Université de Montréal

Cinétique de la nucléation binaire non-isotherme et de la condensation binaire aux conditions dynamiques

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Thèse acceptée le: ....

SOMMAIRE

La présente thèse est consacrée à la théorie de la condensation binaire.

Premièrement, nous considérons la thermodynamique de la nucléation binaire, en nous concentrant sur l'énergie libre de formation d'une goutte et la distribution d'équilibre des gouttes, qui est essentielle pour la vitesse théorique de nucléation et dont le choix n'est toutefois pas unique. Une nouvelle distribution d'équilibre est proposée. Elle permet d'améliorer l'accord des prédictions théoriques avec les données expérimentales pour la vitesse de nucléation.

Deuxièmement, nous développons la théorie cinétique de la nucléation binaire non-isotherme. Cette théorie traite de l'influence des effets thermiques sur la condensation binaire qui sont causés par la chaleur de condensation. Les molécules du mélange de vapeurs absorbées par une goutte de solution binaire lui transmettent de la chaleur de condensation, tandis que les molécules émises par la goutte lui enlèvent une telle chaleur. La température moyenne de la goutte s'accroît au fur et à mesure qu'elle grandit. Cet échauffement des gouttes croissantes diminue la vitesse de nucléation et influence d'autres caractéristiques du processus.
La théorie de la nucléation binaire non-isotherme est développée à partir de l'équation discrète du bilan décrivant l'échange de substance et d'énergie entre le mélange de vapeurs et les gouttes binaires. En réduisant cette équation à la forme différentielle, on obtient l'équation cinétique tridimensionnelle. Nous considérons le cas des chaleurs de condensation arbitraires où l'équation cinétique dépasse les bornes de l'approximation de Fokker et Planck. Dans le cas où les chaleurs de condensation sont très petites par rapport à la fluctuation efficace de l'énergie d'une goutte l'équation cinétique peut être réduite à celle de Fokker et Planck.

L'analyse de l'équation cinétique permet de déterminer la hiérarchie des échelles de temps de la nucléation binaire non-isotherme. Cela rend possible de séparer et décrire analytiquement l'étape de relaxation thermique pendant laquelle la distribution des gouttes selon la température s'approche d'une gaussienne, alors que leur distribution selon les nombres de molécules ne change guère.

À l'étape suivant la relaxation thermique, l'équation cinétique tridimensionnelle peut être résolue en utilisant successivement la méthode de Chapman et Enskog et la méthode de séparation complète des variables. Ces méthodes permettent de réduire notre équation cinétique à l'équation monodimensionnelle de Fokker et Planck dont les coefficients contiennent l'information sur les effets thermiques.

Finalement, nous étudions la condensation binaire isotherme aux conditions dynamiques. Dans ce cas la formation et la croissance des gouttes se passent en même temps que la métastabilité du mélange de vapeurs croît graduellement, atteint son maximum et décroît. C'est ainsi que la condensation binaire se passe le plus souvent dans la nature.

Nous développons la théorie cinétique de ces processus pour les systèmes ouverts ainsi que pour les systèmes fermés (du point de vue de l'échange de matière entre le système où la condensation se passe et son environnement). Les deux sursaturations idéales que les vapeurs du mélange auraient eues en absence d'absorption de la substance par les gouttes sont déterminées par les conditions extérieures: la dépendance temporelle des sursaturations idéales est considérée comme donnée. Le système d'équations intégrales est obtenu pour les processus considérés. La méthode itérative permet de trouver le spectre des dimensions linéaires des gouttes et la distribution des gouttes selon leurs deux variables d'état indépendantes, la précision relative étant assez élevée dès la première itération. De même, cette méthode permet de trouver la dépendance temporelle des sursaturations réelles des deux vapeurs et le nombre total de gouttes.

Tous les résultats théoriques de la thèse sont illustrés avec des calculs numériques.

TABLE DES MATIÈRES

LISTE DES FIGURES

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INTRODUCTION

La condensation binaire c'est la germination et la croissance subséquente des particules d'une solution liquide binaire au sein d'un mélange métastable de deux vapeurs. C'est un processus très répandu dans la nature et dans l'industrie chimique.

La condensation binaire est une transition de phase du premier ordre. Par conséquent, la théorie de la condensation binaire fait partie intégrante de la théorie fondamentale des transitions de phase du premier ordre. En même temps, cette théorie est indispensable pour résoudre différents problèmes appliqués concernant surtout l'industrie chimique et la formation des nuages atmosphériques.

Considérons un mélange de vapeurs de deux espèces chimiques. Supposons que d'une façon ou d'une autre ce mélange devienne métastable. Si une substance se trouve dans un état métastable, elle retournera irrémédiablement dans un état stable. Par example, une vapeur sous-refroidie se condense et se transforme en liquide; un liquide surchauffé finit par s'évaporer. Lorsqu'on considère une vapeur pure son degré de métastabilité est caractérisé par son degré de saturation: la vapeur pure est métastable si elle est sursaturée. La vapeur est dite sursaturée si la pression de cette vapeur est plus élevée que la pression de la vapeur saturée au dessus de la surface plane de sa phase liquide. Quant à un mélange de deux vapeurs, il peut être métastable même si les deux vapeurs sont sous-saturées séparément l'une de l'autre.

La transition de phase du premier ordre peut être soit homogène soit hétérogène.

La transition de phase est dite hétérogène si elle se passe au sein de la phase initiale métastable qui contient différentes inhomogénéités (grains de poussière, grains de sel, ions, etc.) qui servent de centres de formation de la nouvelle phase.

La transition de phase est dite homogène si la phase initiale métastable ne comporte aucun agent nucléant. Les transitions homogènes exigent des degrés de métastabilité beaucoup plus élevés qu'il est nécessaire pour les transitions hétérogènes.

Normalement la transition de phase homogène du premier ordre a un caractère fluctuationnel. C'est grâce aux fluctuations que le travail nécessaire pour la formation de la surface de séparation entre la nouvelle phase et la phase initiale peut être effectué. Par suite des fluctuations, de petites gouttes d'une solution binaire se forment au sein d'un mélange de vapeurs. Si le mélange de vapeurs est stable, ces petits amas restent instables et se désagrègent au cours du temps. Mais si le mélange de vapeurs est métastable, il y a des gouttes qui atteignent certaines dimensions critiques et se retrouvent ainsi en état d'équilibre instable avec le mélange. Dès qu'une telle goutte absorbe (grâce aux fluctuations) une molécule de plus, elle devient stable et continue à croître irréversiblement au cours du temps, en servant de centre de condensation. Une goutte ayant des dimensions critiques et se trouvant ainsi en état d'équilibre instable avec le mélange de vapeurs est désignée sous le terme de "germe". Les dimensions du germe ("dimensions critiques") dépendent du degré de métastabilité de la phase initiale: plus grand le degré de métastabilité est plus petites les dimensions du germe sont.

Le mécanisme hétérogène des transitions de phase du premier ordre est quelque peu différent de celui homogène. La présence des agents nucléants dans la phase métastable cause une grande diminution du degré de métastabilité nécessaire pour déclencher la transition de phase. Qui plus est, à la différence de la transition homogène, la transition hétérogène peut se passer sans barrière (par conséquent, avec une énorme intensité) à métastabilité si basse de la phase maternelle que la transition homogène ne se passe pas du tout. Cela est causé par différents effets, en fonction de la nature de la transition hétérogène. Par exemple, la condensation binaire sur un centre nucléant insoluble peut être considérée comme une formation d'une couche mouillante d'épaisseur arbitraire sur un centre nucléant. Dans ce cas on peut établir que la condensation sans barrière est la conséquence de la concurrence entre la pression capillaire et la pression disjoignante dans les couches minces. Cette concurrence baisse la hauteur de la barrière d'activation de la condensation binaire hétérogène et peut même causer la disparition de cette barrière à très basse métastabilité du mélange de vapeurs. En d'autres termes, les contributions aux potentiels chimiques de deux composantes dans une couche provenant de la pression disjoignante diminuent considérablement ces potentiels en comparaison avec les potentiels chimiques dans une goutte binaire homogène avec les mêmes caractéristiques (rayon et composition) que celles de la couche; cela à son tour baisse considérablement la barrière d'activation de la condensation.

Dans la présente thèse nous ne considérons que les transitions de phase homogènes, mais la théorie sera facile à généraliser pour le cas des transitions de phase hétérogènes.

Habituellement on distingue trois étapes dans une transition de phase du premier ordre.

Pendant la première étape il se forme des embryons de la nouvelle phase (souvent cette étape est appelée "nucléation" ou "germination"). Durant cette étape des embryons ont de petites dimensions: ils ne contiennent que quelques dizaines de molécules chacun. C'est pourquoi, même si le système est fermé, on peut négliger la diminution de la métastabilité de la phase initiale causée par l'absorption de ses molécules par les embryons. Après leur formation ces embryons servent de centres de condensation.

C'est pendant la deuxième étape que la transition de phase proprement dite se passe, car c'est pendant cette étape que la partie bien dominante de la phase métastable se transforme en nouvelle phase stable. Durant cette étape, des particules de la nouvelle phase deviennent si grandes (contenant des milliers de molécules chacune) qu'il est nécessaire de tenir compte de la diminution de la métastabilité de la phase initiale.

Pendant la troisième étape de grandes particules de la nouvelle phase continuent à s'agrandir aux dépens des petites. Cela est causé par la diminution constante de la métastabilité. Cette diminution cause l'augmentation constante des dimensions critiques (du germe). À un moment donné les dimensions du germe s'avèrent plus grandes que celles de certaines gouttes. Ces dernières commencent alors à s'évaporer, ce qui favorise la croissance des gouttes dont les dimensions sont plus grandes que celles du germe.

À présent, il existe une description théorique assez complète et assez adéquate des trois étapes de la condensation monocomposante. Quant à la théorie de la condensation binaire, elle n'a été développée que pour le cas le plus simple où la métastabilité du mélange de vapeurs est créée instantanément et les effets thermiques de la condensation sont négligeables. Et même pour ce cas on ne considère presque pas les deuxième ni troisième étapes de la condensation en se bornant habituellement à développer la thermodynamique et la cinétique de la nucléation.

L'objet de la présente thèse est d'éliminer certaines lacunes de la théorie de la condensation binaire homogène.

Premièrement, nous considérons la thermodynamique de la nucléation binaire. En particulier, nous nous concentrons sur l'énergie libre de formation d'une goutte, le choix de ses variables d'état indépendantes et la distribution d'équilibre des gouttes. Bien que cette dernière joue un rôle essentiel dans la théorie de la nucléation binaire (surtout pour la vitesse de nucléation), son choix n'est pas unique. Ici nous proposons une nouvelle distribution d'équilibre satisfaisant toutes les conditions nécessaires et permettant, dans certains cas, d'améliorer l'accord des prédictions théoriques avec les données expérimentales pour la vitesse de nucléation. Les résultats théoriques sont illustrés avec des calculs numériques.

Deuxièmement, nous développons la théorie cinétique de la nucléation binaire non-isotherme. Cette théorie permet de tenir compte de l'influence des effets thermiques sur le processus de la condensation binaire. Les effets thermiques de la condensation sont causés par la chaleur de condensation. Les molécules du mélange de vapeurs absorbées par une particule de la nouvelle phase (i.e., par une goutte de la solution binaire liquide) lui transmettent de la chaleur de condensation, tandis que les molécules émises par la particule de la solution liquide lui enlèvent de la chaleur de condensation. Car la particule croissante de la solution liquide absorbe plus de molécules qu'elle n'en émet, sa température moyenne augmente au fur et à mesure de sa croissance, la température du mélange de vapeurs étant constante. Cet échauffement de la particule liquide augmente sa faculté d'émettre des molécules. Par conséquent, il cause la diminution de la vitesse de nucléation et l'augmentation de la durée de nucléation. De même, il influence la composition des particules liquides et d'autres caractéristiques du processus.

Nous développons la théorie de la nucléation binaire non-isotherme à partir de l'équation discrète du bilan décrivant l'échange de substance et d'énergie entre le mélange de vapeurs et les particules de solution liquide. Cette équation tridimensionnelle décrit l'évolution temporelle de la distribution de ces particules selon trois variables indépendantes: les nombres de molécules des deux composantes dans une particule liquide et la température de cette particule. En réduisant l'équation discrète du bilan à la forme différentielle, on obtient l'équation cinétique tridimensionnelle de la nucléation binaire non-isotherme. Dans le cas des chaleurs de condensation arbitraires, cette équation cinétique dépasse les bornes de l'approximation de Fokker et Planck. Seulement dans le cas où les chaleurs de condensation sont très petites par rapport à la fluctuation efficace de l'énergie d'une particule liquide, l'équation cinétique peut être réduite à celle de Fokker et Planck. Dans la présente thèse, pourtant, aucune restriction n'est imposée sur les chaleurs de condensation et, par conséquent, l'équation cinétique à résoudre dépasse les bornes de l'approximation de Fokker et Planck.

L'analyse de l'équation cinétique permet de déterminer la hiérarchie des échelles de temps de la nucléation binaire non-isotherme. Cela rend possible de séparer et de décrire analytiquement l'étape de relaxation thermique pendant laquelle la distribution des gouttes selon la température s'approche d'une gaussienne alors que leur distribution selon les nombres de molécules ne change guère.

À l'étape suivant la relaxation thermique, l'équation cinétique tridimensionnelle peut être résolue en utilisant successivement la méthode de Chapman et Enskog et la méthode de séparation complète des variables. L'application successive de ces deux méthodes permet de réduire notre équation cinétique à l'équation monodimensionnelle de Fokker et Planck dont les coefficients contiennent toute l'information sur les effets thermiques. L'analyse d'une telle équation est bien connue et ainsi toutes les caractéristiques de la nucléation binaire non-isotherme peuvent être déterminées. Dans cette thèse, nous présentons les caractéristiques stationnaires: la distribution tridimensionnelle des gouttes, la vitesse de nucléation, la composition et la température moyennes des gouttes. Les résultats théoriques sont illustrés avec des calculs numériques pour les systèmes "éthanol-eau" et "éthanol-hexanol".

La dernière partie de la thèse est consacrée à la condensation binaire isotherme aux conditions dynamiques. Dans ce cas la formation et la croissance des gouttes se passent en même temps que la métastabilité du mélange de vapeurs croît graduellement, atteint son maximum et décroît. C'est ainsi que la condensation binaire se passe le plus souvent dans la nature.

Nous développons la théorie cinétique de ces processus pour les systèmes ouverts ainsi que pour les systèmes fermés (du point de vue de l'échange de matière entre le système où la condensation se passe et son environnement). Les deux sursaturations idéales que les vapeurs du mélange auraient eues s'il n'y avait pas eu de consommation de la substance par les gouttes sont déterminées par les conditions extérieures. Par conséquent, la dépendance temporelle des sursaturations idéales est considérée comme donnée.

Nous considérons le cas où les sursaturations réelles des deux vapeurs atteignent leurs maximums simultanément au moment du maximum de la métastabilité du mélange de vapeurs. Le système d'équations intégrales est obtenu pour les processus considérés. Il est démontré que la méthode itérative permet de construire le spectre des dimensions linéaires des gouttes et la distribution des gouttes selon leurs deux variables d'état indépendantes, la précision relative étant assez élevée dès la première itération. De même, cette méthode permet de trouver la dépendance temporelle des sursaturations réelles de deux composantes du mélange de vapeurs ainsi que le nombre total de gouttes par unité de volume. Les résultats théoriques sont illustrés avec des calculs numériques pour un système ouvert "éthanol - hexanol".

CHAPITRE 1

Thermodynamique de la condensation binaire

Comme nous l'avons déjà noté, pendant la condensation binaire le rôle de la phase métastable est joué par un mélange binaire de vapeurs. Au sein de ce melange il se forme des particules de la phase stable (gouttes de la solution liquide binaire).

Comme ces gouttes représentent la phase condensée, les temps de leurs processus intérieurs de relaxation sont très petits. Toute goutte se trouve donc en état d'équilibre thermodynamique intérieure en possédant la température unique et les potentiels chimiques uniques de ses composantes.

Normalement dans le mélange de vapeurs il y a aussi un gaz qui est passif dans l'échange de matière avec les gouttes mais capable d'un échange thermique avec elles. La concentration assez élevée du gaz passif peut assurer l'égalité entre la température T des gouttes et celle de leur environnement. C'est là que l'on peut négliger les effets thermiques de la condensation qui est dite isothermique dans ce cas.

Habituellement on suppose que le mélange binaire de vapeurs est idéal et qu'il n'y a pas de réactions chimiques.

1.1 L'énergie de formation d'une goutte

Avant de passer à la condensation binaire, rappelons une image simplifiée de la thermodynamique de la condensation monocomposante. La figure 1.1 représente la forme typique de l'énergie libre F de formation d'une goutte monocomposante en fonction du nombre de molécules ν dans la goutte; F représente le travail minimal qu'il faut effectuer pour former une goutte. L'indice "c" marque les valeurs se rapportant au germe. La grandeur ν_c est la dimension du germe. Pour une goutte avec $\nu < \nu_c$ il est énergétiquement plus avantageux de diminuer sa dimension. Mais grâce aux fluctuations certaines gouttes augmentent leurs dimensions jusqu'à ce qu'elles atteignent la dimension ν_c, en devenant germes. Des fluctuations peuvent causer soit le passage du germe dans le domaine $\nu > \nu_c$ soit son retour dans le domaine $\nu < \nu_c$. Une fois passée dans le domaine $\nu > \nu_c$, la goutte commence à grandir irréversiblement.

L'intervalle $\nu_c - \Delta\nu_c < \nu < \nu_c + \Delta\nu_c$ est appelé "voisinage du point critique" ou "voisinage critique". En exprimant l'énergie F en unité $k_B T$ (k_B étant la constante de Boltzmann), la largeur du voisinage critique $\Delta\nu_c$ est définie selon

$$F(\nu_c - \Delta\nu_c) \simeq F(\nu_c + \Delta\nu_c) \simeq F_c - 1 \ .$$

On assume que dans le domaine sub-critique $\nu < \nu_c - \Delta\nu_c$ la distribution des gouttes est celle d'équilibre.

Ainsi l'énergie libre F de formation d'une goutte détermine la barrière d'activation de la nucléation. Toutes les gouttes doivent franchir cette barrière pendant leur formation et leur croissance. Si la vapeur n'est pas sursaturée , F augmente de façon monotone lorsque ν augmente, et F tend à l'infini quand ν tend à l'infini.

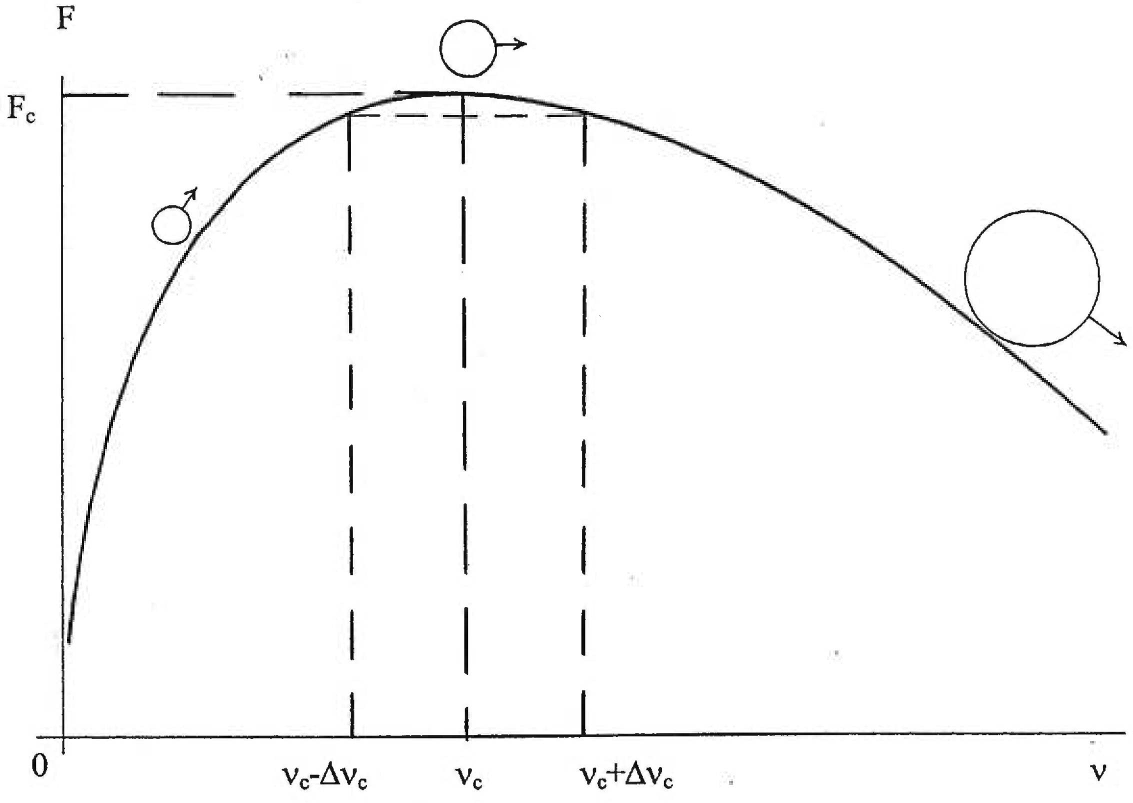

Figure 1.1: La barrière d'activation de la nucléation monocomposante homogène déterminée par l'énergie de formation d'une goutte $F = F(\nu)$. Les cercles représentent la croissance d'une goutte durant son franchissement de la barrière.

Les questions concernant l'énergie de formation d'une goutte binaire ont été étudiées en detail par plusieurs auteurs [1-14].

Soient ν_1 et ν_2 les nombres de molécules des première et deuxième composantes dans une goutte. Dénotons par χ la fraction molaire de la première composante dans une solution à l'intérieur de la goutte. À certaines conditions assez faibles, la valeur de χ est donnée par l'égalité

$$\chi = \nu_1/(\nu_1 + \nu_2). \tag{1.1}$$

Cette variable caractérise la composition d'une goutte.

Introduisons les sursaturations ζ_1 et ζ_2 des composantes 1 et 2 selon les relations

$$\zeta_i = n_i/n_{is} \quad (i = 1, 2), \tag{1.2}$$

où n_i est la densité partielle du nombre de molécules de la composante i dans le mélange de vapeurs; n_{is} est la densité partielle du nombre de molécules de la vapeur de la composante i qui serait saturée au-dessus de la surface plane de sa propre phase liquide.

En exprimant ultérieurement toutes les valeurs énergétiques en unité k_BT, on peut écrire l'énergie de formation d'une goutte $F = F(\nu_1, \nu_2)$ sous la forme

$$F = -\nu_1 b_1 - \nu_2 b_2 + S\gamma\ , \tag{1.3}$$

avec

$$b_1 = \ln[\zeta_1/\chi f_1(\chi)], \;\; b_2 = \ln[\zeta_2/(1-\chi)f_2(\chi)], \tag{1.4}$$

où $f_i(\chi)\,(i = 1, 2)$ est le coefficient d'activité de la composante i dans la solution de composition χ; S est l'aire de la surface d'une goutte; γ représente la tension intérfaciale "goutte - mélange de vapeurs" (en unité k_BT). La figure 1.2 montre la forme typique de la surface énergétique déterminée par la fonction $F = F(\nu_1, \nu_2)$ dans le cas du mélange de vapeurs métastable.

La formule (1.3) a été obtenue à condition que les gouttes soient macroscopiques

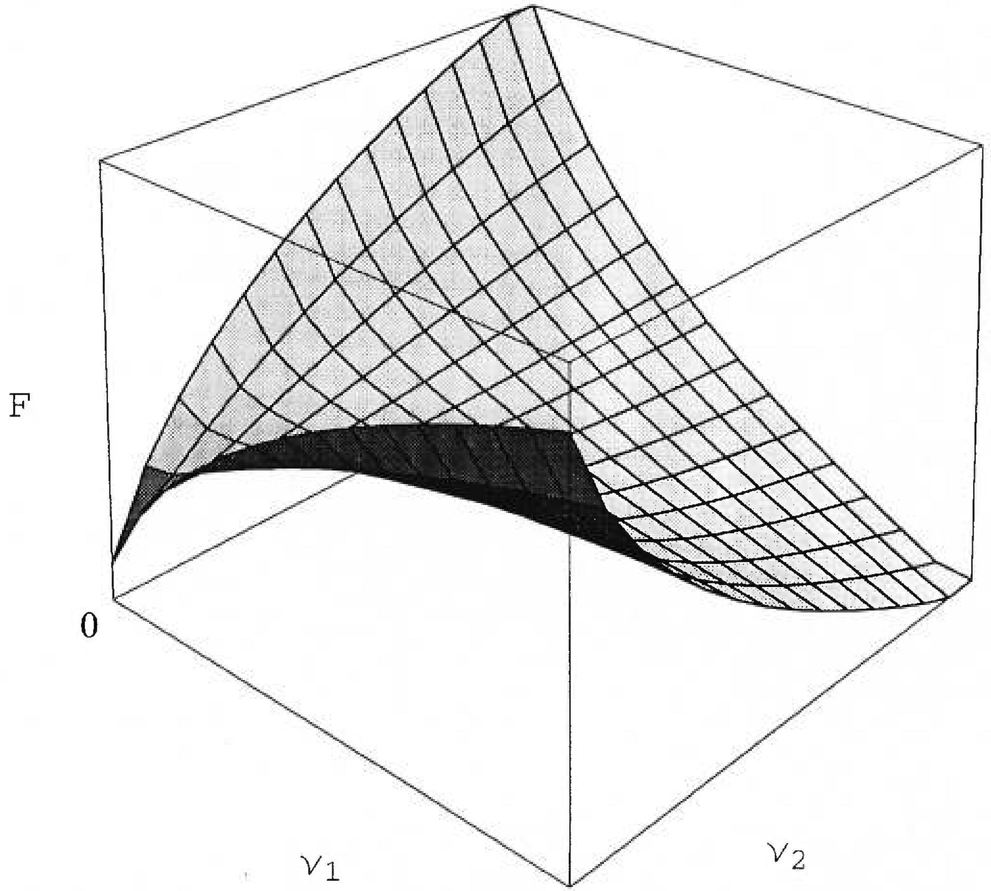

Figure 1.2: La surface énergétique de la nucléation binaire homogène déterminée par l'énergie de formation d'une goutte $F = F(\nu_1, \nu_2)$ dans le cas du mélange de vapeurs métastable.

et décrites par la thermodynamique ordinaire d'équilibre. En utilisant la relation généralisée de Gibbs et Duhem

$$\nu_1 db_1 + \nu_2 db_2 - S d\gamma = 0 \tag{1.5}$$

on peut démontrer que

$$dF = -b_1 d\nu_1 - b_2 d\nu_2 + \gamma dS, \tag{1.6}$$

$$\left(\frac{\partial F}{\partial \nu_1}\right)_{\nu_2} = -b_1 + \frac{2\gamma}{r}\left(\frac{\partial \mu_1}{\partial P}\right)_{\chi}, \quad \left(\frac{\partial F}{\partial \nu_2}\right)_{\nu_1} = -b_2 + \frac{2\gamma}{r}\left(\frac{\partial \mu_2}{\partial P}\right)_{\chi}, \tag{1.7}$$

où μ_i $(i = 1, 2)$ est le potentiel chimique de la composante i dans une goutte; P est la pression à l'intérieur d'une goutte de rayon r.

1.2 La condition de métastabilité du mélange de vapeurs

Introduisons la fonction $b(\chi)$ selon

$$b(\chi) = \chi b_1 + (1-\chi) b_2. \tag{1.8}$$

Dénotant $\nu = \nu_1 + \nu_2$ et tenant compte de (1.8), réduisons (1.3) à

$$F = -\nu b(\chi) + S\gamma\,. \tag{1.9}$$

Selon (1.9) la fonction $b(\chi)$ représente l'énergie de volume d'une goutte par molécule prise avec le signe opposé. Pour que le mélange de vapeurs initial soit métastable il est nécessaire que dans l'intervalle $0 \le \chi \le 1$ il existe les valeurs de χ pour lesquelles l'énergie de volume d'une goutte est negative et, par conséquent, la fonction $b(\chi)$ est positive. La condition nécessaire et suffisante en est évidemment

$$b(\chi_m) > 0, \tag{1.10}$$

où χ_m est la coordonnée du maximum maximal de la fonction $b(\chi)$ dans l'intervalle $0 \le \chi \le 1$. À partir de (1.2),(1.4),(1.8) et tenant compte des propriétés des coefficients d'activité ainsi que de la relation de Gibbs et Duhem on peut obtenir que

$$\left.\frac{db(\chi)}{d\chi}\right|_{\chi=0} = \infty, \quad \left.\frac{db(\chi)}{d\chi}\right|_{\chi=1} = -\infty, \tag{1.11}$$

Ces relations signifient que la fonction $b(\chi)$ n'atteint pas ses maximums aux extrémités de l'intervalle $0 \le \chi \le 1$. Par conséquent, χ_m est la racine de l'équation

$$\left.\frac{db(\chi)}{d\chi}\right|_{\chi=\chi_m} = 0, \tag{1.12}$$

d'où

$$b(\chi_m) = b_1|_{\chi=\chi_m} = b_2|_{\chi=\chi_m}. \tag{1.13}$$

La racine nécessaire pour la formulation de la condition de métastabilité est celle qui assure le maximum maximal de $b(\chi)$.

Si la solution dont les gouttes se forment pendant la condensation binaire est idéale avec $f_1(\chi) = 1$ et $f_2(\chi) = 1$, l'équation (1.12) a une seule racine et à ce point la fonction $b(\chi)$ atteint son maximum. Dans ce cas la condition de métastabilité s'exprime par l'inégalité

$$n_1/n_{1s} + n_2/n_{2s} > 1. \tag{1.14}$$

Il en résulte que la condensation binaire peut se passer même si les vapeurs composant le mélange sont non-saturées séparément l'une de l'autre.

Introduisons la variable κ selon

$$\kappa \equiv (S\gamma)^{3/2} = 6\pi^{1/2}(\nu_1 + \nu_2)\gamma^{3/2}v(\chi). \tag{1.15}$$

où $v(\chi) \equiv V/(\nu_1 + \nu_2) \equiv V/\nu$, et V est le volume d'une goutte. La variable κ représente l'énergie de surface d'une goutte à la puissance $3/2$.

En utilisant (1.15), réduisons (1.9) à la forme

$$F = -\kappa B(\chi) + \kappa^{2/3}, \tag{1.16}$$

où

$$B(\chi) = b(\chi)/[6\pi^{1/2}\gamma^{3/2}v(\chi)], \tag{1.17}$$

L'égalité (1.16) exprime l'énergie de formation comme une fonction des variables d'état κ et χ d'une goutte. La variable κ est extensive ($0 < \kappa < \infty$), tandis que la variable χ est intensive.

Considérons un des maximums positifs de la fonction $B(\chi)$ en dénotant sa coordonnée par χ_c.

En termes de la fonction $B(\chi)$ la condition de métastabilité s'exprime par les relations

$$B(\chi_c) > 0, \quad \left.\frac{dB(\chi)}{d\chi}\right|_{\chi=\chi_c} = 0, \quad \left.\frac{d^2B(\chi)}{d\chi^2}\right|_{\chi=\chi_c} < 0. \tag{1.18}$$

1.3 La barrière d'activation de la nucléation

À l'aide de l'expression (1.16) il est facile d'étudier le comportement de l'énergie de formation F en fonction de κ, la variable χ étant fixée.

Soit χ telle que $B(\chi) > 0$. Dans ce cas lorsque κ varie de 0 à ∞, l'énergie F croît d'abord de façon monotone à partir de 0. Après avoir atteint et traversé son maximum, F commence à diminuer en tendant à $-\infty$. La coordonnée $\kappa_m(\chi)$ du point de col où F atteint son maximum $F_m(\chi)$ est donnée par

$$\kappa_m(\chi) = [2/3B(\chi)]^3. \tag{1.19}$$

Par conséquent,

$$F_m(\chi) = \frac{1}{3}\kappa_m^{2/3}(\chi). \tag{1.20}$$

Maintenant soit χ telle que $B(\chi) \leq 0$. Dans ce cas l'énergie F croît de façon monotone à partir de 0 en tendant vers ∞ lorsque κ varie de 0 à ∞ .

Les propriétés démontrées de l'énergie de formation d'une goutte permettent de bien comprendre son comportement (i.e., le comportement de la barrière d'activation de la nucléation) dans tout le domaine $0 < \kappa < \infty, 0 \leq \chi \leq 1$ des valeurs possibles des variables d'état d'une goutte, κ et χ.

Il est évident que la croissance irréversible d'une goutte (i.e., la croissance irréversible de sa variable κ) n'est possible que pour les valeurs de χ qui satisfont à l'inégalité $B(\chi) > 0$. Cette croissance se passe chaque fois qu'une goutte traverse le point de col de la barrière d'activation.

La ligne de partage des eaux et celle de descente d'eau de la barrière d'activation sont déterminées par les égalités

$$\kappa = \kappa_m(\chi), \tag{1.21}$$

$$\chi = \chi_c. \tag{1.22}$$

Ainsi la ligne de descente d'eau est une droite perpendiculaire à l'axe $\kappa = 0$. La hauteur de la barrière d'activation (i.e., la valeur $F_m(\chi)$ de l'énergie F) sur la ligne de partage des eaux est déterminée par l'égalité (1.20). Si l'équation (1.18) a plusieurs racines χ_c satisfaisant aux inégalités (1.18), à chacune de ces racines correspond son propre maximum de la fonction $B(\chi)$ et, donc, sa propre ligne de descente d'eau.

Les valeurs minimales des fonctions $\kappa_m(\chi)$ et $F_m(\chi)$ sont atteintes au point d'intersection de la ligne de partage des eaux et celle de descente d'eau; à ce point la fonction $B(\chi)$ atteint son maximum positif $B(\chi_c)$. En dénotant ces valeurs par κ_c et F_c nous avons selon (1.19),(1.20):

$$\kappa_c = [2/3B(\chi_c)]^3, \tag{1.23}$$

$$F_c = \frac{1}{3}\kappa_c^{2/3}. \tag{1.24}$$

Le point d'intersection de la ligne de partage des eaux et celle de descente d'eau est le point de selle de la barrière d'activation. C'est à ce point que la hauteur de la barrière est minimale et la ligne de partage des eaux s'approche le plus de l'axe $\kappa = 0$ et devient évidemment parallèle à cet axe, devenant perpendiculaire à la ligne de descente d'eau. Sur le plan des variables κ, χ le point de selle est déterminé par les coodonnées κ_c, χ_c. Dans le voisinage de ce point la barrière d'activation a la forme d'une selle.

Comme la hauteur de la barrière d'activation est minimale au point de selle, le voisinage de ce point est le plus avantageux du point de vue énergétique pour le franchissement de la barrière d'activation par les gouttes. La goutte qui est caractérisée par les coordonnées κ_c, χ_c du point de selle joue le rôle de la goutte critique qui sera désignée sous le terme de germe.

Si l'équation (1.18) a plusieurs racines χ_c satisfaisant aux inégalités (1.18), à chacune de ces racines correspond sa propre ligne de descente d'eau, à laquelle correspond son propre point de selle ainsi que son chemin de franchissement de la barrière d'activation.

Ainsi il peut exister plusieurs canaux de nucléation. Dans tout canal il n'existe qu'un seul point de col de la barrière d'activation. Après avoir franchi ce point, les gouttes grandissent irréversiblement.

Il va sans dire que le canal de nucléation pour lequel la hauteur de la barrière d'activation au point de selle est la plus petite sera le plus avantageux énergétiquement.

1.4 Le voisinage du point de selle de la barrière d'activation

Dans le voisinage du point de selle de la barrière d'activation l'énergie de formation d'une goutte F en fonction des variables ν_1, ν_2 peut être écrite sous la forme bilinéaire

$$F = F_c + \frac{1}{2}\left(\frac{\partial^2 F}{\partial \nu_1^2}\right)_c (\nu_1 - \nu_{1c})^2 + \left(\frac{\partial^2 F}{\partial \nu_1 \partial \nu_2}\right)_c (\nu_1 - \nu_{1c})(\nu_2 - \nu_{2c}) + \frac{1}{2}\left(\frac{\partial^2 F}{\partial \nu_2^2}\right)_c (\nu_2 - \nu_{2c})^2, \tag{1.25}$$

où l'indice inférieur "c" dénote des valeurs au point de selle.

Introduisons les variables x, y au lieu des variables ν_1, ν_2 à l'aide de la transformation linéaire

$$\left.\begin{aligned} x = &\quad c_{11}(\nu_1 - \nu_{1c}) + c_{12}(\nu_2 - \nu_{2c}) \\ y = &\quad c_{21}(\nu_1 - \nu_{1c}) + c_{22}(\nu_2 - \nu_{2c}) \end{aligned}\right\} \tag{1.26}$$

avec

$$\left.\begin{aligned} c_{11} &= \sqrt{-\tfrac{1}{2}\left(\tfrac{\partial^2 F}{\partial \kappa^2}\right)_c}\left(\tfrac{\partial \kappa}{\partial \nu_1}\right)_c, \quad c_{12} = \sqrt{-\tfrac{1}{2}\left(\tfrac{\partial^2 F}{\partial \kappa^2}\right)_c}\left(\tfrac{\partial \kappa}{\partial \nu_2}\right)_c, \\ c_{21} &= \sqrt{\tfrac{1}{2}\left(\tfrac{\partial^2 F}{\partial \chi^2}\right)_c}\left(\tfrac{\partial \chi}{\partial \nu_1}\right)_c, \qquad c_{22} = \sqrt{\tfrac{1}{2}\left(\tfrac{\partial^2 F}{\partial \chi^2}\right)_c}\left(\tfrac{\partial \chi}{\partial \nu_2}\right)_c. \end{aligned}\right\} \tag{1.27}$$

Par rapport aux variables x et y l'approximation bilinéaire de F acquiert la forme diagonale

$$F = F_c - x^2 + y^2 \tag{1.28}$$

Le jacobien de la transformation (1.26),(1.27) n'est pas nul (il est négatif):

$$\frac{\partial(x,y)}{\partial(\nu_1,\nu_2)} = -6\pi^{1/2}\sqrt{-\frac{1}{2}\left(\frac{\partial^2 F}{\partial \kappa^2}\right)_c}\sqrt{\frac{1}{2}\left(\frac{\partial^2 F}{\partial \chi^2}\right)_c}\frac{\gamma^{3/2}}{\nu_{1c}+\nu_{2c}}v_c. \tag{1.29}$$

La simplicité de l'expression (1.28) par rapport à (1.25) signifie que les variables x, y sont plus convenables que les variable ν_1, ν_2 (ou même κ, χ) pour décrire l'énergie de formation d'une goutte et la barrière d'activation de la nucléation dans le voisinage du point de selle. Le fait que les carrés des variables dans (1.28) ont des signes opposés est typique de la théorie des transformations de phase du premier ordre; et cela résulte du caractère de selle de la barrière d'activation. Les signes "-" et "+" dans (1.28) montrent que les variables x et y sont respectivement instable et stable. Et c'est la réduction de l'énergie de formation à la forme diagonale qui a permis de trouver ces variables. Naturellement ces variables égalent zero pour le germe. Leurs valeurs caractéristiques se trouvent évidemment dans l'intervalle de -1 à 1.

1.5 Le facteur de normalisation de la distribution d'équilibre des gouttes

On suppose toujours que la distribution des gouttes dans la région précritique des variables d'état a la forme de la distribution de Gibbs. Cependant le problème de la détermination de son facteur de normalisation est aussi complexe qu'important. En effet, la vitesse de nucléation binaire (c.-à-d., le nombre de gouttes formées en unité de volume par unité de temps) est proportionnelle à la distribution d'équilibre. Toutefois, le facteur de normalisation de cette distribution ne peut pas être déterminé de façon unique. Il existe quelques approches de ce problème dont aucune ne peut être retenue comme la meilleure. Ici nous discutons de ce problème et présentons un nouveau facteur de normalisation qui pourrait assurer, dans certains cas, un meilleur accord entre les prédictions théoriques et les données expérimentales concernant la vitesse de nucléation binaire.

1.5.1 Article 1: *On the equilibrium distribution in the binary nucleation theory*

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On the equilibrium distribution in the binary nucleation theory

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Abstract

In considering a binary nucleation theory, it is shown that the unified approach to the homogeneous and heterogeneous nucleation theories makes it possible to obtain the equilibrium binary distribution satisfying both the mass action law and type II limiting consistency. Theoretical rates of binary nucleation are calculated by using the new equilibrium distribution, the distribution of Reiss, and that of Wilemski and Wyslouzil for the ethanol - hexanol system. Possible causes of the irregularity of discrepancies between theoretical predictions and experimental data are discussed.

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1 Introduction

Lately, a significant progress has been attained in developing different aspects of kinetic theory of binary nucleation and condensation. As there exist some different approaches to this theory in the frameworks of capillarity approximation there appears the need to assess the accuracy of competing approaches as well as to compare their predictions with experimental data. The latter is not always possible because of absence of appropriate experimental results, but for a wide range of situations high quality experimental data are available.

Recently, Wilemski and Wyslouzil (1995) and Wyslouzil and Wilemski (1995, 1996) have obtained a series of very interesting and important results concerning both kinetic and equilibrium aspects of the theory. In particular, they resolved several inconsistencies involving the binary equilibrium distribution. They proposed (Wilemski and Wyslouzil,1995) a new form of the binary equilibrium distribution which obeys the mass action law, reduces to appropriate forms for the unary distributions and yields unique and physically well-behaved evaporation rate coefficients satisfying the new product rule. In this paper we will treat the binary equilibrium distribution proposed by Kuni *et al.* (1990) and Melikhov *et al.* (1990) who generalized ideas developed by Rusanov *et al.* (1987) to the two-component theory. We will show that the distribution of Kuni *et al.* satisfies all principal conditions formulated by Wilemski and Wyslouzil (1995). Then we will calculate the binary nucleation rate using this equilibrium distribution in the kinetic theory of Kuni *et al.* (1990) and Melikhov *et al.* (1990,1991) (yielding the same nucleation rate as Stauffer's theory (1976)) at various values of sticking coefficients. The results of calculations will be compared with each other as well as with the experimental data of Strey and Viisanen (1993) for the ethanol-hexanol system.

2 Binary equilibrium distribution

Let us denote by $f(\nu_1, \nu_2)$ the equilibrium distribution of binary nuclei with respect to the variables ν_1 and ν_2 representing numbers of molecules of first and second components, respectively, in a nucleus. In the capillarity approximation the distribution $f(\nu_1, \nu_2)$ can be presented (Reiss,1950; Wilemski and Wyslouzil,1995) as

$$f(\nu_1, \nu_2) = N \left(\frac{n_1}{n_{1\infty}(\chi)}\right)^{\nu_1} \left(\frac{n_2}{n_{2\infty}(\chi)}\right)^{\nu_2} \exp\left[-F_s(\nu_1, \nu_2)\right], \tag{1}$$

where N is a normalization factor; $n_i\,(i = 1, 2)$ is the number density of molecules of component i in a vapor mixture; $n_{i\infty}(\chi)\,(i = 1, 2)$ is the equilibrium number density of molecules of component i in a vapor saturated over a bulk solution of composition χ, which is defined as $\chi = \nu_1/(\nu_1 + \nu_2)$; $F_s(\nu_1, \nu_2)$ is the contribution to a free energy of formation of a nucleus having variables ν_1, ν_2 due to the nucleus surface (hereinafter, we express all energy quantities in units of thermal energy of the medium k_BT, where k_B is Boltzmann's constant, T is the absolute temperature of the medium).

Wilemski (1995) introduced the term "limiting consistency" in discussing the limiting behaviour of unary distribution. Wilemski and Wyslouzil (1995) discussed two types of limiting consistency. Type I limiting consistency concerns the unary distribution and requires that that distribution equals the number density of molecules in a vapor, when evaluated for "clusters" of single molecules. According to type II limiting consistency, a binary distribution must reduce to an appropriate unary distribution if we let either ν_1 or ν_2 tend to 0.

Besides the two types of limiting consistency, the equilibrium distribution function must satisfy the law of mass action according to which the equilibrium binary distribution must be presentable in the form

$$f(\nu_1, \nu_2) = n_1^{\nu_1} n_2^{\nu_2} K(\nu_1, \nu_2), \tag{2}$$

where $K(\nu_1, \nu_2)$ is the equilibrium constant. If a vapor mixture is considered as ideal, $K(\nu_1, \nu_2)$ can depend on ν_1, ν_2, and T, but never on n_1 nor on n_2. Unlike the limiting consistency conditions, which are imposed for the mathematical convenience, the law of mass action is a fundamental law of statistical physics as it has been shown by Wilemski and Wyslouzil (1995).

So far, the most commonly used form of normalization factor N is that of Reiss (1950):

$$N = n_1 + n_2. \tag{3}$$

This normalization factor, however, violates the mass action law, as it was pointed out by Wilemski (1975). Besides, there is another issue (first pointed out by Katz, according to Wilemski and Wyslouzil (1995)) related with this normalization factor. Actually, according to eqs.(1),(3), the unary distribution of pure nuclei of first component depends linearly on the number density of second component in a vapor mixture if we let ν_2 equal to 0 and vice versa.

Wilemski and Wyslouzil supposed (1995) that the normalization factor N and the normalization factors N_1 and N_2 of unary equilibrium distributions of first and second components are related as

$$N = N_1^{\chi} N_2^{1-\chi}, \tag{4}$$

and they proposed the following form for the binary equilibrium distribution:

$$f(\nu_1, \nu_2) = n_{1\infty}^{\chi} n_{2\infty}^{1-\chi} \exp[\chi\Theta_1 + (1-\chi)\Theta_2] \left(\frac{n_1}{n_{1\infty}(\chi)}\right)^{\nu_1} \left(\frac{n_2}{n_{2\infty}(\chi)}\right)^{\nu_2} \exp[-F_s(\nu_1, \nu_2)], \tag{5}$$

where $\Theta_i = \sigma_i s_i / kT \, (i = 1, 2)$; σ_i and s_i are the surface tension of pure i-component liquid and surface area, respectively, of i-component molecule. This form satisfies both the law of mass action and both types of limiting consistency. Moreover, using this distribution in the relations of detailed balance allows one to obtain fully self-consistent and physically well-behaved expressions for the evaporation coefficients.

3 Unified approach to the homogeneous and heterogeneous nucleation theories

Now, let us consider the method of determination of the normalization factor of the equilibrium binary distribution proposed by Kuni *et al.* (1990) and Melikhov *et al.* (1990). This method extends ideas developed earlier by Rusanov *et al.* (1987) for treating the homogeneous unary nucleation as a heterogeneous one occurring not on foreign heterogeneous centers but on molecules themselves of condensing vapor to the two-component theory . The reasoning of interest is as follows.

Taking into account that each of n_1 molecules of the first component of vapor mixture and each of n_2 molecules of its second component can serve as a heterogeneous center of formation for a nucleus, we have, according to principles of equilibrium statistical thermodynamics:

$$f(\nu_1, \nu_2) = n_1 e^{-F_1} + n_2 e^{-F_2} \tag{6}$$

where F_1 is the work necessary that $\nu_1 - 1$ molecules of the first component of vapor mixture and ν_2 molecules of its second component join a single molecule of first component; F_2 is the work necessary that $\nu_2 - 1$ molecules of second component of vapor mixture and ν_1 molecules of its first component join a single molecule of second component. Though identical nuclei with the variables ν_1 and ν_2 are formed as a result of both works F_1 and F_2, these works in general are not equal to each other. It is because corresponding nuclei are formed on single molecules of different species.

The works F_1 and F_2 do not coincide with the thermodynamic work $F \equiv F(\nu_1, \nu_2)$ either, which, according to its meaning, is required for simultaneous unification of ν_1 molecules of first component of vapor mixture and of ν_2 molecules of its second component in a nucleus situated in a fixed point of condensing system. Of course, the differences between F_1, F_2, and F have only a statistico-thermodynamical character, but not a mechanical one.

It has been shown by Kuni *et al.* (1987) that

$$F_1 = F - \ln[n_{1s}/n_1], F_2 = F - \ln[n_{2s}/n_2], \tag{7}$$

where n_{1s} and n_{2s} are the number densities of molecules of first and second components, respectively, in a liquid solution of composition χ.

Substituting eq.(7) in eq.(6), we have

$$f(\nu_1, \nu_2) = \frac{1}{v(\chi)} e^{-F}, \tag{8}$$

where $v(\chi) = 1/[n_{1s}(\chi) + n_{2s}(\chi)]$ is the nucleus volume per molecule. Denoting by v_1 and v_2 the partial molecular volume of first and second component, respectively, in their pure liquids, and taking into account that F can be expressed through $F_s \equiv F_s(\nu_1, \nu_2)$ as

$$F = F_s - \nu_1 \ln \frac{n_1}{n_{1\infty}(\chi)} - \nu_2 \ln \frac{n_2}{n_{2\infty}(\chi)}, \tag{9}$$

one can rewrite eq.(8) as

$$f(\nu_1, \nu_2) = \frac{\nu_1 + \nu_2}{\nu_1 v_1 + \nu_2 v_2} \left(\frac{n_1}{n_{1\infty}(\chi)}\right)^{\nu_1} \left(\frac{n_2}{n_{2\infty}(\chi)}\right)^{\nu_2} \exp[-F_s]. \tag{10}$$

Since here the normalization factor $(\nu_1 + \nu_2)/(\nu_1 v_1 + \nu_2 v_2)$ does not depend on n_1 nor n_2, this equilibrium distribution automatically satisfies the mass action law. As for the limiting consistency, equilibrium distribution (10) evidently satisfies that of type II ($1/v_1$ and $1/v_2$ being the normalization factors of respective unary distributions) but does not satisfy that of type I. It also gives well-behaved evaporation coefficients in the framework of Kelvin model.

Comparing eq.(8) with eqs.(1),(3), we see that the normalization factor of Kuni *et al.* is $q_{KR} = v^{-1}(\chi)(n_1 + n_2)^{-1}$ times as large as that of Reiss (q_{KR} is of the order of 10^4). Comparing eq.(10) with eq.(5), we see that the normalization factor of Kuni *et al.* differs by a factor $q_{KW} = v^{-1}(\chi) n_{1\infty}^{-\chi} n_{2\infty}^{-1+\chi} \exp[-\chi\Theta_1 - (1-\chi)\Theta_2]$

from that of Wilemski and Wyslouzil. This factor (q_{KW}) is rather a complex function of many parameters of condensing system.

It should be noted that in the unary nucleation theory, Reiss *et al.* (1968) and Kikuchi (1969) obtained the corrections to the nucleation free energy like that of Rusanov *et al.* (1987), but they did it by more artificial means. These corrections give the ratio of molecule number density of condensed phase to that of vapor phase as a pre-exponential factor in the classical unary nucleation rate. As shown by Schmitt *et al.* (1983), this factor allows one to obtain a good fit of theoretical predictions and experimental data for the nucleation rate of toluene at physically realistic values of the surface tension and the sticking coefficient.

4 Procedure of numerical calculations

Numerical calculations have been carried out by following the formalism of Kuni's-Melikhov's theory of the binary nucleation. We only remind that the kinetic part of that theory is based on the well-known method of complete separation of variables allowing one to obtain a binary nucleation rate in the most general case like the Stauffer theory.

Briefly, the procedure of our numerical calculations is as follows.

Let us introduce the value κ as

$$\kappa \equiv F_s^{3/2} = 6\pi^{1/2}(\nu_1 + \nu_2)\gamma^{3/2}v, \tag{11}$$

where $v \equiv v(\chi)$; $\gamma \equiv \gamma(\chi)$ is the surface tension of a nucleus of composition χ expressed in units of k_BT.

Considering the variables κ and χ as a couple of independent variables describing the state of a nucleus, we can write the free energy F in the form

(Kuni *et al.*,1990; Melikhov *et al.*,1990,1991)

$$F(\kappa, \chi) = \kappa^{2/3} - \kappa B(\chi), \tag{12}$$

where

$$B(\chi) = [\chi b_1 + (1-\chi)b_2]/[6\pi^{1/2}\gamma^{3/2}v], \tag{13}$$

$$b_1 = \ln\frac{\zeta_1}{\chi f_1(\chi)}, b_2 = \ln\frac{\zeta_2}{(1-\chi)f_2(\chi)}, \tag{14}$$

$$\zeta_i = n_i/n_{i\infty} \quad (i = 1,2), \tag{15}$$

$f_i(\chi)\,(i = 1,2)$ is the activity coefficient of component i in a solution with composition χ; ζ_i would represent the supersaturation of i-component vapor of over the plane surface of its own liquid phase. A typical behaviour of function $B(\chi)$ is shown in Fig.1.

The variables κ_c and χ_c of a critical nucleus are determined as coordinates of the saddle point of the free energy surface given by $F(\kappa, \chi)$:

$$\left.\frac{\partial F(,\kappa,\chi)}{\partial\kappa}\right|_c = 0, \quad \left.\frac{\partial F(,\kappa,\chi)}{\partial\chi}\right|_c = 0 \tag{16}$$

(the subscript "c" marks values at the saddle point, that is, for the critical nucleus). The right-most part of eq.(16) results in the equation $dB(\chi)/d\chi|_c = 0$ determining the composition χ_c of the critical nucleus. To reduce this equation to the correct equation for χ_c (given, e.g., by Wilemski (1984,1987) or by Debenedetti and Reiss (1998)), we have to neglect the derivative $d\gamma/d\chi$, assuming the surface tension of nuclei constant ($\gamma \simeq \gamma_c$) in the near-critical region. For nuclei in this region (which is the most important one for nucleation kinetics), variations of nucleus composition are small enough in order for the assumption $\gamma \simeq \gamma_c$ to be acceptable for most binary systems.

Let us denote by $F''_{\kappa\kappa}$ and $F''_{\chi\chi}$ the second derivatives of the function $F(\kappa, \chi)$ with respect to κ and χ, respectively, at the saddle point and denote by κ'_i and χ'_i the first derivatives of the variables κ and χ with respect to ν_i $(i = 1,2)$, at the saddle point.

Introducing the notations

$$c_{11} = \sqrt{-\frac{1}{2}F''_{\kappa\kappa}}\,\kappa'_1,\ c_{12} = \sqrt{-\frac{1}{2}F''_{\kappa\kappa}}\kappa'_2,\ c_{21} = \sqrt{\frac{1}{2}F''_{\chi\chi}}\,\chi'_1,\ c_{22} = \sqrt{\frac{1}{2}F''_{\chi\chi}}\chi'_2, \tag{17}$$

$$a = W_1 c_{11}^2 + W_2 c_{12}^2,\ \varepsilon = -\frac{W_1 c_{11}^2 + W_2 c_{12}^2}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}},\ p = \frac{W_1 W_2 (c_{11}c_{22} - c_{12}c_{21})^2}{(W_1 c_{11} c_{21} + W_2 c_{12} c_{22})^2}, \tag{18}$$

$$A = \frac{a}{2\varepsilon^2}\{\varepsilon^2 - 1 - p + [(\varepsilon^2 + 1 + p)^2 - 4\varepsilon^2]^{1/2}\}, \tag{19}$$

$$C = \left[6\sqrt{\pi}\sqrt{-\frac{1}{2}F''_{\kappa\kappa}}\sqrt{\frac{1}{2}F''_{\chi\chi}}\frac{\gamma_c^{3/2}}{\nu_{1c} + \nu_{2c}}v_c^2\right]^{-1}, \tag{20}$$

where $W_i\,(i = 1,2)$ is the number of i-component molecules that the critical nucleus absorbs per unit time, the binary nucleation rate J can, finally, be presented as

$$J = ACe^{-F_c}. \tag{21}$$

It is evident that, through W_1 and W_2, the condensation coefficients α_1 and α_2 strongly influence theoretical predictions for the nucleation rate J , which is proportional to a linear combination of these coefficients. At the same time there exist no reliable theoretical nor experimental data for them.

5 Numerical calculations and Conclusions

Numerical calculations have been carried out with the help of *Mathematica* for the ethanol (1) - hexanol (2) system at the same external conditions as the experiments of Strey and Viisanen (1993). Results of calculations are presented by Figure 2a and b in the form of the dependence of $\ln J$ on the mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$. The lines represent theoretical rates corresponding to the fixed values of activity fraction $y = \zeta_2/(\zeta_1 + \zeta_2)$, indicated on Figure 2 over the series. The corresponding experimental data are shown by circles.The theoretical rates were calculated by using the normalization factors of Reiss (eqs.(1),(3): dashed lines in Fig.2), Wilemski and Wyslouzil (eq.(5): dot-dashed lines in Fig.2), and Kuni *et al.* (eq.(8): solid lines in Fig.2). Thermodynamic parameters of the ethanol-hexanol system were taken from Strey and Viisanen (1993). We have presented only a part of results to avoid confusion.

The numerical results shown in Fig.2a correspond to the case of $\alpha_1 = 1$ and $\alpha_2 = 1$. As we can see, the greater y is, the better is the fit of theoretical predictions to experimental data (theoretical rates are greater than experimental ones by a factor of some orders of magnitude), and it is fairly good when y tends to 1. Quite a similar behaviour of predictions for the nucleation rate is observed when Wilemski's - Wyslouzil's equilibrium distribution (5) is used in Stauffer's rate formula (Wilemski and Wyslouzil, 1995). But theoretical rates of Wilemski and Wyslouzil better agree with experimental data than ours (obtained using equilibrium distribution (10) of Kuni *et al.*, i.e. formula (21) for J), since for the considered system the normalization factor of Kuni *et al.* is approximately ten times as large as that of Wilemski and Wyslouzil, that is q_{KW} is of the order of 10. At the same time, q_{KR} is of the order of 10^4 when y is small and tends to the value 10^5 when $y \to 1$ (e.g., $q_{KR} \simeq 8 \times 10^4$ at $y = 0.98$).

Since there exist no theoretical nor experimental data on the sticking coefficients α_1 and α_2 for this system, we could, in principle, try to obtain a fine fit of theoretical rates to experimental data by choosing appropriate values for α_1 and α_2. Magnitudes of α_1 and α_2 must not depend, however, on metastability of a system, though they could be weak functions of temperature. Therefore, within the framework of adequate theory we could obtain a good fit of theoretical predictions to experimental data by means of unique choice of α_1 and α_2 (independent of vapor mixture metastability) for a given system. But for the considered system this does not work. Actually, the theoretical rates of nucleation in the case of $\alpha_1 = 0.2$ and $\alpha_2 = 0.2$ are shown by Fig.2b. Such a choice of α_1 and α_2 allows one to obtain a better fit of theoretical predictions to experimental data, than the couple $\alpha_1 = 1$ and $\alpha_2 = 1$. However, the less is y, the worse the fit remains:

the ratio of the theoretical nucleation rate to the experimental one increases with decreasing y.

Such an irregularity of the discrepancies between the theoretical predictions and the experimental data (but not the discrepancies themselves) can be explained (at least, in part) by the existence of thermal effects of nucleation, which are not taken into account in the classical theory of the binary nucleation, but which can strongly influence nucleation processes under some circumstances.

It is necessary to note that, as pointed out by many authors (Mirabel and Katz, 1977; Wilemski, 1984, 1987; Flageollet-Daniel *et al.*, 1983; Laaksonen, 1992), the most probable explanation for such large discrepancies themselves between the theory and the experiments as observed is the inadequacy of the capillarity approximation in evaluating the free energy of binary nucleation. That approximation uses a bulk surface tension for calculating the nucleus free energy of formation and hence does not take account of the effect of surface enrichment which can considerably change the nucleus surface tension.

Thermal effects cause an increase in the mean temperature of growing nucleus and, consequently, a decrease in the nucleation rate. As well known (Feder *et al.*, 1966; Grinin and Kuni, 1989;Barrett and Clement, 1990; Barrett, 1994), thermal effects can decrease the unary nucleation rate by a factor of up to some thousands. Of course, thermal effects have a significant influence on the nucleation rate only in the case where the number density of carrier gas molecules is not sufficient to ensure the constancy of the nucleus temperature. The carrier gas plays the role of a thermal reservoir and is an effective energy transfer medium. Usually, in experiments on the binary nucleation the carrier gas pressure is as large as possible to weaken the influence of thermal effects on the nucleation as much as possible. Nevertheless, such an influence is always out there, however weak it may be.

On the other hand (Feder *et al.*, 1966; Grinin and Kuni, 1989; Barrett, 1994), the influence of thermal effects on the nucleation rate depends on the ratio of the carrier (passive) gas pressure to the pressure of condensable vapor: the influence increases with decreasing this ratio. In the system considered, the less is the value y, the denser is the vapor mixture ($n_1 + n_2 \approx 5 \times 10^{17} cm^{-3}$ for $y = 0.393$ and $n_1 + n_2 \approx 2 \times 10^{17} cm^{-3}$ for $y = 0.980$) and hence the stronger is the influence of thermal effects on the nucleation rate. Therefore, the fact, that the discrepancies between the theoretical predictions and experimental data increase with decreasing y, can be explained (at least, in part) by the fact that the theory does not allow for thermal effects of nucleation which cause the decrease in the nucleation rate: the smaller is y, the more significant is this decrease.

As clear from Fig.2, the normalization factor of Kuni *et al.* predicts the highest theoretical nucleation rates for the ethanol-hexanol system and Reiss' normalization factor (3) provides the lowest ones, the theoretical rates corresponding to the factor of Wilemski and Wyslouzil being intermediate (but very close to those of Kuni *et al.*). In the case of unary nucleation, according to Figure 3, theoretical predictions for the nucleation rate obtained by using the one-component analogues of these three normalization factors have quite a similar character. Figure 3 shows the logarithm of the nucleation rate J of pure hexanol vs its supersaturation (activity) $\zeta = \zeta_2$. The ellipses represent the experimental nucleation rates measured in a two-piston expansion chamber by Strey *et al.* (1986). Different series correspond to different initial (chamber) temperature T_0. Note that the actual nucleation temperature of nucleation is lower than T_0 and decreases slightly along each $\ln J$-ζ curve. The corresponding nucleation rates calculated by Strey *et al.* (1986) from the classical nucleation theory (i.e., using the one-component analogue of Reiss' normalization factor (3)) are given by the dashed lines. For a comparison, we calculated the theoretical rates using the one-component analogues ofequilibrium distributions (5) and (8) (data of Gallant (1967) were taken for thermodynamic parameters of pure hexanol). The solid lines correspond to the theoretical rates obtained by using the one-component analogue of the normalization factor of Kuni *et al.*. The theoretical predictions obtained by using the Wilemski normalization factor (Wilemski, 1995) are represented by the dot-dashed lines. The initial temperatures are indicated below each series. Evidently, one can conclude that none of these three normalization factors can be given an undeniable priority from the standpoint of the agreement between the theoretical and experimental rates for the considered systems. However, for the homogeneous nucleation of toluene Schmitt *et al.* (1983) showed that the use of the one-component analogue of the normalization factor of Kuni *et al.* brings the theoretical rates into considerably better agreement with the experimental data, the values of the surface tension and the sticking coefficient being physically realistic.

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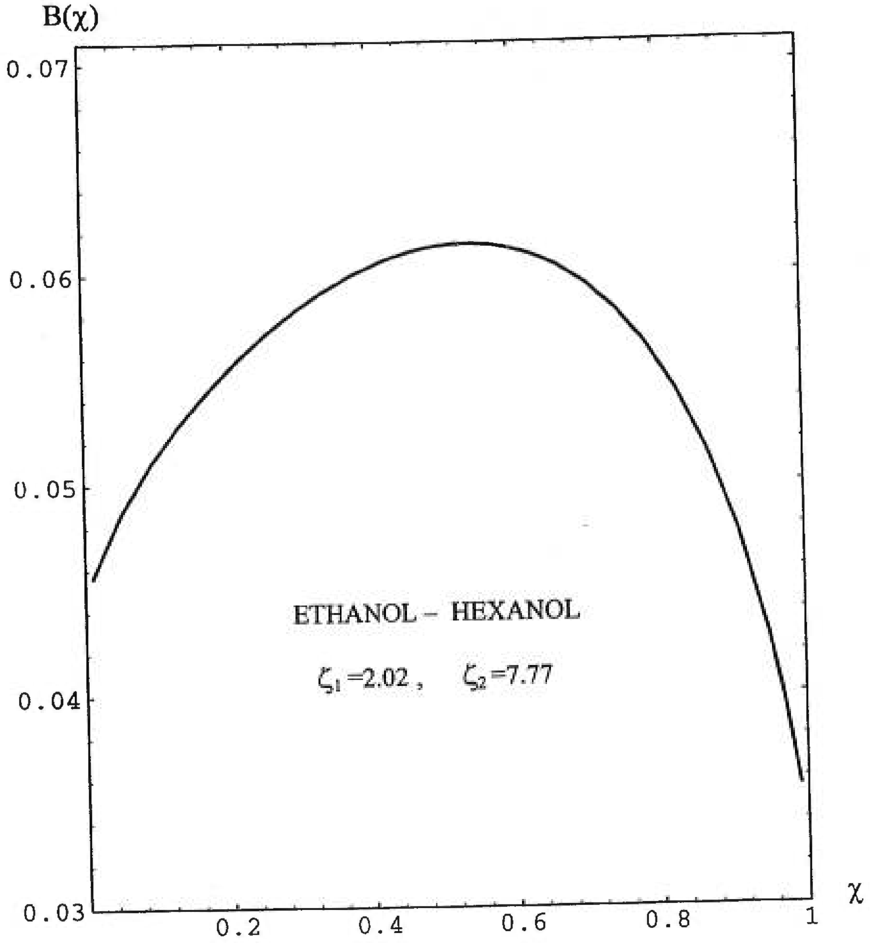

Figure 1. Typical behaviour of function $B(\chi)$ for a metastable binary system, presented by $B(\chi)$ for the ethanol (1) - hexanol (2) system at $\zeta_1 = 2.02, \zeta_2 = 7.77$, and $T = 260K$. We have $\chi_c = 0.54, B(\chi_c) = 0.0619, B''(\chi_c) = -0.1239$.

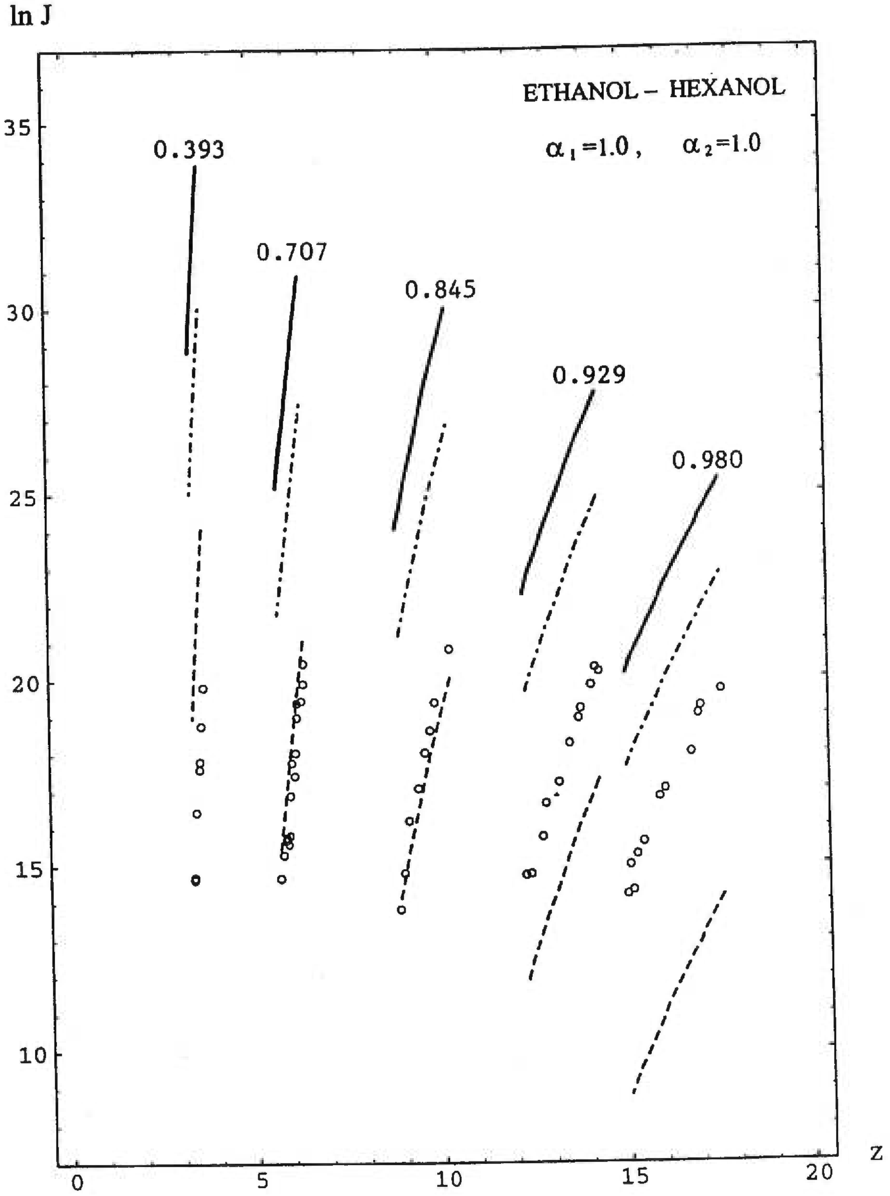

Figure 2a. Logarithm of nucleation rate J in the ethanol (1) - hexanol (2) system plotted vs a mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$, at $T = 260K$. The dimension of J is $cm^{-3}s^{-1}$. The circles are the experimental data of Strey and Viisanen (1993). The lines represent the nucleation rates calculated at the indicated activity fraction $y = \zeta_2/(\zeta_1 + \zeta_2)$ by using the normalization factors of Kuni *et al.* (solid lines), of Wilemski and Wyslouzil (dot-dashed lines), and of Reiss (dashed lines), the sticking coefficients being $\alpha_1 = 1.0$, $\alpha_2 = 1.0$.

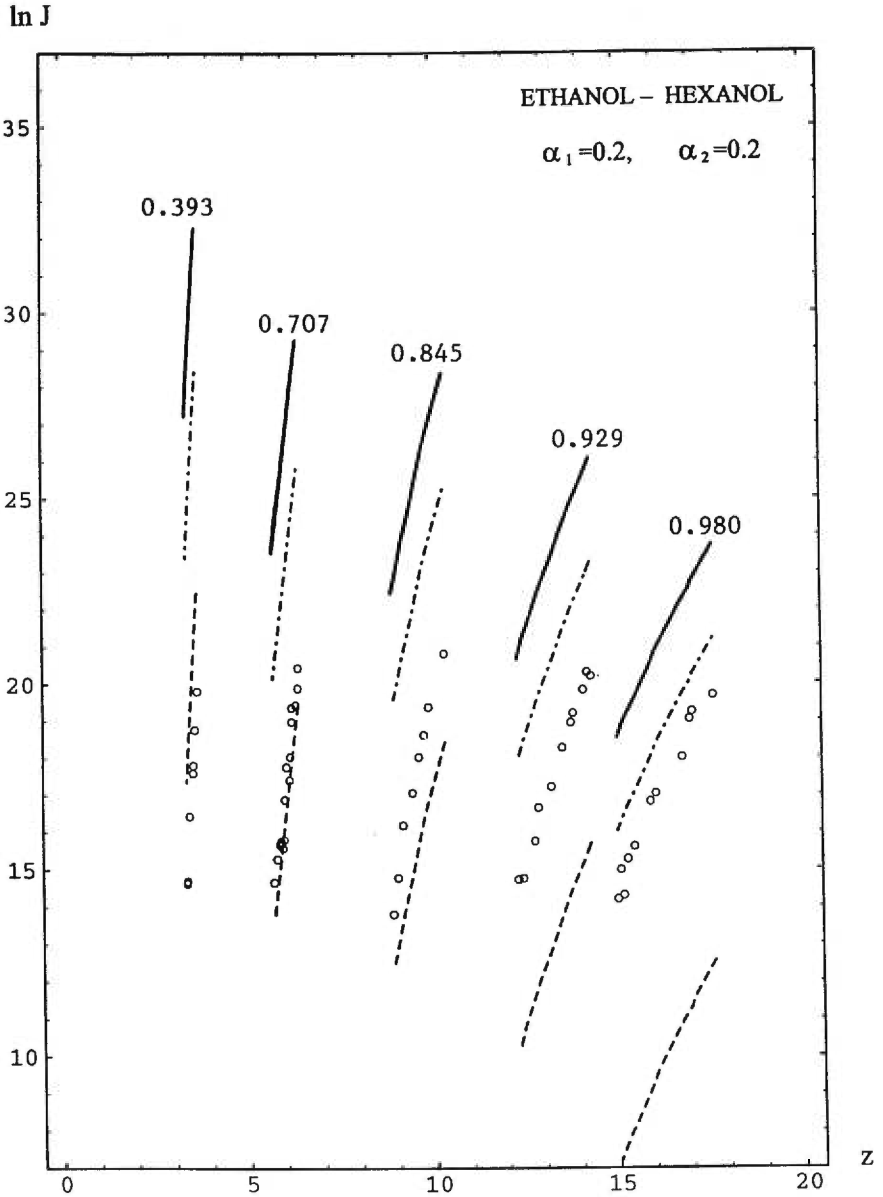

Figure 2b. Logarithm of nucleation rate J in the ethanol (1) - hexanol (2) system plotted vs a mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$, at $T = 260K$. The dimension of J is $cm^{-3}s^{-1}$. The circles are the experimental data of Strey and Viisanen (1993). The lines represent the nucleation rates calculated at the indicated activity fraction $y = \zeta_2/(\zeta_1 + \zeta_2)$ by using the normalization factors of Kuni *et al.* (solid lines), of Wilemski and Wyslouzil (dot-dashed lines), and of Reiss (dashed lines), the sticking coefficients being $\alpha_1 = 0.2$, $\alpha_2 = 0.2$.

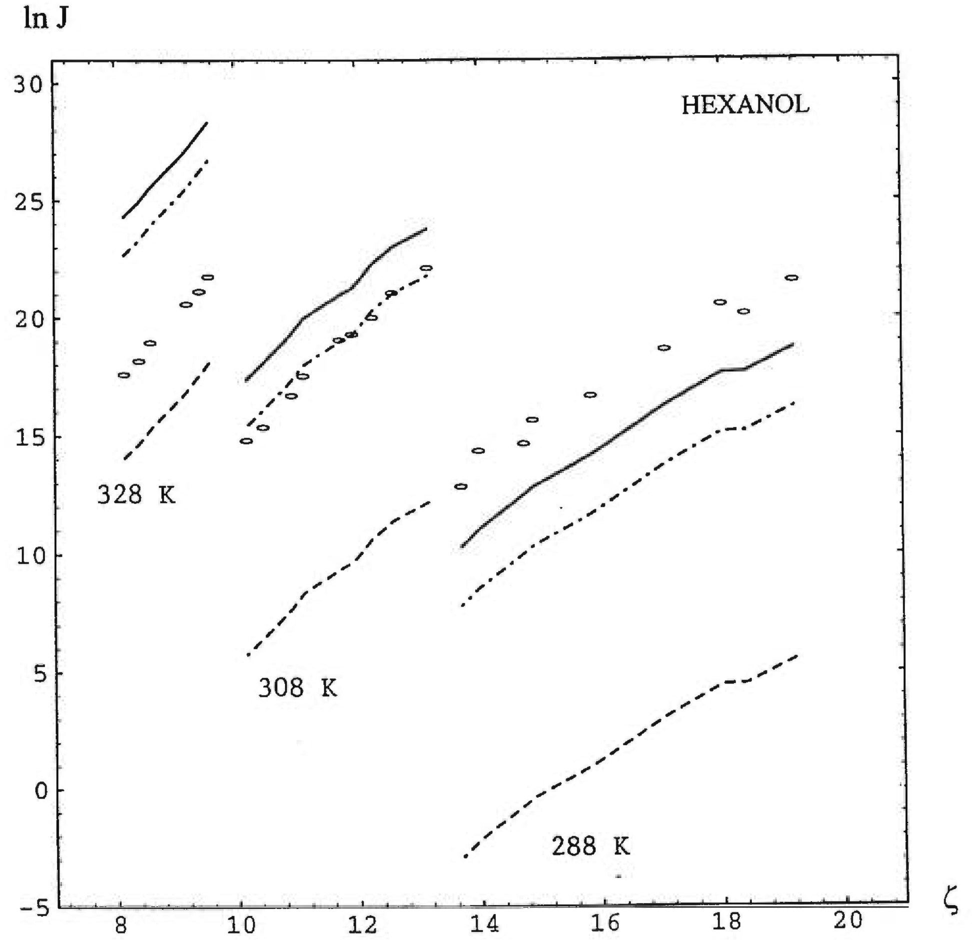

Figure 3. Logarithm of nucleation rate J for pure hexanol vapor plotted vs a supersaturation (activity) $\zeta = \zeta_2$. The dimension of J is $cm^{-3}s^{-1}$. The ellipses are the experimental data of Strey *et al.* (1986). The lines represent the nucleation rates calculated by using the classical nucleation rate expression (dashed lines, calculated by Strey *et al.* (1986)), the one-component analogue of the normalization factor of Kuni *et al.* (solid lines), and the normalization factor of Wilemski (dot-dashed lines). The initial (chamber) temperatures T_0 are indicated below the series. The corresponding nucleation temperatures are: about 258 K for T_0=288 K, about 276 K for T_0=308 K, and about 293 K for T_0=328 K.

CHAPITRE 2

Cinétique de la nucléation binaire non-isotherme

La cinétique de la nucléation binaire non-isotherme tient compte de l'influence des effets thermiques sur le processus de la condensation binaire. Ces effets sont causés par la chaleur de condensation. Les molécules du mélange de vapeurs absorbées par une particule de la nouvelle phase (i.e., par une goutte de la solution binaire liquide) lui transmettent de la chaleur de condensation, tandis que les molécules émises par la particule de la solution liquide lui enlèvent de la chaleur de condensation. Comme la particule croissante de la solution liquide absorbe plus de molécules qu'elle n'en émet, sa température moyenne augmente au fur et à mesure de sa croissance, la température du mélange de vapeurs étant constante. Cet échauffement de la particule liquide augmente sa faculté d'émettre des molécules. Par conséquent, il cause la diminution de la vitesse de nucléation et l'augmentation de la durée de la nucléation. De même, il influence la composition des particules liquides et d'autres caractéristiques du processus.

2.1 L'étape de la relaxation termique

La cinétique de la nucléation binaire non-isotherme est développée à partir de l'équation discrète du bilan décrivant l'échange de substance et d'énergie entre le mélange de vapeurs et les particules de solution liquide. Cette équation tridimensionnelle décrit l'évolution temporelle de la distribution de ces particules selon trois variables indépendantes: les nombres de molécules des deux composantes dans une particule liquide et sa température. En réduisant l'équation discrète du bilan à la forme différentielle, on obtient l'équation cinétique tridimensionnelle de la nucléation binaire non-isotherme. Dans le cas des chaleurs de condensation arbitraires, cette équation cinétique dépasse les bornes de l'approximation de Fokker et Planck. Seulement dans le cas où les chaleurs de condensation sont très petites par rapport à la fluctuation efficace de l'énergie d'une particule liquide, l'équation cinétique peut être réduite à celle de Fokker et Planck. Nous n'imposons pourtant aucune restriction sur les chaleurs de condensation et, par conséquent, l'équation cinétique à résoudre dépasse les bornes de l'approximation de Fokker et Planck.

L'analyse de l'équation cinétique permet de déterminer la hiérarchie des échelles de temps de la nucléation binaire non-isotherme. Cela rend possible de séparer et de décrire analytiquement l'étape de relaxation thermique pendant laquelle la distribution des gouttes selon la température s'approche d'une gaussienne, alors que leur distribution selon les nombres de molécules ne change guère.

2.1.1 Article 2: *Kinetic theory of nonisothermal binary nucleation: the stage of thermal relaxation*

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Kinetic theory of nonisothermal binary nucleation: the stage of thermal relaxation

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Abstract

A generalization of the method used in the kinetics of nonisothermal unary nucleation is proposed to construct the kinetic theory of nonisothermal binary nucleation allowing one to take account of the release of the latent heat of condensation. The three-dimensional balance equation describing the material and heat exchange of liquid solution particles with the surrounding vapor-gas medium is obtained. Independent variables in this equation are the numbers of molecules of each component in a liquid solution nucleus and its temperature. Going beyond the framework of the Fokker-Planck approximation is proposed for the corresponding kinetic equation. A hierarchy of time scales of nonisothermal binary nucleation is established and an analytical description of the thermal relaxation of the nuclei is given. Theoretical results are illustrated by numerical calculations for the nucleation in a water-ethanol system.

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1 Introduction

Binary condensation is a very widespread first-order phase transition and hence is of great interest in many fields. They usually distinguish three stages of any first-order phase transition. During the first of them nuclei of a new phase are formed (this stage is also called the stage of nucleation) which play the role of condensation centers afterwards. It is during the second stage that the phase transition takes place properly - the bulk of a metastable phase passes to a liquid phase. During the third stage the growth of large drops occurs to the detriment of small ones.

It is well known that nonisothermal effects can strongly influence a process of first-order phase transition, particularly a vapor-to-liquid transition. There exist different kinds of nonisothermal effects in the condensation.

First, the heating of the growing nuclei by the latent heat of condensation. This causes a reduction of the nucleation rate in two ways: 1) increasing the ability of the nuclei to emit molecules; 2) decreasing the metastability of vapor phase (owing to the increase in the temperature of condensing system).

Second, temperature fluctuations of nuclei exist even in the absence of matter exchange between the nuclei and the medium. They also influence the emissivity of nuclei.

Third, the nuclei as particles of condensed matter are thermally quasi-isolate from one another being surrounded by the rarefied vapor-gas medium. Consequently, the temperature of a nucleus decreases gradually during each event of emission of a molecule, while the molecule passes from the nucleus through its surface layer to the vapor. Therefore, the emissivity of the nucleus must be determined by some intermediate value of its temperature but neither by the initial one (before the emission event) nor by the final one (after the emission event).

At present, there exists a complete enough and adequate theoretical description of nonisothermal unary nucleation and condensation. Taking account of the release of latent heat, Kantrowitz (1951) obtained the differences between isothermal and nonisothermal nucleation rates, delay times and mean temperatures of nuclei, in terms of a one-dimensional model. Considering the size of a nucleus and its thermal energy as two independent continuous variables determining the state of the nucleus and taking into account the effect of release of latent heat, Feder *et al.* (1966) were the first to develop a two-dimensional kinetic theory of nonisothermal unary nucleation.

A nucleation cutoff being allowed for both by vapor depletion and by rise in temperature from the release of latent heat, Barrett and Clement (1991) derived and solved the coupled equations which give the changes in the aerosol size distribution and vapor saturation during the nucleation of aerosols from a supersaturated vapor. Barrett *et al.* (1993) presented a model of the influence of carrier gas on the nucleation process, based on the changes to the energy distribution of nuclei induced by collisions with carrier gas molecules. Possible differences in nucleus energy distributions between equilibrium and steady state were taken into account by Barrett (1994) in deriving a Fokker-Planck equation for the nucleus distribution in size and energy and presenting an analytical approach to obtaining the steady nucleation rate.

Taking account both of a latent heat release and of temperature fluctuations, Grinin and Kuni (1989) constructed a two-dimensional kinetic theory of nonisothermal nucleation on the basis of a two-dimensional balance equation (number of molecules in a nucleus and its thermal energy being there independent variables) obtained by them earlier in the paper published later (Grinin and Kuni, 1990). They proposed (Grinin and Kuni, 1989) a generalization of the Fokker - Planck approximation in the corresponding kinetic equation which allowed them to take into account large values of latent heat of condensation. They gave (Grinin and Kuni, 1989) the analytical description of the thermal relaxation of nuclei, their subsequent evolution and the final steady state itself. It should be noted that they also showed that the contributions to the nucleus emissivity arisen from the fluctuation and quasi-isolationship effects compensate one another.

Thermal effects in the kinetics of homogeneous condensation under dynamic conditions were taken into account by Kuni (1984,1988). In the kinetics of heterogeneous condensation under dynamic conditions, thermal effects were studied by Grinin *et al.* (1990). The influence of thermal and fluctuation effects on the condensation processes in the supercritical region of the nucleus sizes was investigated by Grinin *et al.* (1992).

Unlikely to the situation in the kinetic theory of the unary nucleation, the kinetic theory of the binary nucleation has been developed almost exclusively (except the recent work of Lazaridis and Drossinos (1997)) for the simplest case where one can neglect the nonisothermal effects of condensation, i.e. the deviation of the temperature of nuclei of liquid phase from the temperature of vapor-gas medium (Reiss, 1950; Stauffer, 1976; Shi and Seinfeld, 1990; Kuni *et al.*, 1990; Melikhov *et al.*, 1990,1991; Wilemski and Wyslouzil, 1995). However, the nucleus temperature has a strong influence on its ability to emit molecules of vapor mixture and, hence, on the whole nucleation process. Of course, the release of condensation heat can substantially increase the nucleus temperature only in the case where the quantity of carrier (passive) gas in the system is so small that its molecules have not sufficient time to take the released heat away from the nucleus. Carrier gas effects in the unary nucleation theory were well investigated by Ford (1992), Barrett *et al.* (1993), and Barrett (1994). It is also evident that the significance of thermal effects for the nucleation kinetics increases with increasing both the condensation heats and the vapor activities of condensable substances (as shown for the unary nucleation by Feder *et al.* (1966), Grinin and Kuni (1989), and Barrett (1994)).

In this work, we intend to develop a kinetic theory of binary nucleation taking into account the effect of latent heat release.

The deviation of the mean temperature of the nuclei from the temperature of the vapor-gas medium is due to the condensation process itself. The condensation heat transferred to a nucleus or extracted from it in individual events of absorption or emission of a vapor mixture molecule by a nucleus is not small in comparison with the rms fluctuation of the nucleus energy. Therefore, for the kinetic theory of the nonisothermal binary nucleation it will not be possible to use the Fokker-Planck approximation.

2 Balance equation

First, let us construct a three-dimensional balance equation of nonisothermal binary nucleation. Let us assume that the metastability of the vapor mixture is created instantaneously and does not change during the whole nucleation process. The temperature T_0 of the vapor mixture and the number density of passive gas molecules are also fixed. We also assume that there are not chemical reactions nor heterogeneous nucleating centers in the condensing system.

It is evident that there are three types of elementary interactions of a nucleus with the vapor-gas medium: 1) absorption of a molecule of 1st or 2nd components of the vapor mixture; 2) emission of a molecule of 1st or 2nd components of the vapor mixture; 3) reflection of a molecule of the vapor-gas medium.

The nuclei formed have so small sizes that the time of their internal relaxation processes are very small in comparison with the time between successive interactions of a nucleus with the vapor-gas medium, and the interactions themselves take place under a free-molecular regime. This allows us to assume that the nucleus attains its internal thermodynamical equilibrium before each successive interaction with the vapor-gas medium.

Let us choose the numbers ν_1 and ν_2 of molecules of 1st and 2nd component in a nucleus and its thermal energy E as its independent characteristics. The thermal energy E of a nucleus is linear in the temperature and will be measured from its value at the temperature T_0 of the vapor-gas medium. Expressing all the quantities which have the dimensions of energy in units of $k_B T_0$ (k_B is Boltzmann's constant), we have

$$E = (c_1\nu_1 + c_2\nu_2)[T/T_0 - 1], \tag{1}$$

where c_i $(i = 1, 2)$ is the molecular specific heat of i-component in a nucleus (all the specific heats are expressed in units of k_B).

Let ε be the thermal energy of molecules striking a nucleus and let ε' be the thermal energy of molecules reflected or emitted by a nucleus. Since the times of internal relaxation processes of nucleus are small, the number W_i^- $(i = 1, 2)$ of molecules of component i which a nucleus emits in unit time as well as the distribution w' of the emitted or reflected molecules with respect to their energy ε' are determined (in consideration of the thermal adaptation of reflected molecules) by the energy of nucleus:

$$W_i^- \equiv W_i^-(\nu_1, \nu_2, E) \ \ (i = 1, 2), w' \equiv w'(\nu_1, \nu_2, E|\varepsilon'). \tag{2}$$

Here the variables ν_1, ν_2, and E correspond to the state of the nucleus before the interaction and we have taken account that the temperature fluctuation effect and the effect of nucleus thermal quasi-isolationship compensate each other. Of course, the distribution $w(\varepsilon)$ of the molecules striking a nucleus with respect to their energy ε is determined by the temperature T_0 of the vapor-gas medium. For the distributions $w(\varepsilon)$ and $w'(\nu_1, \nu_2, E|\varepsilon')$ (which we assume being Maxwellian) we shall use the normalization relations

$$\int_0^\infty d\varepsilon w(\varepsilon) = 1, \quad \int_0^\infty d\varepsilon' w'(\nu_1, \nu_2, E|\varepsilon') = 1. \tag{3}$$

Let us denote by $g(\nu_1, \nu_2, E)$ the distribution of nuclei with respect to the variables ν_1, ν_2, and E at the time t (we shall not indicate the time dependence of values).

Denoting by $W_i(\nu_1, \nu_2)$ and β_i $(i = 1, 2)$ the number of molecules of component i being absorbed by a nucleus per unit time and, respectively, the molecular heat of condensation of component i, let us write the discrete balance equation governing the evolution of the distribution $g(\nu_1, \nu_2, E)$:

$$\frac{\partial g(\nu_1, \nu_2, E)}{\partial t} = D_1^+ + D_1^- + D_2^+ + D_2^- + \frac{1}{2}D_{g1} + \frac{1}{2}D_{g2}, \tag{4}$$

where

$$D_1^+ = \int_0^\infty d\varepsilon[W_1(\nu_1 - 1, \nu_2)w(\varepsilon)g(\nu_1 - 1, \nu_2, E - \beta_1 - \varepsilon) - \\ -W_1(\nu_1, \nu_2)w(\varepsilon)g(\nu_1, \nu_2, E)], \tag{5}$$

$$D_1^- = \int_0^\infty d\varepsilon'[W_1^-(\nu_1 + 1, \nu_2, E + \beta_1 + \varepsilon')w'(\nu_1 + 1, \nu_2, E + \beta_1 + \varepsilon'|\varepsilon') \times \\ g(\nu_1 + 1, \nu_2, E + \beta_1 + \varepsilon') - W_1^-(\nu_1, \nu_2, E)w'(\nu_1, \nu_2, E|\varepsilon')g(\nu_1, \nu_2, E)], \tag{6}$$

$$D_2^+ = \int_0^\infty d\varepsilon[W_2(\nu_1, \nu_2 - 1)w(\varepsilon)g(\nu_1, \nu_2 - 1, E - \beta_2 - \varepsilon) - \\ -W_2(\nu_1, \nu_2)w(\varepsilon)g(\nu_1, \nu_2, E)], \tag{7}$$

$$D_2^- = \int_0^\infty d\varepsilon'[W_2^-(\nu_1, \nu_2 + 1, E + \beta_2 + \varepsilon')w'(\nu_1, \nu_2 + 1, E + \beta_2 + \varepsilon'|\varepsilon') \times \\ g(\nu_1, \nu_2 + 1, E + \beta_2 + \varepsilon') - W_2^-(\nu_1, \nu_2, E)w'(\nu_1, \nu_2, E|\varepsilon')g(\nu_1, \nu_2, E)], \tag{8}$$

$$D_{gi} = \int_0^\infty \int_0^\infty d\varepsilon' d\varepsilon W_i^{ef}(\nu_1, \nu_2)[w(\varepsilon)w'(\nu_1, \nu_2, E - \varepsilon + \varepsilon'|\varepsilon') \times \\ g(\nu_1, \nu_2, E - \varepsilon + \varepsilon') - w(\varepsilon)w'(\nu_1, \nu_2, E|\varepsilon')g(\nu_1, \nu_2, E)], \tag{9}$$

$$W_i^{ef} = \frac{1 - \alpha_{ci}}{\alpha_{ci}}\alpha_{ti}W_i(\nu_1, \nu_2) + \frac{1}{2}\alpha_g W_g(\nu_1, \nu_2) \ \ (i = 1, 2), \tag{10}$$

α_{ci} and α_{ti} $(i = 1, 2)$ are the condensation (sticking) coefficient and coefficient of thermal adaptation, respectively, in a reflection event of i-component molecules;

α_g is the coefficient of thermal adaptation in a reflection event of passive gas molecules; $W_g(\nu_1, \nu_2)$ is the number of molecules of the passive gas striking a nucleus per unit time. It is evident that the sum $W_1^{ef} + W_2^{ef}$ would determine the total number of molecules reflected by a nucleus per unit time if α_{t1}, α_{t1}, and α_g were equal to 1.

Expanding eqs.(5)-(9) in Taylor series in the deviations of nucleus characteristics before the interaction from ν_1, ν_2 and E, effecting some simple transformations and then carrying out partial summing of series obtained, we can reduce eq.(4) to the form

$$\frac{\partial g(\nu_1, \nu_2, E)}{\partial t} = D_1 + D_2 + \frac{\partial}{\partial E} I_E, \tag{11}$$

where

$$D_1 = W_1(\nu_1 - 1, \nu_2) g(\nu_1 - 1, \nu_2, E - \beta_1) - W_1(\nu_1, \nu_2) g(\nu_1, \nu_2, E) +$$
$$+ W_1^-(\nu_1 + 1, \nu_2, E + \beta_1) g(\nu_1 + 1, \nu_2, E + \beta_1) - W_1^-(\nu_1, \nu_2, E) g(\nu_1, \nu_2, E), \tag{12}$$

$$D_2 = W_2(\nu_1, \nu_2 - 1) g(\nu_1, \nu_2 - 1, E - \beta_2) - W_2(\nu_1, \nu_2) g(\nu_1, \nu_2, E) +$$
$$+ W_2^-(\nu_1, \nu_2 + 1, E + \beta_2) g(\nu_1, \nu_2 + 1, E + \beta_2) - W_2^-(\nu_1, \nu_2, E) g(\nu_1, \nu_2, E), \tag{13}$$

$$I_E = - \left[\frac{\beta_1^2}{k_1} W_1 + \frac{\beta_2^2}{k_2} W_2 \right] \left(\frac{E}{c_1 \nu_1 + c_2 \nu_2} + \frac{\partial}{\partial E} \right) g(\nu_1, \nu_2, E), \tag{14}$$

$$\frac{1}{k_i} = \frac{\tilde{c}_i}{\alpha_{ci} \beta_i^2} [\alpha_{ci} + \alpha_{ti}(1 - \alpha_{ci}) + \alpha_g p_i] \quad (i = 1, 2), \tag{15}$$

$$p_i = \left(\frac{m_i}{m_g} \right)^{1/2} \frac{n_g c_g}{2 n_i \tilde{c}_i} \quad (i = 1, 2), \tag{16}$$

$\tilde{c}_i, m_i$, and n_i $(i = 1, 2)$ are the effective (in the sense of energy transfer to the nucleus) specific heat, mass, and number density of molecules , respectively, of component i of the vapor mixture; c_g, m_g, and n_g are the analogous values of the passive gas.

The terms D_1 and D_2 in eq.(11) describe the simultaneous transfer of both the substance and the condensation heat to the nuclei by the molecules of 1st and 2nd components, respectively.

The term $-\partial I_E/\partial E$ in eq.(11) describes the transfer of the kinetic and internal energies to the nuclei by all the molecules of the vapor-gas medium. Its form corresponds to the fulfillment of the condition

$$1/(c_1\nu_1 + c_2\nu_2)^{1/2} \ll 1 \tag{17}$$

which means a smallness of the energy transfer by the molecules of the vapor-gas medium in comparison with the rms fluctuation of the nucleus energy, since the value $(c_1\nu_1 + c_2\nu_2)^{1/2}$ represents, according to the thermodynamic theory of fluctuations, the rms fluctuation of a nucleus energy in the absence of substance exchange between the nucleus and the vapor mixture.

3 Kinetic equation of nonisothermal binary nucleation

Let us introduce the variable ξ instead of variable E as

$$\xi = \frac{E}{[2(c_1\nu_1 + c_2\nu_2)]^{1/2}} \tag{18}$$

and present the distribution $g(\nu_1, \nu_2, E)$ in the form

$$g(\nu_1, \nu_2, E) = [2\pi(c_1\nu_1 + c_2\nu_2)]^{-1/2} e^{-\xi^2} P(\nu_1, \nu_2, \xi), \tag{19}$$

where $P(\nu_1, \nu_2, \xi)$ is some function of ν_1, ν_2, ξ (and of t, too).

Since usually $\beta_i \gg 1$ $(i = 1, 2)$, the parameter

$$\tau_i = \frac{\beta_i}{[2(c_1\nu_1 + c_2\nu_2)]^{1/2}} \quad (i = 1, 2) \tag{20}$$

will not be small despite inequality (17). The parameter τ_i represents the relative condensation heat of component i per molecule, i.e. the condensation heat of component i per molecule expressed in units of rms fluctuation of the nucleus energy and divided by $\sqrt{2}$. Although τ_i is always less than 1, in order of magnitude $\tau_i \sim 1$.

Let us introduce the operator

$$\hat{L}_i \equiv -W_i F_i' - W_i \frac{\partial}{\partial \nu_i} \quad (i = 1, 2), \tag{21}$$

acting on ν_i-dependent functions (here $F_i' \equiv \partial F/\partial \nu_i$, and F is the free energy of formation of the nucleus with the characteristics ν_1, ν_2, and $E = 0$: $F \equiv F(\nu_1, \nu_2, E = 0)$). Let us define the values $\nu_{ic}, \Delta\nu_{ic}$ $(i = 1, 2)$ by the relations

$$F_i'|_{\nu_1=\nu_{1c},\nu_2=\nu_{2c}} = 0, \Delta\nu_{ic} = |2/F_{ii}''||_{\nu_1=\nu_{1c},\nu_2=\nu_{2c}} \quad (i = 1, 2). \tag{22}$$

The values ν_{1c}, ν_{2c} would determine the coordinates of the saddle point of the surface of free energy of nucleation in the isothermal theory. In the capillarity approximation

$$\Delta\nu_{ic}/\nu_{ic} \ll 1, \;\; 1/\Delta\nu_{ic} \ll 1 \quad (i = 1, 2). \tag{23}$$

Hereafter, we will be interested only in the neighborhood of the critical ("saddle") point $|\nu_1 - \nu_{1c}| <\sim \Delta\nu_{1c}$, $|\nu_2 - \nu_{2c}| <\sim \Delta\nu_{2c}$. This "near-critical region" is the most important one for the nucleation kinetics. In the near-critical region, $\Delta\nu_{ic}$ represents a characteristic scale of change of ν_i-dependent functions and, consequently, we have the operator estimate $\partial/\partial\nu_i \sim 1/\Delta\nu_{ic}$. On the other hand, $|F_i'| <\sim 1/\Delta\nu_{ic}$ $(i = 1, 2)$ in this region, according to eq.(22). Therefore, in the near-critical region, the second term on the RHS of eq.(21) is dominant and we have the following operator estimates:

$$\frac{1}{W_i}\hat{L}_i \sim \frac{\partial}{\partial \nu_i} \sim \frac{1}{\Delta\nu_{ic}} \quad (i = 1, 2). \tag{24}$$

Let us transform eq.(11) into a differential equation for the distribution $P(\nu_1, \nu_2, \xi)$ in the standard way, by expanding the terms D_1 and D_2 in Taylor series in the deviations of $\nu_i \pm 1$ from ν_i and $E \pm \beta_i$ from E $(i = 1, 2)$ and retaining only the leading terms in the small parameters $1/\Delta\nu_{1c}$ and $1/\Delta\nu_{2c}$:

$$\begin{aligned}\frac{\partial P}{\partial t} \;=\; & -\frac{\partial}{\partial \nu_1}\left(\hat{L}_1 - W_1 \sum_{m=1}^{\infty} \frac{\tau_1^m}{m!}\frac{\partial^m}{\partial \xi^m}\right) P - \frac{\partial}{\partial \nu_2}\left(\hat{L}_2 - W_2 \sum_{m=1}^{\infty} \frac{\tau_2^m}{m!}\frac{\partial^m}{\partial \xi^m}\right) P + \\ & + \sum_{m=1}^{\infty} \frac{(-1)^m}{m!}(\tau_1^m \hat{L}_1 + \tau_2^m \hat{L}_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m P - \\ & - \sum_{m \neq l=1}^{\infty} \frac{(-1)^l}{m!l!}(\tau_1^{m+l} W_1 + \tau_2^{m+l} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^l \frac{\partial^m}{\partial \xi^m} P + \\ & + \left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial \xi} - 2\xi\right)\frac{\partial}{\partial \xi} - \right. \\ & \left. - \sum_{m=2}^{\infty} \frac{(-1)^m}{m!m!}(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m \frac{\partial^m}{\partial \xi^m}\right] P. \end{aligned} \tag{25}$$

For simplicity, the independent arguments ν_1, ν_2 and ξ are omitted and τ_1 and τ_2 are assumed to be constant and equal to their magnitudes for the critical nucleus. The terms $\partial L_i P/\partial \nu_i$ $(i = 1, 2)$ in the RHS of eq.(25) have the second order of smallness in $1/\Delta\nu_{ic}$, but they will be important afterwards. According to eq.(19),characteristic values of ξ lie in the interval $|\xi| <\sim 1$ where we have the estimates

$$\partial/\partial\xi \sim \xi \sim 1. \tag{26}$$

Therefore, τ_1 and τ_2 are the expansion parameters in the series in m and l. Retaining all the terms of the series means that we extend the theory to values $\tau_i \sim 1$ $(i = 1, 2)$ and go beyond the framework of the Fokker-Planck approximation.

Let us establish a relative importance of the terms on the RHS of eq.(25), taking into account the estimates (24),(26), and $|F_i'| <\sim 1/\Delta\nu_{ic}$ $(i = 1, 2)$.

Since the 1st, 2nd and 3rd terms contain the operators $L_1, \partial/\partial\nu_1, L_2$, and $\partial/\partial\nu_2$, we conclude that their ratios to the last, fifth, term do not exceed $1/\Delta\nu_{1c}$ or $1/\Delta\nu_{2c}$ (which are much less than 1) in order of magnitudes.

Comparing the first member of the last term on the RHS of eq.(25) with the second member, we conclude that the first member is the main one in this term, because of the inequalities $(k_i + 1)/k_i > 1$ $(i = 1, 2)$ and factorial factors m!m!. One can also see that the ratio of the fourth term to the last term does not exceed the parameter

$$\Theta \equiv \frac{1}{2} \frac{k_1 k_2 (\tau_1^3 W_1 + \tau_2^3 W_2)}{(k_1+1)k_2\tau_1^2 W_1 + k_1(k_2+1)\tau_2^2 W_2}.$$

assumed to be much less than unity: $\Theta \ll 1$. Thus, we conclude that on the RHS of eq.(25) the last term is the main one.

Equation (25) governs the time evolution of the three-dimensional distribution P. The hierarchy of terms established above corresponds to the hierarchy of time scales in the development of the distribution P.

The eigenfunctions of the principal operator of the governing equation, i.e. of the operator of the dominant term on the RHS of eq.(25), are the Hermite polynomials $H_j \equiv H_j(\xi)(H_0 = 1, H_1 = 2\xi, H_2 = 4\xi^2 - 2, ...)$, satisfying the recursion relations

$$\frac{\partial}{\partial \xi} H_j = 2j H_{j-1}, \left(\frac{\partial}{\partial \xi} - 2\xi\right) H_j = -H_{j+1}. \tag{27}$$

Hence,

$$\left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial \xi} - 2\xi\right)\frac{\partial}{\partial \xi} - \right.$$
$$\left. - \sum_{m=2}^{\infty} \frac{(-1)^m}{m!m!}(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m \frac{\partial^m}{\partial \xi^m}\right] H_j = -j\lambda_j H_j, \tag{28}$$

where $j = 0, 1, 2, ...$ and

$$\lambda_j = 2\frac{k_1+1}{k_1}\tau_1^2 W_1 + 2\frac{k_2+1}{k_2}\tau_2^2 W_2 + (j-1)! \sum_{m=2}^{j} \frac{2^m(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)}{m!m!(j-m)!}. \tag{29}$$

We can conclude that $-j\lambda_j$ $(j = 0, 1, 2, ...)$ are the eigenvalues of the principal operator. They all are negative except that for $j = 0$ which is equal to 0. For $j = 0$ and $j = 1$ the sum over m in (29) is absent. Obviously, $\lambda_1 < \lambda_2 < ....$

The Hermite polynomials form a complete system of eigenfunctions satisfying the orthogonality and normalization relations

$$(H_j, H_k) = \delta_{jk} 2^j j! \quad (j, k = 0, 1, 2, ...), \tag{30}$$

where δ_{jk} is the Kronecker delta and the scalar product (Φ, Ψ) of function Φ and Ψ of ξ is defined as

$$(\Phi, \Psi) = \pi^{-1/2} \int_{-\infty}^{\infty} d\xi \, e^{-\xi^2} \Phi \Psi. \tag{31}$$

From eqs.(19),(31) and $H_0 = 1$ it follows that the two-dimensional distribution $f \equiv f(\nu_1, \nu_2)$ of the nuclei with respect to variables ν_1 and ν_2 is given by the equation $f = (H_0, P)$, i.e. the two-dimensional distribution f is the projection of the three-dimensional one P on H_0.

Let us take the projection of governing equation (25) on H_0. According to eqs.(27) and (30), only the first and second terms (which are the smallest ones, of order of $1/(\Delta\nu_{1c})^2$ or $1/(\Delta\nu_{2c})^2$) make contributions to this projection. Since $f = (H_0, P)$, we obtain

$$\frac{\partial f}{\partial t} = -\frac{\partial J_1}{\partial \nu_1} - \frac{\partial J_2}{\partial \nu_2}, \tag{32}$$

where

$$J_i = \left(H_0, \left(\hat{L}_i - W_i \sum_{m=1}^{\infty} \frac{\tau_i^m}{m!} \frac{\partial^m}{\partial \xi^m} \right) P \right) \quad (i = 1, 2) \tag{33}$$

is the flux (averaged over ξ) of nuclei along the ν_i-axis.

4 Stage of thermal relaxation

Retaining in the RHS of governing equation (25) only the leading term, we obtain

$$\frac{\partial P}{\partial t} = \left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial \xi} - 2\xi\right)\frac{\partial}{\partial \xi} - \right.$$
$$\left. - \sum_{m=2}^{\infty} \frac{(-1)^m}{m!m!}(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m \frac{\partial^m}{\partial \xi^m}\right] P. \tag{34}$$

The solution of eq.(34) is given, according to relations (28),(29), by

$$P = f + \sum_{j=1}^{\infty} e^{-j\lambda_j t} f_j H_j, \tag{35}$$

where f and f_j do not depend on ξ nor t and can be presented, by virtue of definition (31), as

$$f = (H_0, P) = (H_0, P|_{t=0}), f_j = (2^j j!)^{-1}(H_j, P|_{t=0}) \tag{36}$$

($P|_{t=0}$ is the three dimensional distribution P at $t = 0$). It follows from eq.(36) that f still represents the two-dimensional distribution with respect to ν_1, ν_2 and it does not change as long as P is governed by eq.(34). Therefore, eq.(34) describes the thermal relaxation of nuclei. The relaxation is described by the spectrum of times $1/j\lambda_j$ $(j = 1, 2, ...)$, which decrease with increasing j.

It is evident from eqs.(19) and (31) that if Φ is some function of the variable ξ, its average value Φ with respect to the variable ξ is determined as $\bar{\Phi} = (\Phi, P)/f$. Therefore, mean values with respect to ξ will also change together with P in the process of thermal relaxation.

At the end of the thermal relaxation, as follows from eq.(35), we have

$$P \simeq f \quad (t >\sim t_\xi), \tag{37}$$

$$t_\xi = 1/\lambda_1 = \frac{1}{2}\frac{k_1 k_2}{k_2(k_1+1)\tau_1^2 W_1 + k_1(k_2+1)\tau_2^2 W_2}, \tag{38}$$

where t_ξ is the principal thermal relaxation time. Since f does not depend on ξ and taking eqs.(19),(37) into account, we can conclude that the distribution of nuclei with respect to the temperature approaches a quasiequilibrium Gaussian distribution by the end of the thermal relaxation stage, the duration of which is given by the time t_ξ.

Let us denote by t_ν the characteristic time of change of two-dimensional distribution f. In order to obtain an estimate for t_ν at the end of the stage of thermal relaxation, let us replace P by f in eq.(33) (it is correct enough by virtue of eq.(37)) and then substitute J_1 and J_2 in eq.(32). Using estimates (24), one can obtain for t_ν:

$$t_\nu \sim \frac{(\Delta\nu_{1c})^2(\Delta\nu_{2c})^2}{W_1(\Delta\nu_{2c})^2 + W_2(\Delta\nu_{1c})^2}. \tag{39}$$

Accordingly, we have:

$$\frac{t_\xi}{t_\nu} \sim \frac{1}{2}\frac{k_1k_2\,[W_1/(\Delta\nu_{1c})^2 + W_2/(\Delta\nu_{2c})^2]}{(k_1+1)k_2\tau_1^2W_1 + k_1(k_2+1)\tau_2^2W_2} \ll 1. \tag{40}$$

This inequality expresses the hierarchy of time scales which has allowed us to separate the thermal relaxation stage. During this stage the distribution of nuclei with respect to the variable ξ approaches the quasiequilibrium distribution, while the distribution with respect to ν_1 and ν_2 practically does not change.

The quasiequilibrium distribution is an eigenfunction of the principal operator of governing equation (25) with zero eigenvalue. Therefore, as follows from eq.(37), the operators of the first four terms on the RHS of eq.(25) also become important at the end of the stage of thermal relaxation.

5 Numerical calculations

To illustrate our theoretical results by numerical calculations we considered the binary nucleation in the vapor mixture of water (1st component) and ethanol (2nd component) at $T_0 = 293.15$ K. Air at the normal atmospheric pressure was chosen as carrier gas. All the physical properties of both components required for calculations are well determined for both liquid and vapor phases. Besides, accurate fits of several thermodynamic properties vs. composition are required

Table 1.

Main theoretical characteristics of the nonisothermal nucleation on the stage of thermal relaxation for the water(1)-ethanol(2) system at $T_0 = 293.15$ K (air at the normal atmospheric pressure being a carrier gas); α_{ci} and α_{ti} are the sticking and thermal accommodation coefficients of component i; α_g is the thermal accommodation coefficient of carrier gas; ζ_i and τ_i are the vapor activity and the molecular relative condensation heat of component i; t_ξ and t_ν are the time of thermal relaxation and the characteristic time of change of the distribution of nuclei with respect to numbers of molecules.

	$\alpha_{t1} = 1,\ \alpha_{t2} = 1$							
	$\alpha_g = 1$							
	$\alpha_{c1} = 1,\ \alpha_{c2} = 1$				$\alpha_{c1} = 0.5,\ \alpha_{c2} = 0.5$			
ζ_1	1.4		1.5		1.4		1.5	
ζ_2	1.0	1.25	1.0	1.25	1.0	1.25	1.0	1.25
τ_1	0.34	0.39	0.39	0.44	0.34	0.39	0.39	0.44
τ_2	0.33	0.38	0.37	0.42	0.33	0.38	0.37	0.42
t_ξ, ns	0.93	0.74	0.84	0.68	1.68	1.33	1.51	1.23
t_ν, μs	0.04	0.06	0.03	0.04	0.08	0.11	0.06	0.07

	$\alpha_{c1} = 0.5,\ \alpha_{c2} = 0.5$							
	$\alpha_{t1} = 0.5,\ \alpha_{t2} = 0.5$							
	$\alpha_g = 0.5$				$\alpha_g = 0.1$			
ζ_1	1.4		1.5		1.4		1.5	
ζ_2	1.0	1.25	1.0	1.25	1.0	1.25	1.0	1.25
t_ξ, ns	1.85	1.46	1.66	1.34	2.00	1.57	1.79	1.43

	$\alpha_{c1} = 0.5,\ \alpha_{c2} = 0.5$							
	$\alpha_{t1} = 0.1,\ \alpha_{t2} = 0.1$							
	$\alpha_g = 0.5$				$\alpha_g = 0.1$			
ζ_1	1.4		1.5		1.4		1.5	
ζ_2	1.0	1.25	1.0	1.25	1.0	1.25	1.0	1.25
t_ξ, ns	1.86	1.47	1.67	1.35	2.02	1.58	1.81	1.44

for water (1) - ethanol (2) liquid solution and they are fortunately also available.

The specific heats of pure water and ethanol in liquid and vapor phases were determined with the help of formulas given in *Thermophysical Properties of Matter* (1970). The latent heat of pure water was calculated from the formula given by Feder *et al.* (1966) and that of pure ethanol was obtained by linearly extrapolating data in *CRC Handbook of Chemistry and Physics* (1992-1993). The equilibrium vapor pressure of pure water was taken from *CRC Handbook of Chemistry and Physics* (1992-1993), and that of pure ethanol was calculated from the formula given by Mirabel and Katz (1977). The partial molar volumes v_1 and v_2 of pure liquid water and ethanol, respectively, were computed from the density values given by *CRC Handbook of Chemistry and Physics* (1992-1993) and the the volume V of the nucleus was related to v_1 and v_2 as $V = \nu_1 v_1 + \nu_2 v_2$. As for the surface tension σ of water-ethanol liquid solution, we, following Wilemski (1987), fitted $\ln \sigma$ with a third-order polynomial in the variable $4(1-\chi)/(4-3\chi)$, using data in Timmermans (1960). Following Mirabel and Katz (1977) and Wilemski (1987), the liquid phase activity coefficients were determined from the three-parameter Redlich-Kister equation of d'Avila and Silva (1970).

Since there exist no theoretical nor experimental data on the thermal accommodation and sticking coefficients, calculations were carried out at various values of $\alpha_{ci}, \alpha_{ti}\,(i = 1, 2)$, and α_g in order to illustrate the influence of these parameters on theoretical predictions. To illustrate the dependence of theoretical predictions on the degree of vapor mixture metastability, calculations were performed for four couples of water and ethanol activities ζ_1, ζ_2 at each set of coefficients $\alpha_{ci}, \alpha_{ti}\,(i = 1, 2)$, and α_g (activity $\zeta_i\,(i = 1, 2)$ is defined as $\zeta_i = n_i/n_{si}$, where n_i is the number density of i-component molecules in the vapor mixture, and n_{si} is the equilibrium number density of i-component molecules in a vapor saturated over the pure bulk liquid of this component). Results of calculations are presented in Table 1.

Since the values $\tau_i\,(i = 1, 2)$ do not depend on $\alpha_{ci}, \alpha_{ti}\,(i = 1, 2)$, and α_g and the time t_ν does not depend on $\alpha_{t1}, \alpha_{t2}, \alpha_g$, we presented τ_i $(i = 1, 2)$, and t_ν only in the first part of Table 1.

Figure 1 shows the time dependence of the first mode of the deviation $P - f$ of the distribution of nuclei with respect to the temperature from a Gaussian equilibrium distribution at the stage of thermal relaxation not only for the binary nucleation in the water-ethanol system (using equation (35)) but also for the unary nucleation of pure water vapor (according to Grinin and Kuni (1989)). According to eq.(35) and to the analogous equation of the one-component theory (Grinin and Kuni, 1989), the first mode of the deviation $P - f$ corresponds to the greatest relaxation time (t_ξ) and, therefore, is the slowest (the most "long-lived") mode of $P - f$. The second mode decreases with time about three times as fast as the first one. Air at the normal atmospheric pressure was a carrier gas in both system and the thermal accommodation coefficients of both water and ethanol were equal to 1. Figure 1a corresponds to the binary system and Figure 1b represents the nucleation of pure water. The curves of series **A** were obtained for the case where the sticking coefficients α_{c1} and α_{c2} of water and ethanol were both equal to 0.5; series **B** corresponds to the case where α_{c1} and α_{c2} were both equal to 0.1. In each series, the values of the thermal accommodation coefficient of air were taken as follows: $\alpha_g = 1$ for the boldest (lower) curve; $\alpha_g = 0.5$ for the dashed (medium) curve; $\alpha_g = 1$ for the thinnest (upper) curve. According to Fig.1, the supersaturation (activity) of pure water vapor has to be equal to about 3.5 so that the time of thermal relaxation of the unary nucleation should be the same as (or close to) the time of thermal relaxation of the binary nucleation of water and ethanol at the activities $\zeta_1 = 1.5$ and $\zeta_2 = 1.0$.

As shown in Section 3, the strong inequalities $\tau_1 \ll 1$ and $\tau_2 \ll 1$ are necessary for the validity of the Fokker-Planck approximation in kinetic equation (25). Since under the considered external conditions the molecular relative condensation heats τ_1 and τ_2 of water and ethanol are not much less than 1, going beyond the Fokker-Planck approximation is quite founded.

Numerical calculations show that Θ is less than 0.2, that is, the strong inequality $\Theta \ll 1$ is well satisfied. Therefore, the transition from eq.(25) to eq.(34) is quite founded. Table 1 clearly confirms the strong inequality (40) reflecting the established hierarchy of time scales of the development of the distribution P. Table 1 also shows a strong dependence of the duration t_ξ of thermal relaxation stage on the sticking coefficients α_{c1} and α_{c2}; this is due both to the linear dependence of $W_i\,(i = 1, 2)$ on α_{ci} and to the dependence of $k_i\,(i = 1, 2)$ on α_{ci} in eq.(38). The dependence of t_ξ on α_g is significantly weaker and t_ξ is almost unsensitive to the thermal accommodation coefficients α_{t1} and α_{t2} of reflected vapor molecules (at least, when p_1 and p_2 are greater than or of the order of some units).

Note that, according to eqs.(15),(16), the dependence of the theory on the quantity of carrier gas in the system is implemented through the product $\alpha_g n_g$. This means that the time t_ξ of thermal relaxation identically depend on α_g and n_g. Therefore, Table 1 and Figure 1 allow us to conclude that the greater is the number density of carrier gas molecules, the faster is the thermal relaxation of nuclei and hence the weaker is the influence of the release of condensation heat on the nucleation. Such a dependence is in accordance with the results of Barrett (1994) and Barrett *et al.* (1993) for the one-component nucleation. According to Table 1, there exists also a very weak dependence of the time of thermal relaxation on the activities of condensable components: t_ξ decreases slightly with increasing ζ_1 and ζ_2 (of course, this does not mean at all any decrease of the influence of thermal effects on the nucleation).

6 Conclusions

Taking account of the increase in the nucleus temperature due to the latent heat of condensation, we have considered the homogeneous binary nucleation in the case of instantaneous creation of a metastable vapor mixture.

First, we have constructed the discrete balance equation (4) for the time evolution of the three-dimensional distribution of nuclei with respect to the numbers of molecules of both species in the nucleus and its temperature. That balance equation takes into account all the possible types of elementary interactions of the nucleus with the vapor-gas medium: both the absorption and emission of a molecule of 1st or 2nd components of the vapor mixture and the reflection of a molecule of the vapor-gas medium.

Next, reducing balance equation (4) to a continual form, we have obtained three-dimensional kinetic equation (25) of the nonisothermal binary nucleation reaching beyond the framework of the Fokker-Planck approximation. Our kinetic equation (25) governs the time evolution of the three-dimensional distribution not only in the case where the latent heats per molecule for both components are much less than the rms equilibrium fluctuation of the nucleus energy, but also in the case where these latent heats are of the same order of magnitude as the rms fluctuation of the nucleus energy. The kinetic equation of Lazaridis and Drossinos (1997) describes only the first of these situations: the Fokker-Planck approximation in the case of small latent heats of both components becomes acceptable and our kinetic equation (25) can then be reduced to theirs.

Conditions (23) of the capillarity approximation being fulfilled, we have established the hierarchy of the terms on the RHS of eq.(25). Such a hierarchy corresponds to the hierarchy of time scales in the development of the three-dimensional distribution of nuclei (expressed by strong inequality (40)). This is what has allowed us to separate the stage of thermal relaxation of nuclei. At that stage the distribution of nuclei with respect to the temperature approaches a quasiequilibrium Gaussian distribution, while the distribution with respect to the numbers of molecules ν_1 and ν_2 practically does not change. The three dimensional distribution at the stage of thermal relaxation is given by eq.(35) obtained by solving the kinetic equation (34) to which is reduced eq.(25) at this stage.

The theoretical results have been illustrated by numerical calculations for the nucleation in the water-ethanol system with air as a carrier gas for various values of sticking and thermal adaptation coefficients. Numerical results are presented by Table 1 and Figure 1. Calculations have shown that, as expected, condition (40) of hierarchy of time scales is well fulfilled. This means that, as known from the one-component theory of Grinin and Kuni (1989), the thermal relaxation of the nuclei occurs much faster than the evolution with respect to numbers of molecules in the nucleus. The influence of the quantity of carrier gas on the importance of thermal effects is also predicted to be similar to that of the one-component theory (Barrett, 1994; Barrett *et al.*, 1993): the greater is the carrier gas pressure, the slighter is the influence of the release of condensation heat on the nucleation. At present, it is not possible to make a comparison between our theoretical predictions and experimental data because even the most modern experimental methods (Strey and Viisanen, 1993; Viisanen *et al.*, 1994; Viisanen *et al.*, 1997)can not provide any data about the time dependence of the distribution of binary nuclei with respect to the temperature. Evidently, such a comparison will be necessary to do when appropriate experimental data become available. Besides, it would be very interesting to compare the predictions (concerning the time of thermal relaxation t_ξ) of the theory developed with results that can be obtained with the help of the method of numerical solution of birth-death equations proposed by Wyslouzil and Wilemski (1995).

In order to describe the evolution of the system after the stage of thermal relaxation (that is, for $t >\sim t_\xi$) and to obtain an exact expression for the rate of binary nonisothermal nucleation with the help of relation (33), we have to solve the eq.(25) taking account of all the terms on its RHS. These problems will be objects of our further research. Of course, as long as there are no experimental nor theoretical data about sticking and thermal accommodation coefficients α_{ci}, α_{ti} $(i = 1,2), \alpha_g$, theoretical predictions will remain uncertain enough. Nevertheless, we will be able to get approximative magnitudes of these coefficients by making a comparison between theoretical predictions and experimental data on nucleation rates.

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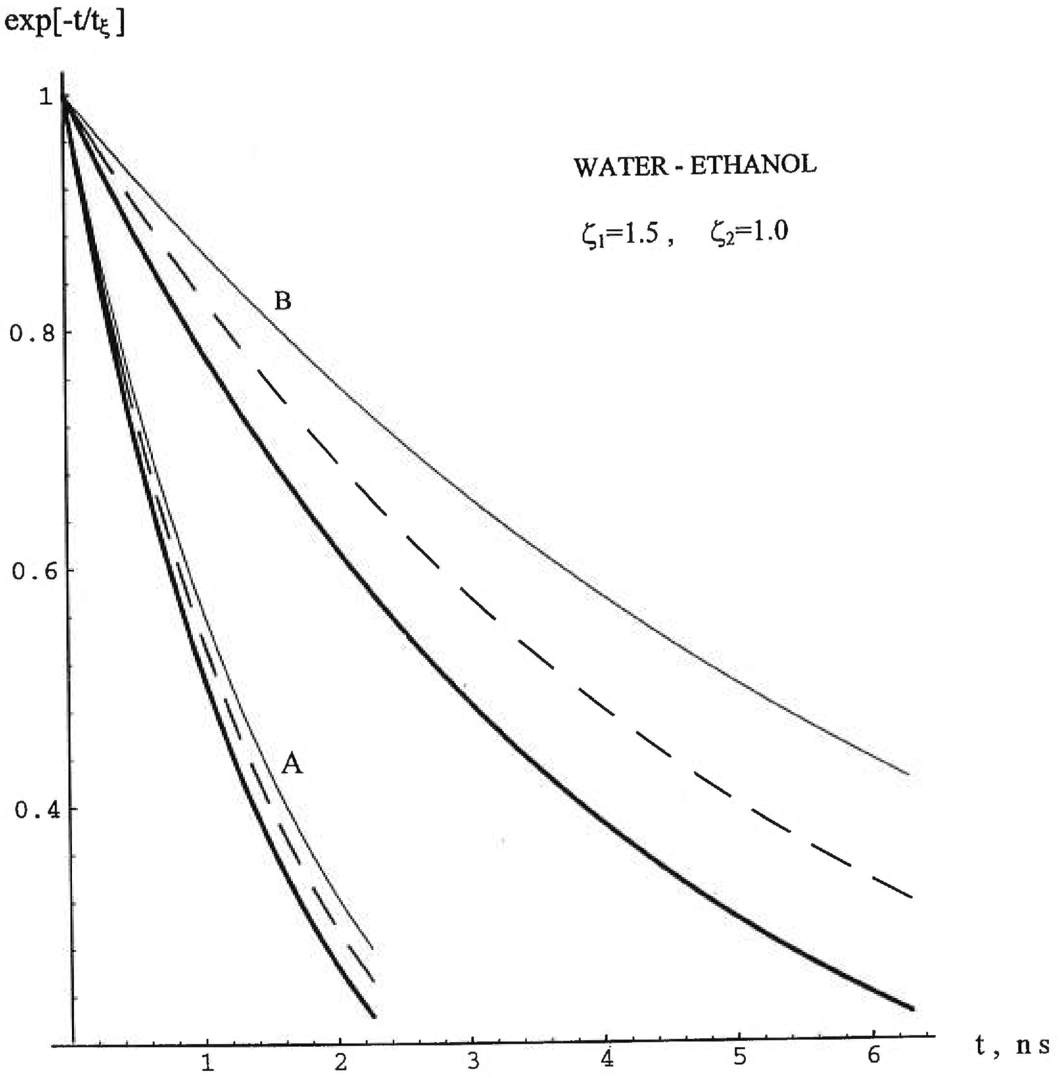

Figure 1a. Thermal relaxation stage of the binary nucleation in the water(1)-ethanol(2) system the activities being $\zeta_1 = 1.5$ and $\zeta_2 = 1.0$ at $T_0 = 293.15$ K with air as a carrier gas. The curves show the time dependence of the slowest (first) mode of the deviation $P - f$ of the distribution of nuclei with respect to temperature from a quasiequilibrium Gaussian distribution (equation (38)). Series **A** corresponds to the sticking coefficients $\alpha_{c1} = 0.5$ and $\alpha_{c2} = 0.5$; series **B** corresponds to $\alpha_{c1} = 0.1$ and $\alpha_{c2} = 0.1$. In each series, the values of the thermal accommodation coefficient of air are: $\alpha_g = 1$ for the boldest (lower) curve; $\alpha_g = 0.5$ for the dashed (medium) curve; $\alpha_g = 0.1$ for the thinnest (upper) curve.

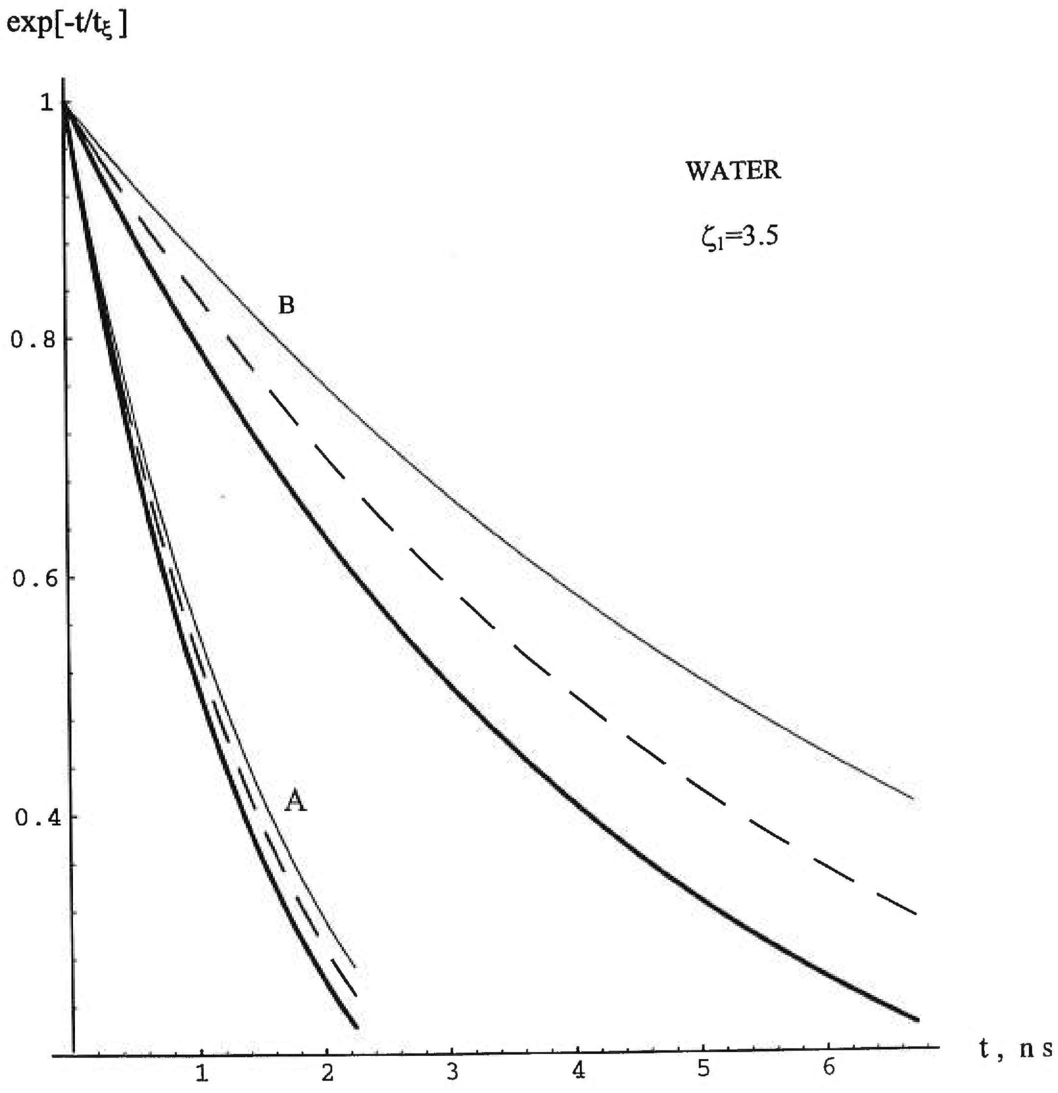

Figure 1b. Thermal relaxation stage of the unary nucleation of pure water at $\zeta_1 = 3.5$, $T_0 = 293.15$ K with air as a carrier gas. The curves show the time dependence of the slowest (first) mode of the deviation $P - f$ of the distribution of nuclei with respect to temperature from a quasiequilibrium Gaussian distribution (equation (38)). Series **A** corresponds to the sticking coefficient $\alpha_{c1} = 0.5$; series **B** corresponds to $\alpha_{c1} = 0.1$. In each series, the values of the thermal accommodation coefficient of air are: $\alpha_g = 1$ for the boldest (lower) curve; $\alpha_g = 0.5$ for the dashed (medium) curve; $\alpha_g = 0.1$ for the thinnest (upper) curve.

2.2 L'étape suivant la relaxation thermique

À l'étape suivant la relaxation thermique, l'équation cinétique tridimensionnelle peut être résolue en utilisant successivement la méthode de Chapman et Enskog et celle de séparation complète des variables. L'application successive de ces deux méthodes permet de réduire notre équation cinétique à l'équation monodimensionnelle de Fokker et Planck dont les coefficients contiennent toute l'information sur les effets thermiques. L'analyse d'une telle équation est bien connue. Ainsi toutes les caractéristiques de la nucléation binaire non-isotherme peuvent être déterminées. Ici nous présentons les caractéristiques stationnaires: la distribution tridimensionnelle des gouttes, la vitesse de nucléation, la composition et la température moyennes des gouttes.

2.2.1 Article 3: *Kinetic theory of nonisothermal binary nucleation: the stage following thermal relaxation*

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Kinetic theory of nonisothermal binary nucleation: The stage following thermal relaxation

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Abstract

A kinetic theory is constructed for a nonisothermal binary nucleation at the stage following the thermal relaxation of nuclei. The three-dimensional kinetic equation to be solved reaches beyond the framework of the Fokker-Planck approximation even if one of two components has a large value of condensation heat. It is shown that, by successively applying the method of Enskog-Chapman and the method of complete separation of variables to that kinetic equation, one can reduce the problem of constructing the three-dimensional kinetic theory to the well investigated problem of solving an one-dimensional kinetic equation of first-order phase transition, in the non-stationary case as well as in the stationary one. For the steady state, the main characteristics of nucleation, including the nucleation rate, are found. Theoretical results are numerically evaluated for the nucleation in ethanol-hexanol system and compared with predictions of classical (isothermal) theory and experimental data.

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1 Introduction

Binary nucleation is the first stage of any first order phase transition in two-component systems, in particular, of the binary condensation consisting of the formation and growth of drops of a liquid solution of two substances in a metastable mixture of vapors of these substances. During the nucleation the nuclei of a liquid phase are formed. They play the role of condensation centers afterwards.

At present, there exists an adequate theoretical description of main aspects of one-component nucleation. At the same time the kinetic theory of binary nucleation has been developed almost exclusively for the case where the metastability of two-component vapor mixture is created instantaneously and both thermal effects of condensation and presence of heterogeneous nucleation centers are neglected (Reiss [1]; Stauffer [2]; Shi and Seinfeld [3]; Wilemski and Wyslouzil [4]). However, it is well known, that heterogeneous nucleation can occur at much lower degrees of metastability than the homogeneous one. Besides, as follows from the nonisothermal one-component nucleation theory (Kantrowitz [5]; Feder *et al.* [6]; Grinin and Kuni [7]; Barrett and Clement [8]; Barrett [9]), nonisothermal effects can have a substantial influence on the kinetics of the process.

As discussed earlier (Djikaev *et al.* [10]) there exist several kinds of nonisothermal effects, but the most important of them is the effect due to the condensation heat transferred to a nucleus or extracted from it in all individual events of absorption or emission of a vapor molecule by a nucleus. As first pointed out by Feder *et al.* [6], in the case of one-component nucleation that effect can diminish the nucleation rate as many as hundreds of times relatively to the nucleation rate in the isothermal theory. Such a decrease is physically easy explained. Firstly, the temperature of a growing nucleus gradually increases with the growth of its size because of the release of the condensation heat. The increase in the temperature of nucleus causes an increase in its ability to emit molecules what naturally slows down its growth. Secondly, the increase in the temperature of nuclei causes an increase in the average temperature of vapor-gas medium and this is what decreases the metastability (supersaturation) of the condensing system.

Obviously, in the case of binary nucleation the thermal effect influences the nucleation rate in the same ways as mentioned above. Therefore, the nonisothermal nucleation rate should be less than the isothermal (classical) one. That is why it is not easy to explain the result of Lazaridis and Drossinos [11]: following the approach developed earlier by Langer [12] and extending the Barrett's [9] analysis of the one-component nucleation to the binary nucleation, they obtained an explicit analytical expression for the total rate of steady-state binary nonisothermal nucleation, but when applied to the water-ethanol system, their model predicts a nucleation rate that is higher than the classical (isothermal) nucleation rate.

As pointed out by many authors (Wyslouzil *et al.*, [13]; Wilemski and Wyslouzil, [4]), the classical (isothermal) theory of binary nucleation predicts nucleation rates much higher than experimental results (including the water-alcohol systems, in the cluster models of Flageollet-Daniel *et al.* [14] and Laaksonen [15]). Although most of those authors agree that those discrepancies are the most probably accounted for by the effect of surface enrichment (Mirabel and Katz [16]; Wilemski [17,18]; Flageollet-Daniel *et al.* [14]; Laaksonen [15]), taking account of thermal effects, nevertheless, can improve an agreement between theoretical predictions and experimental data on the nucleation rate. Evidently, such an improvement will be noticeable only if the quantity of the carrier gas in the system during experiments is not sufficient to ensure the constancy of nucleus mean temperature (an extensive treatment of carrier-gas effects is given by Ford [19] and Barrett *et al.* [20]).

In this paper we continue to develop the approach to the kinetic theory of nonisothermal binary nucleation proposed by Djikaev *et al.* [10] on the basis of the method developed by Grinin and Kuni [7] in constructing a kinetic theory of nonisothermal one-component nucleation. As shown by Djikaev *et al.* [10], that approach allows one to analytically describe the stage of thermal relaxation of nuclei at which their distribution with respect to the temperature approaches a quasiequilibrium Gaussian distribution while their distribution with respect to numbers of both components practically does not change. In this paper we will analytically describe both the subsequent evolution (after the stage of thermal relaxation) of nuclei and the final steady state of system. Theoretical results will be numerically evaluated and compared with experimental data and predictions of isothermal theory.

2 Kinetic equation of nonisothermal binary nucleation

Let ν_i $(i = 1, 2)$ be the number of i-component molecules in a nucleus, and let E be the thermal energy of such a nucleus. The thermal energy is linear in the temperature T of a nucleus and is measured from its value at $T = T_0$, where T_0 is the temperature of the vapor-gas medium. Expressing all values having the dimensions of energy in units of k_BT_0 (k_B is Boltzmann's constant), we have

$$E = (c_1\nu_1 + c_2\nu_2)[T/T_0 - 1], \tag{1}$$

where c_i $(i = 1, 2)$ is the molecular specific heat of component i in the nucleus (all specific heats are expressed in units of k_B).

Choosing the values ν_1, ν_2, and E as independent characteristics of the nucleus, let us denote by $g(\nu_1, \nu_2, E, t)$ the distribution of the nuclei with respect to the variables ν_1, ν_2, and E at the time t. Introducing the variable ξ as

$$\xi = E/[2(c_1\nu_1 + c_2\nu_2)]^{1/2}, \tag{2}$$

let us present the distribution $g(\nu_1, \nu_2, E, t)$ in the form

$$g(\nu_1, \nu_2, E, t) = [2\pi(c_1\nu_1 + c_2\nu_2)]^{-1/2}e^{-\xi^2}P(\nu_1, \nu_2, \xi), \tag{3}$$

where $P(\nu_1, \nu_2, \xi, t)$ is a function of ν_1, ν_2, ξ, and t.

Following the approach of Feder *et al.* [6] and that of Grinin and Kuni [7] to the construction of the kinetic equation of nonisothermal one-component nucleation, Djikaev *et al.* [10] obtained the equation governing the time evolution of the function $P(\nu_1, \nu_2, \xi, t)$:

$$\begin{aligned}
\frac{\partial P}{\partial t} = & -\frac{\partial}{\partial \nu_1}\left(\hat{L}_1 - W_1 \sum_{m=1}^{\infty} \frac{\tau_1^m}{m!}\frac{\partial^m}{\partial \xi^m}\right) P - \frac{\partial}{\partial \nu_2}\left(\hat{L}_2 - W_2 \sum_{m=1}^{\infty} \frac{\tau_2^m}{m!}\frac{\partial^m}{\partial \xi^m}\right) P + \\
& + \sum_{m=1}^{\infty} \frac{(-1)^m}{m!}(\tau_1^m \hat{L}_1 + \tau_2^m \hat{L}_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m P - \\
& - \sum_{m \neq l=1}^{\infty} \frac{(-1)^l}{m!l!}(\tau_1^{m+l} W_1 + \tau_2^{m+l} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^l \frac{\partial^m}{\partial \xi^m} P + \\
& + \left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial \xi} - 2\xi\right)\frac{\partial}{\partial \xi} - \right. \\
& \left. - \sum_{m=2}^{\infty} \frac{(-1)^m}{m!m!}(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m \frac{\partial^m}{\partial \xi^m}\right] P.
\end{aligned} \tag{4}$$

where, for simplicity of the notation, the independent arguments ν_1, ν_2, ξ, and t are omitted and

$$\hat{L}_i \equiv -W_i F_i' - W_i \frac{\partial}{\partial \nu_i} \quad (i = 1, 2), \tag{5}$$

$$\tau_i = \frac{\beta_i}{[2(c_1\nu_1 + c_2\nu_2)]^{1/2}} \quad (i = 1, 2), \tag{6}$$

$$\frac{1}{k_i} = \frac{\tilde{c}_i}{\alpha_{ci}\beta_i^2}[\alpha_{ci} + \tilde{\alpha}_i(1 - \alpha_{ci}) + \alpha_g p_i], \; p_i = \left(\frac{m_i}{m_g}\right)^{1/2} \frac{n_g c_g}{2 n_i \tilde{c}_i} \quad (i = 1, 2). \tag{7}$$

Here W_i and β_i $(i = 1, 2)$ are the number of i-component molecules being absorbed by a nucleus per unit time and the condensation heat of component i per molecule, respectively; α_{ci} and α_{ti} $(i = 1, 2)$ are the condensation (sticking) coefficient and the coefficient of thermal adaptation in a reflection event of i-component molecules, respectively; α_g is the coefficient of thermal adaptation in a reflection event of passive gas molecules ; $\tilde{c}_i, m_i$, and n_i $(i = 1, 2)$ are the effective (in the sense of energy transfer to the nucleus) specific heat, mass and number density of molecules of component i of the vapor mixture, respectively;c_g, m_g, and n_g are the analogous quantities for the passive gas; $F_i' \equiv \partial F/\partial \nu_i$, F being the free energy of formation of a nucleus in the thermal equilibrium with the medium, i.e. with the characteristic $E = 0$.

Retaining all terms of the series in the RHS of eq.(4) means extending the theory to values $\tau_i \sim 1 \;\; (i = 1, 2)$ and thus going beyond the framework of the Fokker-Planck approximation. If both τ_1 and τ_2 are much smaller than 1, the Fokker-Planck approximation becomes acceptable and eq.(4) can be reduced to the kinetic equation of Lazaridis and Drossinos [11].

In the case of one-component nucleation where either $\hat{L}_2 = 0$, $\tau_2 = 0$ or $\hat{L}_1 = 0$, $\tau_1 = 0$ (i.e. only one component is present in the system), eq.(4) transforms itself into the kinetic equation of nonisothermal one-component nucleation of Kuni and Grinin [7].

In the variables ν_1 and ν_2, we are interested only in the near-critical region $|\nu_i - \nu_{ic}| <\sim \Delta\nu_{ic} \;\; (i = 1, 2)$, which is the most important one for the nucleation kinetics; the parameters ν_{ic} and $\Delta\nu_{ic}$ are defined as

$$F_i'|_{\nu_1=\nu_{1c},\nu_2=\nu_{2c}} = 0, \Delta\nu_{ic} = |2/F_{ii}''||_{\nu_1=\nu_{1c},\nu_2=\nu_{2c}} \;\; (i = 1, 2). \tag{8}$$

The values ν_{1c}, ν_{2c} would determine the coordinates of the saddle point of the surface of free energy of nucleation in the isothermal theory. Within the framework of the capillarity approximation

$$\Delta\nu_{ic}/\nu_{ic} \ll 1, \;\; 1/\Delta\nu_{ic} \ll 1 \quad (i = 1, 2). \tag{9}$$

As in the near-critical region $|F_i'| <\sim 1/\Delta\nu_{ic} \;\; (i = 1, 2)$, the following operator estimates can be obtained for that region:

$$\frac{1}{W_i}\hat{L}_i \sim \frac{\partial}{\partial\nu_i} \sim \frac{1}{\Delta\nu_{ic}} \quad (i = 1, 2). \tag{10}$$

3 Stage of thermal relaxation of nuclei

Taking into account that characteristic values of ξ lie, according to eq.(3), in the interval $|\xi| <\sim 1$ where $\partial/\partial\xi \sim 1$ and using conditions (9) and operator estimates (10), one can establish the relative importance of the terms on the RHS of eq.(4). The ratios of the first, second, and third terms to the last (fifth) term do not exceed $1/\Delta\nu_{1c}$ and $1/\Delta\nu_{2c}$ (much less than 1) in the order of magnitude. The ratio of the fourth term to the last one does not exceed the parameter

$$\frac{1}{2}\frac{k_1k_2(\tau_1^3W_1+\tau_2^3W_2)}{(k_1+1)k_2\tau_1^2W_1+k_1(k_2+1)\tau_2^2W_2} \tag{11}$$

assumed to be much less than 1 (in the last term itself, the first two members are evidently the main ones). Such a hierarchy of terms on the RHS of eq.(4) corresponds to the hierarchy of time scales in the evolution of the distribution P. It allowed Djikaev *et al.* [10] to separate the stage of thermal relaxation of nuclei and, retaining in the RHS of eq.(4) only the leading (fifth) term, to find the distribution P for that stage as

$$P = f + \sum_{j=1}^{\infty} e^{-j\lambda'_j t} f_j H_j \quad (t <\sim t_\xi), \tag{12}$$

where $H_j \equiv H_j(\xi)$ $(j = 0, 1, 2, ...)$ are the Hermite polynomials $(H_0 = 1,\ H_1 = 2\xi,\ H_2 = 4\xi^2 - 2, ...)$,

$$\lambda'_j = 2\frac{k_1+1}{k_1}\tau_1^2W_1 + 2\frac{k_2+1}{k_2}\tau_2^2W_2 + (j-1)!\sum_{m=2}^{j}\frac{2^m(\tau_1^{2m}W_1+\tau_2^{2m}W_2)}{m!m!(j-m)!}, \tag{13}$$

$$t_\xi = 1/\lambda'_1 = \frac{1}{2}\frac{k_1k_2}{k_2(k_1+1)\tau_1^2W_1+k_1(k_2+1)\tau_2^2W_2}, \tag{14}$$

$$f = (H_0, P) = (H_0, P|_{t=0}), f_j = (2^j j!)^{-1}(H_j, P|_{t=0}) \tag{15}$$

with the scalar product (Φ, Ψ) of the functions Φ and Ψ of ξ defined as

$$(\Phi, \Psi) = \pi^{-1/2}\int_{-\infty}^{\infty} d\xi\, e^{-\xi^2}\Phi\Psi \tag{16}$$

(for $j = 0$ and $j = 1$ the sum over m is absent from eq.(13)).

The Hermite polynomials H_j $(j = 0, 1, 2, ...)$ are eigenfunctions of the principal operator in the governing equation, i.e. of the operator in the leading (fifth) term on the RHS of eq.(4). They satisfy the recursion relations

$$\frac{\partial}{\partial \xi} H_j = 2j H_{j-1}, \left(\frac{\partial}{\partial \xi} - 2\xi \right) H_j = -H_{j+1}. \tag{17}$$

and form a complete system of eigenfunctions satisfying also the orthogonality and normalization conditions

$$(H_j, H_k) = \delta_{jk} 2^j j! \quad (j, k = 0, 1, 2, ...), \tag{18}$$

where δ_{jk} is Kronecker's delta. Obviously, $-j\lambda'_j$ $(j = 0, 1, 2, ...)$ represents the eigenvalue corresponding to H_j. All the eigenvalues are negative except that for $j = 0$ which is equal to 0.

The function $f \equiv f(\nu_1, \nu_2, t)$ in eq.(12) represents the two-dimensional distribution of nuclei with respect to ν_1, ν_2. Its time evolution is given by the equation

$$\frac{\partial f}{\partial t} = -\frac{\partial J_1}{\partial \nu_1} - \frac{\partial J_2}{\partial \nu_2}, \tag{19}$$

where

$$J_i = \left(H_0, \left(\hat{L}_i - W_i \sum_{m=1}^{\infty} \frac{\tau_i^m}{m!} \frac{\partial^m}{\partial \xi^m} \right) P \right) \quad (i = 1, 2) \tag{20}$$

is the flux (averaged on ξ) of nuclei along the ν_i-axis. As can be seen (Djikaev *et al.* [10], during the stage of thermal relaxation $t <\sim t_\xi$ the distribution of nuclei with respect to ν_1 and ν_2 does not change while the distribution with respect to the variable ξ approaches a quasiequilibrium Gaussian distribution by the end of that stage, and

$$P \simeq f \quad (t >\sim t_\xi) \tag{21}$$

as follows from eq.(12) (t_ξ represents the principal relaxation time).

4 Evolution of nuclei after the stage of thermal relaxation

The quasiequilibrium distribution is an eigenfunction of the main operator of the governing equation (4), the corresponding eigenvalue being zero. Therefore, as follows from eq.(21), the operators of the first four terms on the RHS of eq.(4) also become important at the end of thermal relaxation stage. However, the operator of the last term is still the main one when acting on the deviation of P from f: according to eq.(15), this deviation is orthogonal to the eigenfunction H_0 with the zero eigenvalue. This makes it possible to construct a solution of governing eq.(4) for $t >\sim t_\xi$ with the help of the Enskog - Chapman method.

4.1 Method of Enskog and Chapman

Following Grinin and Kuni [7], let us choose the quasiequilibrium distribution as a zeroth approximation and present the distribution P as

$$P = f + \sum_{j=1}^{\infty}(2\tau_1)^{-j} z_j(f) H_j, \tag{22}$$

$$z_j(f) = \sum_{l=1}^{\infty} z_j^{(l)}(f), \tag{23}$$

where the correction terms depend on the time only through the time dependence of the two-dimensional distribution f; the superscript indicates the number of the approximation and the subscript indicates the number of the mode. The components of the binary system are supposed to be numbered so that $\tau_1 \geq \tau_2$.

Taking eqs.(17),(18) into account, let us substitute expression (22) in eq.(20):

$$J_i = \hat{L}_i f - W_i \sum_{j=1}^{\infty} \tau_{21}^{j} z_j(f) \quad (i = 1, 2) \tag{24}$$

($\tau_{21} \equiv \tau_2/\tau_1$).Obviously, in order that the substitution of eq.(24) in eq.(20) bring us to an explicit equation governing the time evolution of the two-dimensional distribution f, we have to explicitly find the correction terms $z_j(f)$.

Estimates (10) and eqs.(19) and (24) allow us to conclude that when finding the correction term in l-th approximation $z_j^{(l)}$ from eq.(4) in the main order in $1/\Delta\nu_{1c}$ and $1/\Delta\nu_{2c}$, one can neglect both the LHS and the first term on the RHS of eq.(4) already from the first approximation. Besides, already from the second approximation one can neglect also the second term on the RHS of eq.(4). Thus, as the operator of the fifth term on the RHS of eq.(4) is more important than the operators of its third and forth terms when applied to the deviation $P - f$, one can obtain the following expression for the correction terms:

$$z_j^{(1)}(f) = \frac{(2\tau_1^2)^{j-1}}{j!j\lambda_j}[\hat{L}_1 + \tau_{21}^j \hat{L}_2]f, \; z_j^{(l)}(f) = \sum_{m=1}^{\infty}{}' \Gamma_{jm} z_m^{(l-1)}(f) \quad (l \geq 2), \tag{25}$$

where

$$\Gamma_{jm} = -\frac{m!}{j\lambda_j} \sum_{k=r_{jm}}^{m} \frac{(2\tau_1^2)^{j-m+k-1}[W_1 + W_2 \tau_{21}^{j-m+2k}]}{k!(m-k)!(j-m+k)!}, \tag{26}$$

$$r_{jm} = \begin{cases} 1 & (j > m), \\ j - m + 1 & (j < m), \end{cases}$$

$$\lambda_j = \lambda_j'/(2\tau_1^2) \tag{27}$$

(the prime in the sum over m in eq.(25) eliminates the term with $j = m$ what means $\Gamma_{mm} = 0$ for any m).

Rewriting eqs.(25) in the form

$$z_j^{(l)}(f) = a_j^{(l)} \hat{L}_1 f + b_j^{(l)} \hat{L}_2 f, \tag{28}$$

$$a_j^{(1)} = \frac{(2\tau_1^2)^{j-1}}{j!j\lambda_j}, \; a_j^{(l)} = \sum_{m=1}^{\infty}{}' \Gamma_{jm} a_m^{(l-1)} \quad (l \geq 2), \tag{29}$$

$$b_j^{(1)} = \frac{(2\tau_1^2)^{j-1}}{j!j\lambda_j}\tau_{21}^j, \; b_j^{(l)} = \sum_{m=1}^{\infty}{}' \Gamma_{jm} b_m^{(l-1)} \quad (l \geq 2), \tag{30}$$

and substituting $z_j^{(l)}$ in eq.(23), we have

$$z_j(f) = a_j \hat{L}_1 f + b_j \hat{L}_2 f, \tag{31}$$

$$a_j = \sum_{l=1}^{\infty} a_j^{(l)}, \; b_j = \sum_{l=1}^{\infty} b_j^{(l)} \tag{32}$$

Eqs.(31),(24), and (19) result in the equation governing the time evolution of two-dimensional distribution f:

$$\frac{\partial f}{\partial t} = -\Theta_1 \frac{\partial}{\partial \nu_1} \hat{L}_1 f - \Theta_2 \frac{\partial}{\partial \nu_2} \hat{L}_2 f + \delta_1 \frac{\partial}{\partial \nu_1} \hat{L}_2 f + \delta_2 \frac{\partial}{\partial \nu_2} \hat{L}_1 f, \tag{33}$$

with

$$\Theta_1 = 1 - W_1 \sum_{j=1}^{\infty} a_j,\ \Theta_2 = 1 - W_2 \sum_{j=1}^{\infty} b_j \tau_{21}^j,\ \delta_1 = \sum_{j=1}^{\infty} b_j,\ \delta_2 = \sum_{j=1}^{\infty} a_j \tau_{21}^j. \qquad (34)$$

Thus, according to eqs.(3),(22),(31), and (33), the problem of finding the three-dimensional distribution $g(\nu_1, \nu_2, E, t)$ in the nonisothermal theory is reduced to the well investigated problem of finding the two-dimensional distribution $f(\nu_1, \nu_2, t)$. However, equation (33) for f significantly differs from the Reiss' kinetic equation of isothermal binary nucleation: both the difference of Θ_1 and Θ_2 from 1 and the presence of the third and forth terms on the RHS of eq.(33) are exclusively due to thermal effects. Nevertheless, eq.(33) is still an equation of the Fokker-Planck type. Therefore, to solve this equation, one can apply the method of complete separation of variables used earlier in a kinetic theory of isothermal binary nucleation by Kuni *et al.* [21] and by Melikhov *et al.* [22]. The following section is based on those two works. (The most general form of that method for a two-dimensional kinetic theory of first-order phase transition is given by Kuni and Melikhov [23], and its covariant formulation for a multidimensional theory is provided by Kuni *et al.* [24].)

4.2 Method of complete separation of variables

4.2.1 Reduction of the two-dimensional problem to the one-dimensional one

Let us introduce the variables χ and κ as

$$\chi = \nu_1/(\nu_1 + \nu_2),\ \kappa = 6\pi^{1/2}(\nu_1 + \nu_2)\gamma^{3/2}v \qquad (35)$$

where γ is the surface tension of a nucleus in units of the thermal energy of medium $k_B T_0$; v is the volume of the nucleus per molecule. Choosing the variables χ and κ as independent characteristics of a nucleus (in the framework of two-dimensional theory, of course), the free energy F of formation of the nucleus will take the form

$$F = \kappa^{2/3} - \kappa B(\chi), \tag{36}$$

where

$$B(\chi) = [\chi b_1 + (1-\chi) b_2]/[6\pi^{1/2}\gamma^{3/2} v], \tag{37}$$

$$b_1 = \ln \frac{\zeta_1}{\chi f_1(\chi)}, b_2 = \ln \frac{\zeta_2}{(1-\chi) f_2(\chi)}, \tag{38}$$

$$\zeta_i = n_i/n_{i\infty} \quad (i = 1,2), \tag{39}$$

n_i is the number density of i-component molecules in a vapor mixture; n_{is} is the number density of molecules of i-component pure vapor saturated over a plane surface of its own pure liquid phase; $f_1(\chi)$ and $f_2(\chi)$ are the activity coefficients of the first and second components in a solution with concentration χ.

The variables χ and κ representing respectively the concentration of solution in the nucleus and its surface energy in power 3/2 are very good for the description of a global behaviour of free energy surface (Kuni *et al.* [21]; Melikhov *et al.* [25]). However, when considering the vicinity of the saddle point (near-critical region) which is most important for the nucleation kinetics, it is more convenient to introduce the variables x and y as

$$x = c_{11}(\nu_1 - \nu_{1c}) + c_{12}(\nu_2 - \nu_{2c}), \; y = c_{21}(\nu_1 - \nu_{1c}) + c_{22}(\nu_2 - \nu_{2c}), \tag{40}$$

where

$$c_{11} = \sqrt{-\frac{1}{2}\left(\frac{\partial^2 F}{\partial \kappa^2}\right)_c} \left(\frac{\partial \kappa}{\partial \nu_1}\right)_c, \; c_{12} = \sqrt{-\frac{1}{2}\left(\frac{\partial^2 F}{\partial \kappa^2}\right)_c} \left(\frac{\partial \kappa}{\partial \nu_2}\right)_c,$$
$$c_{21} = \sqrt{\frac{1}{2}\left(\frac{\partial^2 F}{\partial \chi^2}\right)_c} \left(\frac{\partial \chi}{\partial \nu_1}\right)_c, \; c_{22} = \sqrt{\frac{1}{2}\left(\frac{\partial^2 F}{\partial \chi^2}\right)_c} \left(\frac{\partial \chi}{\partial \nu_2}\right)_c \tag{41}$$

(subscript "c" marks magnitudes corresponding to the saddle point). In the near-critical region, the variables x and y represent the deviations of the variables κ and χ, respectively, from their values κ_c and χ_c at the saddle point, linearized in $\nu_1 - \nu_{1c}$ and $\nu_2 - \nu_{2c}$ and normalized by their rms fluctuations.

In the near-critical region the free energy F can be approximated by the bilinear form which in the variables x and y becomes a quadratic one:

$$F = F_c - x^2 + y^2. \tag{42}$$

Let us denote by $n(x, y, t)$ the distribution of nuclei with respect to the variables x and y at the moment t and turn to the variables x and y in eq.(33). Replacing v by v_c in the vicinity of the saddle point and taking eq.(42) into account, we obtain

$$n(x, y, t) = v_c C f(\nu_1, \nu_2, t), \tag{43}$$

$$C = \left[6\pi^{1/2}\sqrt{-\frac{1}{2}\left(\frac{\partial^2 F}{\partial\kappa^2}\right)_c}\sqrt{\frac{1}{2}\left(\frac{\partial^2 F}{\partial\chi^2}\right)_c}\ \frac{\gamma^{3/2}}{\nu_{1c}+\nu_{2c}}v_c^2\right]^{-1} \tag{44}$$

$$\begin{aligned}\partial_t n(x, y, t) \ &= \ a\Big\{\partial_x(\partial_x - 2x) - \varphi^{-1}\partial_x(\partial_y + 2y) \\ &\quad -\varepsilon^{-1}\partial_y(\partial_x - 2x) + (\varphi\varepsilon)^{-1}(1+p)\partial_y(\partial_y + 2y)\Big\}\, n(x, y, t)\end{aligned} \tag{45}$$

where

$$a = W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1W_2(\delta_1 + \delta_2)c_{11}c_{12} \tag{46}$$

$$\begin{aligned}\varphi \ &= \ -\frac{W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1W_2(\delta_1+\delta_2)c_{11}c_{12}}{W_1\Theta_1 c_{11}c_{21} + W_2\Theta_2 c_{12}c_{22} - W_1W_2(\delta_1 c_{11}c_{22} + \delta_2 c_{12}c_{21})} \\ \varepsilon \ &= \ -\frac{W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1W_2(\delta_1+\delta_2)c_{11}c_{12}}{W_1\Theta_1 c_{11}c_{21} + W_2\Theta_2 c_{12}c_{22} - W_1W_2(\delta_1 c_{12}c_{21} + \delta_2 c_{11}c_{22})}\end{aligned} \tag{47}$$

$$p = W_1W_2(\Theta_1\Theta_2 - W_1W_2\delta_1\delta_2)(c_{11}c_{22} - c_{12}c_{21})^2\varphi\varepsilon/a^2, \tag{48}$$

and abbreviated notations $\partial_t \equiv \partial/\partial t, ...$ have been introduced for differentiation operators.

As the two-dimensional equilibrium distribution of nuclei $f_e(\nu_1, \nu_2)$ with respect to the variables ν_1 and ν_2 is (Kuni *et al.* [21]; Melikhov *et al.* [25])

$$f_e(\nu_1, \nu_2) = v^{-1}e^{-F(\nu_1,\nu_2)}, \tag{49}$$

the two-dimensional equilibrium distribution $n_e(x,y)$ with respect to x and y takes the form

$$n_e(x,y) = Ce^{-F_c}e^{x^2}e^{-y^2} \tag{50}$$

(we again replaced v by v_c). Thus, the variables x and y have been separated in the equilibrium distribution. This allows one to conclude that the variable x is unstable and the variable y is stable. Therefore, the ordinary boundary conditions are applied to eq.(45):

$$n(x,y,t)/n_e(x,y) = \begin{cases} 1 & (x \to -\infty), \\ 0 & (x \to \infty). \end{cases} \tag{51}$$

(for arbitrary y).

To ensure the complete separation of variables both in the equilibrium distribution and in the kinetic equation, let us introduce the new variables u and η with the help of the Lorentz transformation

$$u = (1-\alpha^2)^{-1/2}(x+\alpha y), \; \eta = (1-\alpha^2)^{-1/2}(y+\alpha x), \tag{52}$$

the transformation parameter α satisfying the restriction $-1 < \alpha < 1$. The Jacobian of transformation (52) is equal to unity.

Passing from the variables x and y to the variables u and η and choosing the parameter α as

$$\alpha = \frac{1}{2\varepsilon}\left\{\varphi\varepsilon + 1 + r \mp \left[(\varphi\varepsilon + 1 + r)^2 - 4\varphi\varepsilon\right]^{1/2}\right\}, \tag{53}$$

we obtain

$$n(u,\eta) = n(x,y), \tag{54}$$

$$F = F_c - u^2 + \eta^2, \tag{55}$$

$$n_e(u,\eta) = Ce^{-F_c}e^{u^2}e^{-\eta^2}, \tag{56}$$

$$\begin{aligned} \partial_t n(u,\eta,t) \;&=\; A\left\{\partial_u(\partial_u - 2u) + \frac{1}{\varepsilon}\frac{\varphi-\varepsilon}{\varphi-\alpha}\partial_u(\partial_\eta + 2\eta) + \right. \\ &\left. \frac{\varphi}{\varepsilon}\frac{(1-\varepsilon\alpha)^2}{\alpha^2 r}\partial_\eta(\partial_\eta + 2\eta)\right\} n(u,\eta,t), \end{aligned} \tag{57}$$

where

$$A = a(1 - \frac{\alpha}{\varphi}) = \frac{a}{2\varphi\varepsilon}\left\{\varphi\varepsilon - 1 - r \pm [(\varphi\varepsilon + 1 + r)^2 - 4\varphi\varepsilon]^{1/2}\right\}. \qquad (58)$$

The expression under the square root sign in eq.(53) must not be negative so that α should be real; this imposes the restriction $(\varphi\varepsilon + 1 + r)^2 \geq -4p$ on the parameters φ, ε, and r. The sign of the square root in eq.(53) is chosen so that the conditions $|\alpha| < 1$ and $A > 0$ be also fulfilled. For example, in the case where $r > 0$ and $\varphi = \varepsilon$, all these three conditions are automatically satisfied by choosing the minus sign for the square root in eq.(53). According to eq.(47), the equality $\varphi = \varepsilon$ is equivalent to the equality $\delta_1 = \delta_2$ which is verified, for example, in any of the following particular situations: 1) $\tau_1 = \tau_2$; 2) the first approximation is satisfactory in calculating a_j and b_j; 3) $\alpha_{12} \simeq \alpha_{12}^2$ and the small terms of order τ_1^6, τ_1^8, ... are neglected in finding a_j and b_j.

According to eqs.(55),(52), the variable u is unstable and the variable η is stable. This allows one to apply to eq.(57) the usual (in the nucleation kinetics) boundary conditions:

$$n(u,\eta,t)/n_e(u,\eta) = \begin{cases} 1 & (u \to -\infty), \\ 0 & (u \to \infty) \end{cases} \qquad (59)$$

for arbitrary η.

As shown by Kuni and Melikhov [7], the solution of eq.(57) with boundary conditions (59) is given by

$$n(u,\eta,t) = \pi^{-1/2}\rho(u,t)e^{-\xi^2}, \qquad (60)$$

where the time evolution of the function $\rho(u,t)$ is governed by the one-dimensional equation

$$\partial_t\rho(u,t) = A\partial_u(\partial_u - 2u)\rho(u,t) \qquad (61)$$

with the boundary conditions

$$\rho(u,t)/\rho_e(u) = \begin{cases} 1 & (u \to -\infty), \\ 0 & (u \to \infty), \end{cases} \qquad (62)$$

the function ρ_e being defined as

$$\rho_e(u) = C\pi^{1/2}e^{-F_c}e^{u^2}. \tag{63}$$

According to eq.(60),

$$\rho(u,t) = \int_{-\infty}^{\infty} d\eta\, n(u,\eta,t). \tag{64}$$

This shows that $\rho(u,t)$ represents the one-dimensional distribution of nuclei with respect to the unstable variable u.

Eq.(57) can be presented in the form of two-dimensional continuity equation

$$\partial_t n(u,\eta,t) = -\partial_u j_u - \partial_\eta j_\eta, \tag{65}$$

where j_u and j_η are the flux densities of nuclei along the u- and η-axes. Evidently, distribution (60) makes the flow j_η vanish, what means that in the variables u, η the two-dimensional flow of nuclei is parallel to the u-axis.

Let us present equation (61) in the form

$$\partial_t \rho(u,t) = -\partial_u J_u,\ J_u = -A(\partial_u - 2u)\rho(u,t), \tag{66}$$

where J_u (function of u and t) is the one-dimensional flow of nuclei along u-axis integrated over the stable variable.

In the near-critical region $|u| <\sim 1$ we have the estimates $\partial/\partial u \sim u \sim 1$ (without paying attention to signs) which, with the help of eq.(60),(61), allow us to conclude that the characteristic time t_u of the change of the distribution of nuclei with respect to unstable variable in that region can be estimated as

$$t_u \sim A^{-1}. \tag{67}$$

Obviously, t_u will also represent the time in which the steady state is established in the entire near-critical region $|u| <\sim 1$.

In the steady state J_u is independent of u and t. Therefore, according to eqs.(66),(62), for the one-dimensional steady-state nucleation flux $(J_u)_s$ and distribution $\rho_s(u)$ we have:

$$(J_u)_s = \pi^{-1/2} A \rho_e(u)\Big|_{u=0}\,, \quad \rho_s(u) = \pi^{-1/2} \rho_e(u) \int_u^{\infty} du' e^{-u'^2} \qquad (68)$$

(subscript "s" marks steady-state values).

4.2.2 Invariance with respect to the choice of the unstable variable

Let us show the invariance of the theory with respect to the choice of the unstable characteristic of a nucleus.

By virtue of eqs.(52),(54), and (57), the distribution

$$n(x,y,t) = \pi^{-1/2} \rho(\frac{x+\alpha y}{\sigma}, t) \exp\left[-(\frac{y+\alpha x}{\sigma})^2\right], \qquad (69)$$

in which $\sigma = (1-\alpha^2)^{1/2}$, is the solution of eq.(45) with boundary conditions (51). Defining the one-dimensional distribution of nuclei $p(x,t)$ with respect to x as

$$p(x,t) = \int_{-\infty}^{\infty} dy\, n(x,y,t) \qquad (70)$$

and substituting eq.(69) in eq.(70), we obtain

$$p(x,t) = \frac{\sigma}{\pi^{1/2}|\alpha|} \int_{-\infty}^{\infty} du \exp\left[-\left(\frac{u-\sigma x}{\alpha}\right)^2\right] \rho(u,t) \qquad (71)$$

According to eqs.(70),(50), and (51), this function satisfies the boundary conditions

$$p(x,t)/p_e(x) = \begin{cases} 1 & (x \to -\infty), \\ 0 & (x \to \infty). \end{cases} \qquad (72)$$

with

$$p_e(x) = C\pi^{1/2} e^{-F_c} e^{x^2} \qquad (73)$$

Let us differentiate eq.(71) with respect to t. Making several simple transformations in the RHS of obtained equation with the help of eqs.(66) and (71), one can rewrite it in the form

$$\partial_t p(x,t) = -\partial_x J_x, \;\; J_x = -A(\partial_x - 2x)p(x,t), \tag{74}$$

where J_x (function of x and t) is the one-dimensional flux density of nuclei along the x-axis integrated over the stable variable.

The variables x, y defined as

$$x = \sigma^{-1}(u - \alpha\eta), \;\; y = \sigma^{-1}(\eta - \alpha u) \tag{75}$$

can be assigned to an arbitrary value of α satisfying the restriction $|\alpha| < 1$. It is the most general definition of the unstable (x) and stable (y) characteristics of a nucleus ensuring the quadratic form for F. Eqs.(72)-(74) confirm the invariance of the theory with respect to the choice of the unstable variable of a nucleus as they transform themselves into eqs.(62),(63), and (66) if $\alpha = 0$.

For the steady state, eqs.(56),(63),(68),(69),(50), and (73) allow one to find:

$$n_s(x,y) = \pi^{-1/2} n_e(x,y) \int_{\frac{x+\alpha y}{\sigma}}^{\infty} du'\, e^{-u'^2}, \tag{76}$$

$$p_s(x) = \pi^{-1/2} p_e(x) \int_{x}^{\infty} dx'\, e^{-x'^2}. \tag{77}$$

Comparing eqs.(63) and (73), we conclude that the dependence of the one-dimensional equilibrium distributions $p_e(x)$ and $\rho_e(u)$ on the unstable variable is identical. In addition, the comparison of eqs.(68) and (77) shows that the one-dimensional steady-state distributions $p_s(x)$ and $\rho_s(u)$ also have an identical dependence on the unstable variable. Besides, as follows from eqs.(66) and (74),

$$(J_x)_s = (J_u)_s. \tag{78}$$

Therefore, the one-dimensional flux density $(J_u)_s$ given by eq.(68), determines the steady-state rate of binary nonisothermal nucleation J_s which can be presented as

$$J_s = ACe^{-F_c}. \tag{79}$$

Using results of the one-dimensional theory and taking account of eq.(66), one can obtain the estimate

$$\partial_u - 2u \simeq -2u \quad (u >\sim 1), \tag{80}$$

and the relation

$$J_u \simeq \dot{u}\rho(u,t), \;\; \dot{u} = 2Au \quad (u >\sim 1). \tag{81}$$

The value $\dot{u}$ represents the rate of regular growth in time of the unstable variable u. Obviously, for the unstable variable x one could write the identical estimate and relation, as follows from (74). Equation (81) allows one to conclude that the fluctuation-induced nucleation is completed in the region $|u| <\sim 1$ of the variables u, η (in the variables x, y it is completed in the region $|x| <\sim 1$). To the left of the region $|u| <\sim 1$ (or $|x| <\sim 1$) the nuclei are still in equilibrium, while to the right of it they already grow irreversibly.

5 Mean values of composition and temperature of the nucleus

Equation (66) with boundary conditions (62) (or eq.(74) with boundary conditions (72)) is well known and investigated in the one-dimensional theory of first-order phase transitions. Accordingly, we can use the results of one-dimensional theory for the one-dimensional distribution $\rho(u,t)$ (or $p(x,t)$) and the nucleation rate J_u (or J_x). Thus, eqs.(69),(43),(22), and (3) determine the three-dimensional distribution of nuclei with respect to the variables ν_1, ν_2, and E in the nonisothermal binary nucleation. The rate of nucleation is given by eq.(66) (or (74)). In the particular case of steady-state nucleation the one-dimensional distribution $\rho_s(u)$ is given by the second of eq.(68) and the expression for $n(x,y,t)$ is reduced to eq.(76); the nucleation rate is then determined by eq.(79).

The average value $\overline{y}(x)$ of the stable variable y (which is a linearized and normalized concentration of solution in the nucleus) at a given value of the unstable variable x is defined as

$$\overline{y}(x) = \frac{1}{p(x,t)} \int_{-\infty}^{\infty} dy\ yn(x,y,t). \tag{82}$$

Taking eqs.(69),(70),(74) into account and making several simple transformations, one can obtain

$$\overline{y}(x) = -\frac{\alpha}{2Ap(x,t)} J_x. \tag{83}$$

As follows from eqs.(79),(77), and (73), in the steady state we have

$$\overline{y}_s(x) = -\frac{1}{2}\alpha e^{-x^2} \Big/ \int_x^{\infty} dx'\, e^{-x'^2}\ . \tag{84}$$

The average value $\overline{\xi}(\nu_1, \nu_2)$ of the temperature of nuclei with given ν_1, ν_2 is defined as

$$\overline{\xi}(\nu_1, \nu_2) = (\xi, P)/f. \tag{85}$$

Taking eqs.(16),(22) and (31) into account, one can obtain

$$\overline{\xi}(\nu_1, \nu_2) = \frac{1}{2\tau_1} \frac{1}{f(\nu_1, \nu_2, t)} (a_1 \hat{L}_1 + b_1 \hat{L}_2) f(\nu_1, \nu_2, t) \tag{86}$$

Evidently, the steady-state value can be obtained with the help of eqs.(43), (76), (50), (40), and (5).

6 Correction terms

As it can be readily seen, the influence of thermal effects on the results of the theory developed is implemented through the correction terms a_j and b_j defined by eqs.(32). Since Γ_{jk} does not depend on the number of approximation, eqs.(29),(30), and (32) allow one to obtain two infinite sets of simultaneous equations for a_j and b_j respectively:

$$a_j = {\sum_{m=1}^{\infty}}' \Gamma_{jm} a_m + \frac{(2\tau_1^2)^{j-1}}{j! j \lambda_j} \quad (j = 1, 2, 3, ...), \tag{87}$$

$$b_j = {\sum_{m=1}^{\infty}}' \Gamma_{jm} b_m + \frac{(2\tau_1^2)^{j-1}}{j! j \lambda_j} \tau_{21}^j \quad (j = 1, 2, 3, ...). \tag{88}$$

They are very convenient for finding a_j and b_j in the form of asymptotics in τ_1^2. For example, using eq.(26), neglecting the terms of order $\tau_1^6, \tau_1^8, \ldots$ and solving equations (87) and (88), one can find:

$$a_1 = \frac{1}{\lambda_1} + \tau_1^2 K_1 + \tau_1^4 Q_1,\ a_2 = \tau_1^2 K_2 + \tau_1^4 Q_2,\ a_3 = \tau_1^4 Q_3, \tag{89}$$

$$\begin{aligned}
K_1 &= -\frac{1}{2\lambda_1\lambda_2}U_3 + \frac{1}{2\lambda_1^2\lambda_2}U_3^2, \quad K_2 = \frac{1}{2\lambda_2} - \frac{1}{2\lambda_1\lambda_2}U_3, \\
Q_1 &= -\frac{2}{9\lambda_1\lambda_3}U_4 + \frac{1}{3\lambda_1\lambda_2\lambda_3}U_3(U_3+U_4) + \frac{2}{9\lambda_1^2\lambda_3}U_4^2 - \frac{1}{4\lambda_1^2\lambda_2^2}U_3^3 \\
&\quad -\frac{2}{3\lambda_1^2\lambda_2\lambda_3}U_3^2U_4 - \frac{1}{2\lambda_1\lambda_2^2\lambda_3}U_3^3 - \frac{1}{2\lambda_1^2\lambda_2^2\lambda_3}U_3^4 - \frac{1}{\lambda_1\lambda_2^2\lambda_3^2}U_3^4, \\
Q_2 &= -\frac{1}{3\lambda_2\lambda_3}U_3 + \frac{1}{4\lambda_1\lambda_2^2}U_3^2 + \frac{1}{3\lambda_1\lambda_2\lambda_3}U_3U_4 + \frac{1}{2\lambda_2^2\lambda_3}U_3^2 \\
&\quad -\frac{1}{4\lambda_1^2\lambda_2^2}U_3^2 - \frac{1}{\lambda_1\lambda_2^2\lambda_3}U_3^2, \\
Q_3 &= \frac{2}{9\lambda_3} - \frac{2}{9\lambda_1\lambda_3}U_4 - \frac{1}{3\lambda_2\lambda_3}U_3 + \frac{1}{3\lambda_1\lambda_2\lambda_3}U_3^2,
\end{aligned}$$

$$b_1 = \frac{\tau_{21}}{\lambda_1} + \tau_1^2 R_1 + \tau_1^4 S_1,\ b_2 = \tau_1^2 R_2 + \tau_1^4 S_2,\ b_3 = \tau_1^4 S_3, \tag{90}$$

$$\begin{aligned}
R_1 &= -\frac{\tau_{21}^2}{2\lambda_1\lambda_2}U_3 + \frac{\tau_{21}}{2\lambda_1^2\lambda_2}U_3^2, \quad R_2 = \frac{\tau_{21}^2}{2\lambda_2} - \frac{\tau_{21}}{2\lambda_1\lambda_2}U_3, \\
S_1 &= -\frac{2\tau_{21}^3}{9\lambda_1\lambda_3}U_4 + \frac{\tau_{21}^2}{3\lambda_1\lambda_2\lambda_3}U_3(\tau_{21}U_3+U_4) + \frac{2\tau_{21}}{9\lambda_1^2\lambda_3}U_4^2 - \frac{\tau_{21}^2}{4\lambda_1^2\lambda_2^2}U_3^3 \\
&\quad -\frac{2\tau_{21}}{3\lambda_1^2\lambda_2\lambda_3}U_3^2U_4 - \frac{\tau_{21}^2}{2\lambda_1\lambda_2^2\lambda_3}U_3^3 - \frac{\tau_{21}}{2\lambda_1^2\lambda_2^2\lambda_3}U_3^4 - \frac{\tau_{21}}{\lambda_1\lambda_2^2\lambda_3^2}U_3^4, \\
S_2 &= -\frac{\tau_{21}^3}{3\lambda_2\lambda_3}U_3 + \frac{\tau_{21}^2}{4\lambda_1\lambda_2^2}U_3^2 + \frac{\tau_{21}}{3\lambda_1\lambda_2\lambda_3}U_3U_4 + \frac{\tau_{21}^2}{2\lambda_2^2\lambda_3}U_3^2 \\
&\quad -\frac{\tau_{21}}{4\lambda_1^2\lambda_2^2}U_3^2 - \frac{\tau_{21}}{\lambda_1\lambda_2^2\lambda_3}U_3^2, \\
S_3 &= \frac{2\tau_{21}^3}{9\lambda_3} - \frac{2\tau_{21}}{9\lambda_1\lambda_3}U_4 - \frac{\tau_{21}^2}{3\lambda_2\lambda_3}U_3 + \frac{\tau_{21}}{3\lambda_1\lambda_2\lambda_3}U_3^2
\end{aligned}$$

($U_m \equiv W_1 + \tau_{21}^m W_2$ with arbitrary m). As follows from eqs.(29), (30), and (26), the values $a_4, a_5, \ldots$ and $b_4, b_5, \ldots$ are of order $\tau_1^6, \tau_1^8, \ldots$ and hence they are not taken into account in solving equations (87) and (88).

7 Comparison with results of isothermal theory and experimental data

To illustrate the theory developed we have carried out numerical calculations for the condensation in the system “ethanol (first component) - hexanol (second component)” at the same external conditions as the experiments of Strey and Viisanen [26]. All the physical properties of both components required for calculations are well determined for both liquid and vapor phases. Besides, accurate fits of several thermodynamic properties vs. composition are required for ethanol (1) - hexanol (2) liquid solution and they are fortunately also available.

The equilibrium vapor pressures of pure ethanol and hexanol as well as the dependence of surface tension γ and mean molecular volume v on the concentration χ were taken following Strey and Viisanen [26].The liquid phase activity coefficients f_1 and f_2 were assumed to be equal to unity. The condensation heat of pure ethanol was obtained by linearly extrapolating data in *CRC Handbook of Chemistry and Physics* [27]. The condensation heat of pure hexanol and its specific heat in a vapor phase were taken in the work of Gallant [28]. The specific heats of pure ethanol in liquid and vapor phases, as well as those of liquid hexanol and gaseous argon (passive gas) were determined with the help of *Thermophysical Properties of Matter* [29]. The sticking coefficients α_{c1} and α_{c2} were assumed to be equal to unity. At such a choice of sticking coefficients the theory does not depend on magnitudes of the thermal accommodation coefficients α_{t1} and α_{t2} of condensing components. As for the thermal accommodation coefficient of argon it was set equal to 0.1 and 0.01.

Results of numerical calculations are presented by Figure 1a and b (for $\alpha_g = 0.1$ and $\alpha_g = 0.01$ respectively) in the form of the dependence of $\ln J_s$ on the mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$. The solid lines represent nucleation rates in our nonisothermal theory obtained with the help of eq.(79) and corresponding to the fixed values of activity fraction $q = \zeta_2/(\zeta_1 + \zeta_2)$, indicated on the Figure over the lines; the dashed lines represent nucleation rates according to the isothermal nucleation kinetics. The corresponding experimental data are shown by series of circles. To avoid possible confusion, we have presented only a part of results.

As was expected, Figure 1 shows that thermal effects diminish the nucleation rates up to tens of times in comparison with the predictions of isothermal theory; the smaller is the value q, the stronger is the decrease in the nucleation rate. This is readily accounted for by the fact that, in the considered system, the smaller is the value q, the denser is the vapor mixture (since the equilibrium pressure of ethanol vapor is by far greater than that of hexanol vapor), and also the stronger is the influence of thermal effects on the nucleation rate. Figure also shows that taking account of thermal effects approaches theoretical nucleation rates to experimental data though there still remains a large discrepancy between them that may be explained by the effect of surface enrichment. Evidently, by virtue of the structure of the parameters k_1 and k_2, the smaller n_g and/or α_g are, the more significant are the influence of thermal effects on the nucleation and, consequently, the improvement of the fit of theoretical predictions to experimental data. This is confirmed by comparing Fig.1a with Fig.1b showing the numerical calculations for two different values of α_g (0.1 and 0.01, respectively).

8 Conclusions

We have considered the kinetics of nonisothermal binary nucleation at the stage following the stage of thermal relaxation of nuclei. The kinetic equation (4) governing the time evolution of three-dimensional distribution of nuclei was obtained earlier (Djikaev *et al.* [10]) by extending the approach developed by Feder *et al.* [6] and by Grinin and Kuni [7] for the nonisothermal one-component nucleation to the binary nucleation. That kinetic equation (4) reaches beyond the framework of the Fokker-Planck approximation in the variable corresponding to the temperature of nucleus and this is what allows the theory to be valid not only in the case of small condensation heats (both $\tau_1 \ll 1$ and $\tau_2 \ll 1$) but also in the case of large values of condensation heat of any component where at least one of τ_1 or τ_2 is not much less than 1. Such a case is not described by the kinetic equation obtained for the nonisothermal binary nucleation by Lazaridis and Drossinos [11] and solved by them for the steady-state nucleation.

By the end of the stage of thermal relaxation of nuclei theoretically described earlier (Djikaev *et al.* [10]), the three-dimensional distribution of nuclei with respect to ξ approaches a quasiequilibrium Gaussian distribution while the distribution with respect to ν_1 and ν_2 has not sufficient time to change. On the other hand, there exists the hierarchy of the operators in the RHS of eq.(4) when they act on the deviation $P - f$. This is what allows one to construct the solution of eq.(4) at the stage following that of thermal relaxation with the help of the Enskog-Chapman method according to eq.(22). The dependence of correction terms $z_j(f)$ on the time in eq.(22) is implemented through the two-dimensional distribution $f(\nu_1, \nu_2, t)$ with respect to ν_1 and ν_2 according to eq.(31). The time evolution of the function $f(\nu_1, \nu_2, t)$ itself is governed by eq.(33) with the thermal-effect-dependent coefficients $\Theta_1, \Theta_2, \delta_1$, and δ_2. Equation (33) transforms itself into the well known equation of Reiss [1] in the case where the thermal effects are neglected: $\Theta_1 \to 1, \Theta_2 \to 1, \delta_1 \to 0$, and $\delta_2 \to 0$ if $\tau_1 \to 0$ and $\tau_2 \to 0$.

Since eq.(33) is of the Fokker-Planck type, the method of complete separation of variables allows one to reduce the problem of finding the function f to the well investigated problem of constructing the one-dimensional kinetic theory of first order phase transitions. Consequently, by using the results of one-dimensional theory for the distribution ρ governed by eq.(61) with boundary conditions (63), one can determine the three-dimensional distribution g with respect to the variables ν_1, ν_2, and E with the help of eqs. (69),(43),(22), and (3). The rate of nonisothermal binary nucleation can be found by means of either eq.(66) or eq.(74).

Thus, a successive application of the Enskog-Chapman method and the method of complete separation of variables to the kinetic equation (4) allows one to construct the kinetic theory of nonisothermal binary nucleation in the non-stationary case as well as in the stationary one (Lazaridis and Drossinos [1] investigated only the steady-state nucleation). In particular, the steady-state nucleation rate is given by eq.(79), and the steady-state three-dimensional distribution with respect to ν_1, ν_2, and E is given by eqs.(76),(43),(22), and (3). The average values of the temperature of the nucleus and solution concentration in it are given by eqs.(86) and (83).

Finally, numerical calculations were carried out for the nucleation rate in the system "ethanol-hexanol" to illustrate the theory developed. The results were compared with the predictions of the isothermal nucleation theory (Kuni *et al.* [21]; Melikhov *et al.* [22]) and experimental data (Strey and Viisanen [26]). As expected, rates predicted by the nonisothermal theory are substantially lower than rates in the isothermal theory. Consequently, the nonisothermal theory improves the fit of theoretical results and experimental data. The model of Lazaridis and Drossinos [11] predicts nucleation rates that are slightly higher than classical nucleation rates and this is not easy to explain from the physical standpoint.

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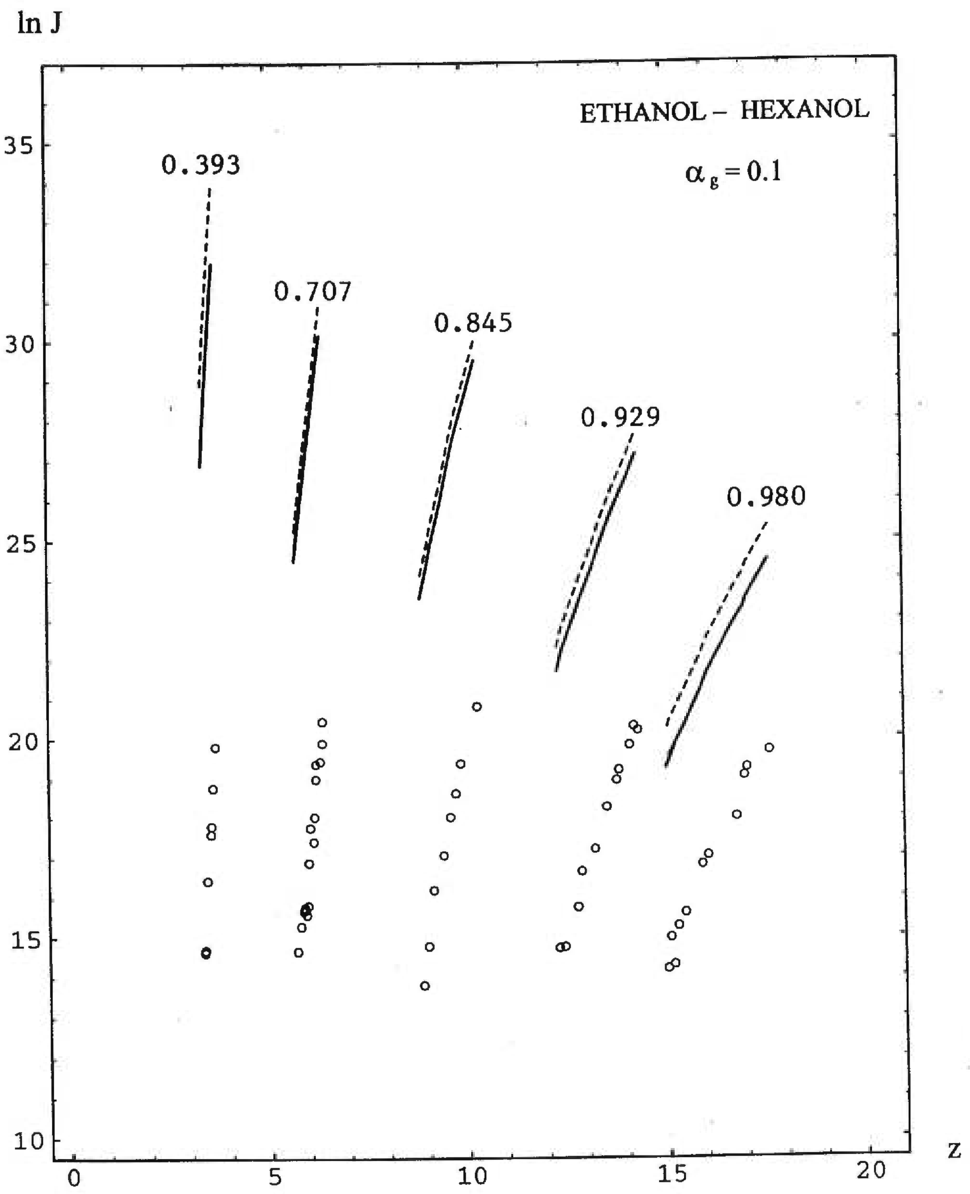

Figure 1a. Natural logarithm of nucleation rate J in the ethanol (1) - hexanol (2) system plotted vs a mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$, at $T_0 = 260K$. The dimension of J is $cm^{-3}s^{-1}$. The circles are the experimental data of Strey and Viisanen (1993). The solid lines are the nonisothermal nucleation rates (equation (79)) calculated at the indicated activity fraction $q = \zeta_2/(\zeta_1+\zeta_2)$; the dashed lines represent the isothermal nucleation rates. The thermal accommodation coefficient of carrier gas (argon) is $\alpha_g = 0.1$.

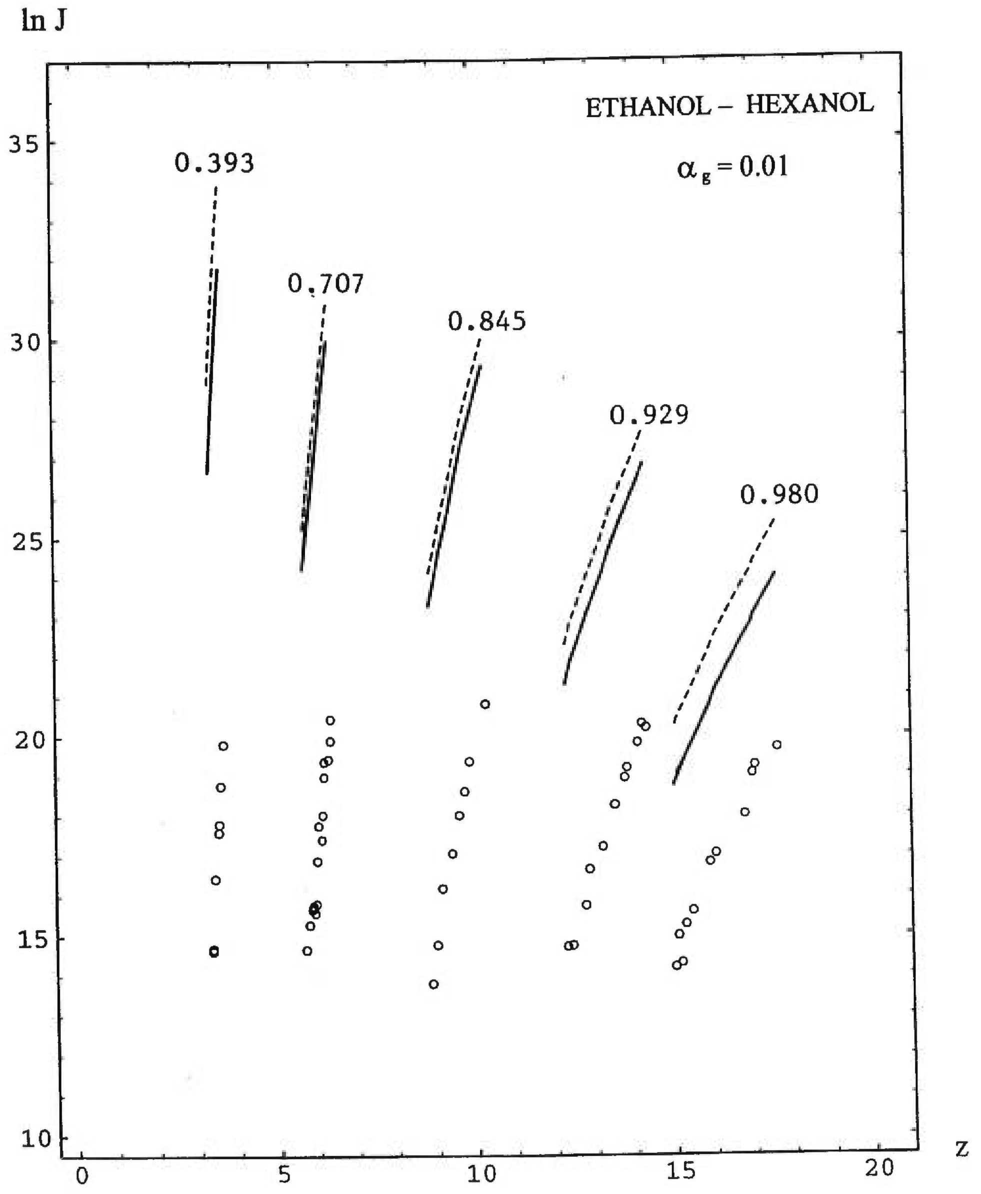

Figure 1b. Natural logarithm of nucleation rate J in the ethanol (1) - hexanol (2) system plotted vs a mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$, at $T_0 = 260K$. The dimension of J is $cm^{-3}s^{-1}$. The circles are the experimental data of Strey and Viisanen (1993). The solid lines are the nonisothermal nucleation rates (equation (79)) calculated at the indicated activity fraction $q = \zeta_2/(\zeta_1+\zeta_2)$; the dashed lines represent the isothermal nucleation rates. The thermal accommodation coefficient of carrier gas (argon) is $\alpha_g = 0.01$.

CHAPITRE 3

Cinétique de la condensation binaire homogène aux conditions dynamiques

Très souvent (et presque toujours dans la nature) la condensation binaire se passe aux conditions dynamiques, c.-à-d., la formation et la croissance des gouttes se passent en même temps que la métastabilité du mélange de vapeurs croît graduellement, atteint son maximum et décroît.

Nous développons la théorie cinétique de ces processus pour les systèmes ouverts ainsi que pour les systèmes fermés (du point de vue de l'échange de matière entre le système où la condensation se passe et son environnement). Les deux sursaturations idéales que les vapeurs du mélange auraient eues en absence de consommation de la substance par les gouttes sont déterminées par les conditions extérieures. Par conséquent, la dépendance temporelle des sursaturations idéales est considérée comme donnée.

Nous considérons le cas où les sursaturations réelles des deux vapeurs atteignent leurs maximums simultanément au moment du maximum de la métastabilité du mélange de vapeurs. Le système d'équations intégrales est obtenu pour les processus considérés. Il est démontré que la méthode itérative permet de construire le spectre des dimensions linéaires des gouttes et la distribution des gouttes selon leurs deux variables d'état indépendantes, la précision relative étant assez élevée dès la première itération. De même, cette méthode permet de trouver la dépendance temporelle des sursaturations réelles des deux composantes du mélange de vapeurs ainsi que le nombre total de gouttes par unité de volume.

3.1 **Article 4:** *Kinetics of two-component condensation under dynamic regime with "synchronous" attainment of the metastability maximum*

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Kinetics of two-component condensation under dynamic regime with ”synchronous” attainment of the metastability maximum

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Abstract

A kinetic theory is presented for isothermal homogeneous two-component condensation under dynamic regime with synchronous attainment of the metastability maximum. It is shown that extending the iteration method of treating of one-component condensation under dynamic conditions to the case of two-component theory makes it possible to construct the spectrum of linear sizes and two-dimensional distribution of two-component droplets, a relative degree of accuracy being high enough even at the first iteration step. This method also allows one to find the time dependence of both real supersaturations as well as the total number of droplets formed per unit volume during two-component condensation.

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1 Introduction

Two-component condensation, i.e. formation and growth of drops of a liquid solution of two substances in a metastable vapor mixture of these substances, is a process widespread in the nature and important for technical applications (we shall use the term "metastable" instead of less general terms "supersaturated", "supercooled", etc...). The theory of two-component condensation is an important part of the theory of first-order phase transitions . At the same time a development of two-component condensation theory is extremely important for various applications, for example, in order to construct the quantitative methodology of forecasting of acid rains.

We usually distinguish three stages of first-order phase transition. During the first of them the embryos of a new phase are formed (this stage is also called the stage of nucleation) which are condensation centers afterwards. It is during the second stage that the phase transition properly takes place - the bulk of a metastable phase passes to a liquid phase. During the third stage the growth of large drops occurs to the detriment of small ones.

At present there exists the complete and adequate theoretical description of all three stages of the one-component condensation. At the same time the kinetic theory of two-component condensation has been developed almost exclusively for the simplest case where the metastability of two-component vapor mixture is created instantaneously (in neglecting both the thermal effects of condensation and presence of heterogeneous nucleation centers). The bases of such binary nucleation theory have been founded by Reiss (1950) who based his argument on the results of Flood (1934) and on the classical one-component nucleation theory of Becker and Döring (1935), Volmer (1939), Kramers (1940), Zeldovitch (1942) and Frenkel (1946). The very important contribution to the theory of binary nucleation has been made by Stauffer (1976), that has corrected the rate of binary nucleation obtained earlier by Reiss (1950). The consistent kinetic theory of binary nucleation has been constructed with the help of the method of complete separation of variables by Kuni *et al.*(1990) and Melikhov *et al.* (1990,1991) who have also found the new normalization factor of equilibrium distribution. Important contributions to the development of stationary theory of binary nucleation have been made by Mirabel and Katz (1974), Hirschfelder (1974), Shugard and Reiss (1976), Wilemsky (1984,1987), Ray *et al.* (1986), Okuyama *et al.* (1988), Shi and Seinfeld (1990) and Grinin *et al.* (1992).

Recently, many very interesting and important results have been obtained by Wilemski and Wyslouzil (1995), and by Wyslouzil and Wilemski (1995, 1996). Particularly, they proposed (Wilemski and Wyslouzil, 1995) a new self-consistent classical size distribution for binary droplets which satisfies the law of mass action and reduces to an one-dimensional distribution for one-component droplets. Studying the transition from binary to unary nucleation Wyslouzil and Wilemski (1995) proposed a modified expression for nucleation rate, prescription of which remains within 10% -20% of the exact numerical rate, when other authors' expressions fail under such a transition. They also investigated (Wyslouzil and Wilemski,1996) the transient behaviour of binary nucleation kinetics by numerically solving the birth-death equations for vapor-to-liquid phase transitions.

Kinetic theory of the second stage of two-component condensation under above mentioned conditions has been constructed by Djikaev (1992) with the help of the iteration method developed by Kuni and Grinin (1984).

The existing theory presented in the above cited papers describes isothermal two-component condensation fairly well in the case where the formation of droplets and their growth take place after the interruption of an external influence on the vapor mixture metastability, that is, in the case of "instantaneous" creation of metastability. Such situations usually occur in most laboratory experiments using piston cloud camera, diffusion cloud camera, supersonic nozzle, particle size magnifier, etc... .

However, there exist many situations (both in the nature and in the industry) in which two-component nucleation begins before the attainment of metastability maximum while the metastability of vapor mixture increases yet. This is, for instance, the case of formation of acid rains where the nucleation of droplets of acid-water solution and their growth take place either under very slow increase in number densities of water and/or acid molecules in atmosphere, or under very slow decrease in atmospheric temperature, or under all these conditions together. Moreover, that problem is well known even to experimenters investigating the condensation under instantaneous creation of metastability. Actually, it is technically very difficult (if not impossible) to "instantaneously" create the metastability, though this is necessary to make a correct comparison between experimental data and data yielded by existing theory of two-component condensation. Therefore, it is very important to know to describe the condensation phenomena under dynamical conditions.

It should be noted that we do not intend to revise the existing theory of binary condensation. The present paper is an attempt to construct the theory of two-component condensation under a new statement of problem. This statement is as follows. We intend to construct the kinetic theory of isothermal two-component condensation for dynamical conditions, when the metastability of two-component vapor mixture increases gradually. Unlike the existing theory in the present statement of problem it is not required that the formation of droplets and their growth take place after the interruption of the external influence on the vapor mixture metastability, and we shall take into account both changes of metastability caused by an external influence and the consumption of vapor mixture by droplets.

This problem will be solved by extending the method of treating of one-component condensation under dynamic conditions developed by Kuni (1984,1988) to the case of two-component theory, and we shall also need main results of the classical theory of binary condensation. Since it is a new statement of problem, no theoretical results are available with which we could compare the results of our approach (except results of Kurasov (1990), using the same method). There are no experimental data on binary condensation under dynamical conditions either; such experiments have never been carried out because the appropriate theory had not existed yet. Certainly, it would be very interesting to make a comparison between our results and results of other approaches to the problem. Besides, experimental data on the time dependence of real supersaturations and average concentration of solution in a droplet as well as on the total quantity of droplets formed during the condensation would be the best verification of present theory.

The applicability of the theory is limited only by the conditions of validity of the classical capillarity approximation. It means that the droplets must be large enough, they hold at least some tens of molecules. The formation of droplets demands their passage through a high activation barrier, i.e. has a pure fluctuation character.

It is supposed that the condensing system and its environment do not exchange droplets. At the same time we shall consider materially open systems, in which the condensing substances sources exist being homogeneously distributed within system, as well as materially closed systems. The absolute temperature T and volume V of materially open system are assumed fixed. In a materially closed system a vapor mixture metastability changes as a result of the changes of T and V, which we shall naturally take into account. It is also supposed that there are no heterogeneous nucleation centers in the vapor mixture, and that no chemical reaction occurs in considered system.

2 Complete set of equations of the kinetics of two-component condensation

Let us denote by ζ_i $(i = 1, 2)$ the supersaturation of the vapor of i-component over the plane surface of its own liquid phase:

$$\zeta_i = n_i/n_{is} \qquad (i = 1, 2), \tag{1}$$

where n_i is the number density of molecules of i-component in a vapor mixture; n_{is} is the number density of molecules of i-component vapor saturated over a plane surface of its own liquid phase (obviously, n_{is} depends on temperature T).

Let us introduce the value

$$\Phi_i = n_{itot}/n_{is} \qquad (i = 1, 2), \tag{2}$$

where n_{itot} is the total quantity (in the vapor mixture as in the droplets) of molecules of i-component in the system volume unit. Obviously, Φ_i represents the "ideal supersaturation" of i-component which could be observed in the system at the same external conditions if there was no consumption of this component by the droplets. In materially open system T, V, n_{1s} and n_{2s} are constant, and Φ_1 and Φ_2 change only as a result of injections of corresponding component by external sources. In materially closed system the total quantities of molecules of both components remain constant, i.e. $Vn_{itot} = Const \ \ (i = 1, 2)$. Therefore, in materially closed system the following equations are observed:

$$n_{is*}V_*/n_{is}V = \Phi_i/\Phi_{i*} \qquad (i = 1, 2), \tag{3}$$

where the subscript "*" marks the values at some moment t_*, when a nucleation rate is maximal. For the theory that is intended to be developed this moment coincides with the moment when a vapor mixture metastability is maximal, i.e. a critical embryo formation free energy is minimal.

Usually in addition to the droplets and binary vapor mixture participating in a material exchange with the droplets, in a condensing system there is some passive gas the molecules of which do not participate in a material exchange with the droplets. Let us suppose the passive gas concentration is high enough. Then non-isothermal effects of condensation will not be important, and the equation of state of the passive gas and character of thermal contact of the system with the environment will determine the unambiguous relationship between n_{is} $(i = 1, 2)$ and V. Taking eq.(3) into account, let us present this relationship as a parametric one:

$$n_{is*}/n_{is} = S_i(\Phi_i) \qquad (i = 1, 2), \tag{4}$$

$$V_*/V = \Phi_i/\Phi_{i*} S_i(\Phi_i) \qquad (i = 1, 2), \tag{5}$$

where $S_i(\Phi_i)$ is some function (we do not indicate its dependence on Φ_{i*}). With the help of Clapeyron's-Clausius' formula one can rewrite eq.(4) as

$$T/T_* = [S_i(\Phi_i)]^{1/\beta_{i*}} \qquad (i = 1, 2), \tag{6}$$

where β_i is the partial molecule heat of condensation of i-component taken in units of $k_B T$ (k_B is Boltzmann's constant). Ordinarily, β_i is of the order of some tens.

The functions $S_i(\Phi_i)$ $(i = 1, 2)$, which are determined by the character of thermal contact of a system with an environment, are assumed to be known. In the cases of isothermal compression, of isochoric cooling and of adiabatic expansion these functions are given, respectively, by expressions:

$$\begin{aligned} S_i(\Phi_i) &= 1, \\ &= \Phi_i/\Phi_{i*}, \qquad\qquad (i = 1, 2), \\ &= [\Phi_i/\Phi_{i*}]^{k_i+1} \end{aligned} \tag{7}$$

where

$$k_i = 1/[(\kappa - 1)\beta_{i*} - 1] \qquad (i = 1, 2), \tag{8}$$

and κ is the adiabatic constant of passive gas. The condition

$$[k_i(k_i + 1)^2/2\beta_{i*}] \ln^2(\Phi/\Phi_{i*}) \ll 1, \tag{9}$$

is that of validity of the third of expressions (7). Obviously, $k_i > 0$ and $k_i \ll 1$ for β_{i*} is a value of the order of 10. The inequalities $\beta_{i*} \gg 1$ and $k_i \ll 1$ guarantee the inequality (9) even if the difference between Φ_i and Φ_{i*} is great.

In accordance with eqs.(7), the function $S_i(\Phi_i)$ increases monotonically or remains constant with increasing Φ_i; at $\Phi_i = \Phi_{i*}$ it is equal to 1. Let us suppose that $S_i(\Phi_i)$ has the same properties also in general case of any materially closed system.

Contrary to the supersaturations ζ_i, the supersaturations Φ_i are completely determined by the external conditions in which the condensing system is, and can be controlled from outside.

During the period of intensive nucleation which is very short the time dependence of Φ_i can be well approximated by the expressions

$$\Phi_i = \begin{cases} (t/t_i)^{m_i} & (t < t_{0i}), \\ \Phi_{0i} \equiv (t_{0i}/t_i)^{m_i} & (t \geq t_{0i}) \end{cases} \quad (i = 1, 2), \tag{10}$$

with the independent positive parameters m_i, t_i and t_{0i}. The time is counted off from the moment when the ideal supersaturations were equal to zero. The moment t_{0i} corresponds to a stabilization of Φ_i on its maximal magnitude Φ_{0i} (obviously, for the materially closed system $t_{01} = t_{02}$). In fact, the approximations (10) will be necessary only during the intensive formation of embryos.

The approximations (10) together with eqs.(4)-(6) determine the time dependences of n_{1s}, n_{2s}, V, and T in materially closed system.

The supersaturations of both components determine the metastability of system. Since a nucleation rate is very sensitive to the metastability, the accuracy of the approximations (10) must be very high during the intensive formation of embryos.

Supposing $t_* \leq min(t_{01}, t_{02})$ (that means the attainment of metastability maximum before the stabilization of any of ideal supersaturations) and assuming t_*, Φ_{i*} and $(d\Phi_i/dt)|_{t=t_*}$ to be known (at $t_* = min(t_{01}, t_{02})$ the derivative corresponds to the approach to $t = t_*$ from left side), we have for the optimum values of parameters m_i, t_i in eq.(10):

$$m_i = (t_*/\Phi_{i*})(d\Phi_i/dt)|_{t=t_*}, \ t_i = t_*/\Phi_{i*}^{1/m_i} \quad (i = 1, 2). \tag{11}$$

Let us name the supercritical embryo of liquid phase (growing irreversibly) for "the droplet". Only such droplets participate perceptibly in the consumption of the vapor mixture. The regime of molecule exchange between the droplets and the vapor mixture is assumed to preserve the free molecular character even for the largest droplets considered in theory.

Let us denote by ν_1 and ν_2 the numbers of molecules of the first and second components, respectively, in the droplet. Let us choose the values ρ and χ determined according to

$$\rho = (\nu_1 + \nu_2)^{1/3}, \ \ \chi = \nu_1/(\nu_1 + \nu_2) \tag{12}$$

as the droplet state variables. The variable ρ represents the linear size of droplet, and variable χ represents the composition of the solution in a droplet. Let us denote by $n(\rho, \chi, t)$ the distribution (corresponding to unit volume and expressed in units of n_{1s}) of droplets with respect to the variables ρ and χ at moment t. It has been shown (Kuni *et al.*,1990; Melikhov *et al.*,1990; Melikhov *et al.*,1991) that the variable χ is the stable one in near-critical region. According to Dzhikaev(1992), during the second stage of two-component condensation at the instantaneous creation of metastability the distribution of droplets has a Gaussian dependence on the variable χ in supercritical region, and an average magnitude χ_0 of variable χ is determined by means of quasistationary condition on χ. Therefore, it is natural to assume that in the present theory the distribution of droplets with respect to the stable variable χ in the supercritical region also has a form of Gaussian distribution, and that an average magnitude χ_0 of variable χ in this region is determined by means of quasi-stationary condition $\dot{\chi} = d\chi/dt = 0$ leading to the transcendental equation

$$\alpha_{c1} v_{T1} n_{1s} (1 - \chi_0)[\zeta_1 - \chi_0 f_1(\chi_0)] = \alpha_{c2} v_{T2} n_{2s} \chi_0 [\zeta_2 - (1 - \chi_0) f_2(\chi_0)], \tag{13}$$

where α_{ci} and v_{Ti} $(i = 1, 2)$ are respectively the condensation coefficient and average thermal velocity of molecule of i-component in vapor mixture; $f_1(\chi)$ and $f_2(\chi)$ are the activity coefficients of the first and second components in a liquid solution with composition χ. Therefore, the distribution $n(\rho, \chi, t)$ has the form

$$n(\rho, \chi, t) = p(\rho, t)[2\pi(\Delta\chi)^2]^{-1/2} \exp\left[-\frac{(\chi - \chi_0)^2}{2(\Delta\chi)^2}\right], \tag{14}$$

where $\Delta\chi$ is an equilibrium value of the rms fluctuation of solution concentration in a droplet. The function $p(\rho, t)$ represents obviously the one-dimensional distribution (corresponding to unit volume and expressed in units of n_{1s}) of droplets with respect to variable ρ at moment t.

It has been shown (Dzhikaev, 1992) that a linear size of droplet, practically immediately after its formation, increases with time with the rate independent of linear size:

$$\dot{\rho} = \frac{d\rho}{dt} = \frac{n_{1s}}{n_{1s*}} \frac{\alpha_{c1}}{\tau_{1*}} [\zeta_1 - \chi_0 f_1(\chi_0)] + \frac{n_{2s}}{n_{2s*}} \frac{\alpha_{c2}}{\tau_{2*}} [\zeta_2 - (1 - \chi_0) f_2(\chi_0)], \tag{15}$$

$$\tau_i = [v_{Ti} n_{is} (\pi v^2/48)^{1/3}]^{-1} \quad (i = 1, 2). \tag{16}$$

Here $v \equiv v(\chi)$ is the droplet volume per molecule (it is supposed that it depends only on χ). In eqs.(15),(16) the temperature dependence of α_{ci}, v_{Ti} and v is much slighter than that of n_{is}, and one can neglect it.

Under the conditions of validity of macroscopic theory of condensation the characteristic size of droplets is much greater than their sizes at moment of formation. Therefore, the solution of equation (15) has to satisfy the initial condition

$$\rho(t)|_{t=0} = 0. \tag{17}$$

Taking into account that for all the droplets $\dot{\rho}$ does not depend on ρ and there is no droplet exchange between the system and environment, one can (Kuni, 1984; Kuni, 1988) present the distribution $p(\rho, t)$ in the form

$$p(\rho, t) = \frac{n_{1s*}V_*}{n_{1s}V}\theta(\rho)f(z-\rho). \tag{18}$$

Here

$$\theta(u) = \begin{cases} 1 & (u \geq 0), \\ 0 & (u < 0). \end{cases}$$

is theta-function; f is some function which depends on ρ and t by means of the argument $z - \rho$; z is the coordinate moving along the ρ-axis with the rate $\dot{\rho}$ of increasing of linear size of droplet. The correctness of the expression (18) is evident as it ensures the conservation of the total quantity of droplets of the system $n_{1s}Vp(\rho, t)d\rho$ in the element $d\rho$ during the movement of that element along the ρ-axis with the rate of coordinate z movement.

In order to remove an arbitrariness in the definition of coordinate z let us assume that the equation

$$\frac{dz}{dt} = \frac{n_{1s}}{n_{1s*}}\frac{\alpha_{c1}}{\tau_{1*}}[\zeta_1 - \chi_0 f_1(\chi_0)] + \frac{n_{2s}}{n_{2s*}}\frac{\alpha_{c2}}{\tau_{2*}}[\zeta_2 - (1-\chi_0)f_2(\chi_0)] \tag{19}$$

satisfies the initial condition

$$z(t)|_{t=t_*} = 0, \tag{20}$$

with $z < 0$ for $t < t_*$ and $z > 0$ for $t > t_*$.

Instead of the variable ρ let us introduce the variable

$$x = z - \rho \qquad (x \leq z). \tag{21}$$

The variables $x < 0$ correspond to the droplets formed at time moments $t < t_*$, and the variables $x > 0$ correspond to the droplets formed at time moments $t > t_*$. Since z and ρ increase with the same rate, every droplet has its own magnitude of variable x during whole its growth after its formation. Let us denote by $t(x)$ the moment of formation of the droplet characterized by value x.The more x is the later the droplet was formed and the more $t(x)$ is. All the time dependent values together with t will be x-dependent functions. At $x = 0$ those functions are equal to their magnitudes at time moment t (which are marked by subscript "$*$") and at $x = z$ they are equal to their current magnitudes.

In view of eq.(21) one can rewrite the expression (18) in the form

$$p(\rho, t) = \frac{n_{1s*} V_*}{n_{1s} V} \theta(z - x) f(x). \tag{22}$$

The function $f(x)$ characterizes the spectrum of linear sizes of droplets. Figure 1 shows the dependence of spectrum f on variable ρ and illustrates what is $f(x)$. As it has been shown by Dzhikaev (1992), under the condition of validity of the classical capillarity approximation one can assume that during the two-component nucleation the state of embryos having the linear sizes in the region $0 < \rho <\sim (2 \div 3)\rho_c$ is quasistationary, ρ_c being the linear size of critical embryo. At any current magnitudes of ζ_1 and ζ_2 this state is described by stationary one-dimensional distribution $f_s(\zeta_1, \zeta_2)$ independent of ρ. Thus, one can use $f_s(\zeta_1, \zeta_2)$ as a boundary condition to $p(\rho, t)$. Taking into account that during the first stage $n_{is} V \approx n_{is*} V_*$, we obtain from eq.(22)

$$f(x) = f_s(\zeta_1(x), \zeta_2(x)), \tag{23}$$

where $\zeta_i(x)$ $(i = 1, 2)$ is the magnitude of the supersaturation ζ_i at time $t(x)$ when the droplets with given x were formed.

According to Kuni *et al.* (1990), Melikhov *et al.* (1991), Dzhikaev (1992), the distribution f_s expressed in units of n_{1s} has the form

$$f_s(\zeta_1, \zeta_2) = K(\zeta_1, \zeta_2) \exp[-F(\zeta_1, \zeta_2)], \tag{24}$$

where the dependence of the pre-exponential factor $K(\zeta_1, \zeta_2)$ on ζ_1, ζ_2 is a power one; $F(\zeta_1, \zeta_2)$ is the height of activation barrier of two-component nucleation at saddle point, i.e. critical embryo formation free energy, expressed in units of $k_B T_*$, at the current magnitudes of supersaturations ζ_1, ζ_2. For $F(\zeta_1, \zeta_2)$, in accordance with Kuni *et al.* (1990), Melikhov *et al.* (1990) one can obtain the expression

$$F(\zeta_1, \zeta_2) = 16\pi\gamma_*^3 v^2(\chi_c)/3[\chi_c \ln\zeta_1 + (1-\chi_c)\ln\zeta_2 - G(\chi_c)]^2, \tag{25}$$

where

$$G(\chi_c) = \chi_c \ln[\chi_c f_1(\chi_c)] + (1-\chi_c)\ln[(1-\chi_c)f_2(\chi_c)], \tag{26}$$

χ_c is the composition of solution in a critical embryo; γ_* is the surface tension of embryo in units of $k_B T_*$ (assumed independent of the composition of solution in an embryo).

The expressions (14),(13),(19),(22)-(24) represent the solution of the kinetic equation of two-component condensation (obtained first by Reiss (1950)) for the considered supercritical droplets. In order that this set of equations comprising the unknown functions $\zeta_1(x)$ and $\zeta_2(x)$ becomes consistent it is necessary to add to them the material balance equations for both components:

$$\Phi_i = \zeta_i + g_i \qquad (i = 1, 2), \tag{27}$$

where g_i, according to eqs.(1),(2), represents the total quantity (corresponding to unit volume and expressed in units of n_{1s}) of molecules of i-component condensed in all the droplets. Taking into account the facts that ρ^3 is the total number of molecules in a droplet of linear size ρ and that χ_0 does not depend on ρ, we obtain in view of relations (14),(21) and (22):

$$g_1 = \chi_0 \frac{n_{1s*}V_*}{n_{1s}V} \int_{-\infty}^{z} dx\,(z-x)^3 f(x), \tag{28}$$

$$g_2 = \frac{1-\chi_0}{\chi_0}\frac{n_{1s}}{n_{2s}} g_1. \tag{29}$$

The relations (14),(13),(22)-(24) together with (10),(27)-(29) compose the consistent set of equations of the two-component condensation.The unknowns in this set are the spectrum $f(x)$, coordinate z and composition χ_0.

Let $\rho_{min}(t)$ be the coordinate of the left bound of the region in which the values of the distribution $p(\rho, t)$ are relatively important at time t. Obviously, during a nucleation stage $\rho_{min}(t) = 0$. However, after its end the coordinate $\rho_{min}(t)$ begins moving along the ρ-axis with the rate $\dot{\rho}$ of the increase of linear size of droplet. The decrease of the supersaturations ζ_1 and ζ_2 (on account of the consumption of vapor mixture substances by the ensemble of supercritical droplets) slows the velocity of movement of the coordinate $\rho_{min}(t)$ down, according to eq.(15). The decrease of the supersaturations ζ_1 and ζ_2 (causing the decrease of the metastability of condensing vapor mixture) induces simultaneously the increase of the critical droplet size $\rho_c(\zeta_1, \zeta_2)$ at the current magnitudes of supersaturations. The size $\rho_c(\zeta_1(t), \zeta_2(t))$ begins coming up to the coordinate $\rho_{min}(t)$ on the ρ-axis. The quasistationary distribution of the near-critical droplets is broken and the equation (23) ceases to be observed (in view of the very small intensity of formation of embryos after a nucleation stage end, it's no longer necessary for the developed theory). However, the formula (18) and the set of equations of two-component condensation kinetics remains correct as long as the following constraint is observed:

$$\rho_c(\zeta_1(t), \zeta_2(t)) \leq \rho_{min}(t) \tag{30}$$

i.e. as long as the droplets formed during nucleation stage remain supercritical.

The breakdown of the constraint (30) causes that the droplets formed during a nucleation stage gradually become subcritical (evaporating), and the two-component condensation changes into the two-component coalescence which we shall not consider here.

3 Iteration procedure in the case of continuous increase of both ideal supersaturations

Let us define the parameters Γ_1 and Γ_2 as

$$\Gamma_1 = -\Phi_{1*} \frac{\partial F}{\partial \zeta_1}\bigg|_{\zeta_1=\Phi_{1*}, \zeta_2=\Phi_{2*}}, \quad \Gamma_2 = -\Phi_{2*} \frac{\partial F}{\partial \zeta_2}\bigg|_{\zeta_1=\Phi_{1*}, \zeta_2=\Phi_{2*}}, \tag{31}$$

where $F \equiv F(\zeta_1, \zeta_2)$. Using eqs.(25),(26) one can show that under the condition of validity of the macroscopic description of condensation (when F has the order of some tens) usually

$$\Gamma_i \gg 1 \qquad (i = 1, 2). \tag{32}$$

Later on the correctness of the following estimates will be proved

$$|\zeta_{i*} - \Phi_{i*}|/\Phi_{i*} \ll 1 \qquad (i = 1, 2). \tag{33}$$

Taking eqs.(23),(24),(31)-(33) into account, one can obtain for the spectrum that

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[\frac{\Gamma_1}{\Phi_{1*}}(\zeta_1(x) - \Phi_{1*}) + \frac{\Gamma_2}{\Phi_{2*}}(\zeta_2(x) - \Phi_{2*})\right], \tag{34}$$

where

$$f_s(\zeta_{1*}, \zeta_{2*}) = K(\zeta_{1*}, \zeta_{2*}) \exp[-F(\zeta_{1*}, \zeta_{2*})] \tag{35}$$

(the relative error in (34) has the order of $1/\Gamma_1 + 1/\Gamma_2 \ll 1$).

Let us define the important parameter Γ according to

$$\Gamma = \Gamma_1 + \Gamma_2 \frac{1 - \chi_0}{\chi_0} \frac{\Phi_{1*}}{\Phi_{2*}} \frac{n_{1s}}{n_{2s}}. \tag{36}$$

Introducing the notation

$$P = \frac{1 - \chi_0}{\chi_0} \frac{n_{1tot}}{n_{2tot}} \tag{37}$$

and supposing the condition $P \sim 1$ is observed we conclude that the parameter Γ always satisfies the condition

$$\Gamma \gg 1. \tag{38}$$

Let us define the parameters c_1 and c_2 by relations

$$c_i = \frac{\Gamma_*}{\Phi_{i*}} \frac{d\Phi_i(x)}{dx}\bigg|_{x=0} \qquad (i = 1, 2), \tag{39}$$

where the $\Phi_i(x)$ is the ideal supersaturation Φ_i at time $t(x)$ when the droplets with given x were formed. According to eq.(39), the value $1/c_i$ represents the length on the x-axis on which the relative change of supersaturation Φ_i is $1/\Gamma_*$.

Linearizing $\Phi_i(x)$ in x near $x = 0$ and using eq.(39), we have

$$\Phi_i(x) = \Phi_{i*} + \frac{\Phi_{i*}}{\Gamma_*} c_i x \qquad (i = 1, 2), \tag{40}$$

and the expression (21) takes the form

$$\zeta_i(x) - \Phi_{i*} = \frac{\Phi_{i*}}{\Gamma_*} c_i x - g_i(x) \qquad (i = 1, 2). \tag{41}$$

Inserting eq.(41) in (34) and taking eqs.(29),(36) into account, we obtain

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[cx - \frac{\Gamma}{\Phi_{1*}} g_1(x)\right], \tag{42}$$

where

$$c = \frac{\Gamma_1}{\Gamma_*} c_1 + \frac{\Gamma_2}{\Gamma_*} c_2. \tag{43}$$

During the nucleation stage on account of its relative shortness one can assume $n_{is} = n_{is*}$ $(i = 1, 2), V = V_*$ and $\chi_0 = \chi_{0*}$. Taking eq.(42) into account, we rewrite eq.(28) as

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} dx\, (z - x)^3 \exp\left[cx - \frac{\Gamma}{\Phi_{1*}} g_1(x)\right]. \tag{44}$$

According to the definition of t_* as a time moment of attainment of the metastability maximum, we have

$$\left.\frac{dF}{dt}\right|_{t=t_*} = 0, \tag{45}$$

$$\left.\frac{d^2F}{dt^2}\right|_{t=t_*} > 0. \tag{46}$$

Using eqs.(25),(26), from (45) and (46) we obtain, respectively, the equation

$$\left.\frac{\chi_c}{\zeta_1} \frac{d\zeta_1}{dt}\right|_{t=t_*} + \left.\frac{1 - \chi_c}{\zeta_2} \frac{d\zeta_2}{dt}\right|_{t=t_*} = 0 \tag{47}$$

and the inequality

$$\left.\left[\frac{\chi_c}{1 - \chi_c} \frac{1}{\zeta_1^2} \left(\frac{d\zeta_1}{dt}\right)^2 - \frac{\chi_c}{\zeta_1} \frac{d^2\zeta_1}{dt^2} - \frac{1 - \chi_c}{\zeta_2} \frac{d^2\zeta_2}{dt^2}\right]\right|_{t=t_*} > 0 \tag{48}$$

(it is assumed that the condition of metastability of two-component vapor mixture

(Kuni *et al.*,1990; Melikhov *et al.*,1990) is observed). From equation (47) it follows that the alternative possibilities exist for the behaviour of supersaturations ζ_1 and ζ_2 at the moment t_* - either

$$\left.\frac{d\zeta_1}{dt}\right|_{t=t_*} = \left.\frac{d\zeta_2}{dt}\right|_{t=t_*} = 0 \tag{49}$$

else

$$\left.\frac{d\zeta_1}{dt}\right|_{t=t_*} = -\left.\frac{1-\chi_c}{\chi_c}\frac{\zeta_1}{\zeta_2}\frac{d\zeta_2}{dt}\right|_{t=t_*} \neq 0. \tag{50}$$

The fulfillment of the equalities (49) corresponds to a synchronous attainment of metastability maximum when the supersaturations ζ_1 and ζ_2 attain their maximums simultaneously at the moment t_*. The fulfillment of (50) corresponds to a non-synchronous attainment of metastability maximum when at the moment t_* one of the supersaturations (ζ_1 else ζ_2) already passed its maximum and decreases, another (ζ_2 else ζ_1) did not attain its maximum yet and increases. What kind of attainment occurs depends on both external influences and physical properties of condensing system. In this paper we shall consider almost the case of synchronous attainment of metastability maximum because it is easier to extend to this case the iteration method developed by Kuni (1984,1988) for description of unary condensation under dynamic conditions.

Let the equalities (49) be observed. Differentiating eq.(41) with respect to x and taking into account that $\zeta_i'(x) = 0$ $(i = 1, 2)$ at $x = 0$, we obtain

$$g_1'(0) = \frac{\Phi_{1*}}{\Gamma_*}c_1\,,\; g_2'(0) = \frac{\Phi_{2*}}{\Gamma_*}c_2 \tag{51}$$

(the prime indicates the first derivative). The equations (51) compose the set of linearly independent equations with respect to the variables Φ_{1*} and Φ_{2*}.

With the help of eqs.(29),(36) and (43) from eq.(51) we obtain the useful equation

$$g_1'(0) = \frac{\Phi_{1*}}{\Gamma_*}c. \tag{52}$$

The relations (44),(52) compose the consistent set of equations with respect to $g_1(z)$ and $f_s(\Phi_{1*}, \Phi_{2*})$ (the composition χ_{0*} figuring in this set as a parameter obeys the equation (13)). This set can be solved with the help of the iteration method which has been developed by Kuni (1984,1988) for the construction of kinetic theory of one-component condensation under dynamic conditions.

Let us construct the first approximation corresponding to the insertion of the equality $g_1(x) = 0$ in the RHS of eq.(44). In this approximation the accumulation of substance by the droplets occurs more rapidly than it occurs in reality.

We have

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} dx\,(z-x)^3 e^{cx}, \qquad (53)$$

$$g_1'(0) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \frac{6}{c^3},$$

and also

$$f_s(\Phi_{1*}, \Phi_{2*}) = \frac{\Phi_{1*}}{6\Gamma_* \chi_{0*}} c^4. \qquad (54)$$

Taking into account (54) and equality

$$\int_{-\infty}^{x} dx\,(z-x)^3 e^{c} x = \frac{6}{c^4} e^{cz}, \qquad (55)$$

it follows from eq.(53) that

$$g_1(z) = \frac{\Phi_{1*}}{\Gamma_*} e^{cz}. \qquad (56)$$

By using eq.(27) at $x = 0$ and the equalities (56) and (29), one can obtain the relations

$$\zeta_{1*} = \Phi_{1*}(1 - 1/\Gamma_*), \quad \zeta_{2*} = \Phi_{2*}\left[1 - P_* \frac{1}{\Gamma_*}\right], \qquad (57)$$

which, in view of eqs.(32),(36)-(38), justify the estimates (33) at the first step of iteration procedure.

Let us construct the second approximation corresponding to the insertion of eq.(56) in the RHS of eq.(44). In this approximation the accumulation of substance by the droplets occurs more slowly than it occurs in reality.

We have

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} dx\,(z-x)^3 \exp\left[cx - e^{cx}\right], \tag{58}$$

$$g_1'(0) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \frac{3b_2}{c^3}, \tag{59}$$

and also

$$f_s(\Phi_{1*}, \Phi_{2*}) = \frac{\Phi_{1*}}{3b_2 \Gamma_* \chi_{0*}} c^4, \tag{60}$$

where

$$b_q = \int_0^\infty d\xi\, \xi^q \exp\left[-\xi - e^{-\xi}\right] \quad (q = 0, 1, 2, \ldots). \tag{61}$$

Numeric calculations show that

$$b_0 = 1 - 1/e = 0.632,\ b_1 = 0.797,\ b_2 = 1.78,\ b_3 = 5.66. \tag{62}$$

Denoting by symbol δ the difference between the magnitudes of value in the first and second approximations, one can, with the use of eq.(10), establish

$$\frac{\delta\Phi_{1*}}{\Phi_{1*}} = \left(\frac{2}{b_2} - 1\right) \Big/ \left[\Gamma_1 + \frac{m_2}{m_1}\Gamma_2\right] = 0.12/\left[\Gamma_1 + \frac{m_2}{m_1}\Gamma_2\right],$$

$$\frac{\delta\Phi_{2*}}{\Phi_{2*}} = \left(\frac{2}{b_2} - 1\right) \Big/ \left[\frac{m_1}{m_2}\Gamma_1 + \Gamma_2\right] = 0.12/\left[\frac{m_1}{m_2}\Gamma_1 + \Gamma_2\right]. \tag{63}$$

Inserting eq.(60) in (58) and using eq.(61), we obtain

$$g_1(z) = \frac{\Phi_{1*}}{3b_2\Gamma_*} c^4 \int_{-\infty}^{z} dx\,(z-x)^3 \exp\left[cx - e^{cx}\right], \tag{64}$$

$$g_1(0) = \frac{b_3}{3b_2} \frac{\Phi_{1*}}{\Gamma_*}. \tag{65}$$

With the help of eq.(27) at $x = 0$ and eqs.(65),(29) one can obtain the relations

$$\zeta_{1*} = \Phi_{1*}\left[1 - \frac{b_3}{3b_2}\frac{1}{\Gamma_*}\right],\ \zeta_{2*} = \Phi_{2*}\left[1 - P_* \frac{b_3}{3b_2}\frac{1}{\Gamma_*}\right] \tag{66}$$

which, in virtue of eqs.(32),(36)-(38) and (62), justify the estimates (33) at the second step of iteration procedure.

Marking with superscripts 0,1,2,... the values at the corresponding iteration step, let us compare the first approximation with the second one.

From eqs.(10) and (63) it follows that

$$\frac{\delta t_*}{t_*} = \left(\frac{2}{b_2} - 1\right) \Big/ (m_1\Gamma_1 + m_2\Gamma_2) = \frac{0.12}{m_1\Gamma_1 + m_2\Gamma_2}, \tag{67}$$

i.e. the moment $t_*^{(2)}$ has become a little more than the moment $t_*^{(1)}$ (we exclude from considering theory very small m_1 and m_2, assuming $m_1\Gamma_1 + m_2\Gamma_2 \gg 1$) owing to the more slow accumulation of substance by the droplets in second approximation. The increase of the duration of droplet growth clears the result $g_1^{(2)}(0) > g_1^{(1)}(0)$ following from eqs.(56),(65) and (62).

Inserting eqs.(54),(56) and then the eqs.(60),(64) in (42), we find the spectrum $f(x)$ in the first and second approximations, respectively:

$$f^{(1)}(x) = \frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}} c^4 \exp\left[cx - e^{cx}\right], \tag{68}$$

$$f^{(2)}(x) = \frac{\Phi_{1*}}{3b_2\Gamma_*\chi_{0*}} c^4 \exp\left[cx - \frac{c^4}{3b_2}\int_{-\infty}^{x} dx'\,(x-x')^3 \exp\left(cx' - e^{cx'}\right)\right] \tag{69}$$

(in view of eqs.(63),(32),(38) we suppose $\Phi_{1*}, \Phi_{2*}, \Gamma_*$, and c are the same in first and second approximations).

From eqs.(19),(20),(67) and (10) it follows that in second approximation the beginning of z-axis shifts by

$$\delta z = \left(\frac{2}{b_2} - 1\right) \Big/ c = 0.12/c \tag{70}$$

compared with that of first approximation.

Substituting in eqs.(56),(68) the variables z and x corresponding to the second approximation and taking eq.(55) into account, we obtain

$$g_1^{(1)}(z) = \frac{\Phi_{1*}}{3b_2\Gamma_*} c^4 \int_{-\infty}^{z} dx\,(z-x)^3 e^{cx}, \tag{71}$$

$$f^{(1)}(x) = \frac{\Phi_{1*}}{3b_2\Gamma_*\chi_{0*}} c^4 \exp\left[cx - \frac{c^4}{3b_2}\int_{-\infty}^{x} dx'\,(x-x')^3 e^{cx'}\right]. \tag{72}$$

Comparing eqs.(64) and (69) respectively with eqs.(71) and (72), we conclude that $g_1^{(2)}(z) < g_1^{(1)}(z)$ and $f^{(2)}(x) > f^{(1)}(x)$. These inequalities would remain true under the use of other variables z, x corresponding to an arbitrary but common choice of the zero point of z-axis. Under common choice of zero point of z-axis the following estimates are also true

$$g_1^{(2)}(z) < g_1(z) < g_1^{(1)}(z), \tag{73}$$

$$f^{(2)}(x) > f(x) > f^{(1)}(x), \tag{74}$$

where $g_1(z)$ and $f(x)$ correspond to the strict solution of the set of equations (44),(52).

Since the value $1/c$ characterizes the scale determining the width of the most important part of spectrum, one may, in virtue of eq.(70), neglect the breakdown of estimates (73),(74) owing to the shift of t_* by δt_* in condition (20), and one may, in the same way, assume that the estimate (74) is true even if the functions $f^{(1)}(x)$ and $f^{(2)}(x)$ are given by eqs.(68),(69). In such a sense we shall understand these functions from now on.

Let us define the left and right spectrum half-widths $\Delta_- x$ and $\Delta_+ x$ as

$$f(-\Delta_- x) = f(0)/e, \quad f(\Delta_+ x) = f(0)/e. \tag{75}$$

Within the interval $\Delta_- x < x < \Delta_+ x$ the relatively important part of spectrum is situated. In first approximation, according to eq.(68), we have

$$\Delta_- x = 1.84/c, \quad \Delta_+ x = 1.15/c. \tag{76}$$

With the help of eqs.(68),(69) and (76) one can obtain the relations

$$\frac{f^{(2)}(x) - f^{(1)}(x)}{f^{(1)}(x)} = \frac{2}{b_2} - 1 = 0.12 \quad (-cx \gg 1),$$

$$\frac{f^{(2)}(0) - f^{(1)}(0)}{f^{(1)}(0)} = \frac{2}{b_2} \exp\left(1 - \frac{b_3}{3b_2}\right) - 1 = 0.059, \tag{77}$$

$$\frac{f^{(2)}(\Delta_+ x) - f^{(1)}(\Delta_+ x)}{f^{(1)}(\Delta_+ x)} = 0.50$$

and the estimate

$$\frac{f^{(2)}(x)}{f^{(2)}(0)} < \exp\left[-\frac{b_1}{b_2}c^2x^2 - \frac{b_0}{3b_2}c^3x^3\right] \quad (x > 0), \tag{78}$$

the analysis of which allows to conclude that already first approximation of spectrum given by eq.(68) is fairly accurate. By this approximation we shall be satisfied afterwards.

4 Simultaneous and non-simultaneous stabilizations of ideal supersaturations after the attainment of the metastability maximum

Above, in the developed iteration procedure it was supposed that the stabilization of ideal supersaturations Φ_1 and Φ_2 occurs after the end of formation of the most important part of spectrum. In the cases where the stabilization of either Φ_1 or Φ_2 and that the stabilization of both Φ_1 and Φ_2 occurs before the end of the stage of formation of the most important part of spectrum, the presented iteration procedure will change a little.

Let us consider at first the case where

$$\Phi_{1*} < \Phi_{01} <\sim \Phi_{1*}(1 + 1.15c_1/c\Gamma_*), \quad \Phi_{02} > \Phi_{2*}(1 + 1.15c_2/c\Gamma_*), \tag{79}$$

i.e. where one of the ideal supersaturations (Φ_1) is stabilized before the end of the stage of formation of the spectrum, and other ideal supersaturation (Φ_2) is stabilized after the end of that stage.

The relations (40) will take the form

$$\begin{aligned} \Phi_1(x) &= \Phi_{1*} + \frac{\Phi_{1*}}{\Gamma_*}c_1 x \quad (x < z_0), \\ &= \Phi_{1*} + \frac{\Phi_{1*}}{\Gamma_*}c_1 z_0 \quad (x \geq z_0), \\ \Phi_2(x) &= \Phi_{2*} + \frac{\Phi_{2*}}{\Gamma_*}c_2 x, \end{aligned} \tag{80}$$

where

$$z_0 = \frac{\Gamma_*}{c_1}(\Phi_{01}/\Phi_{1*} - 1). \tag{81}$$

Respectively instead of eq.(41) we have

$$\begin{aligned}
\zeta_1(x) - \Phi_{1*} &= \frac{\Phi_{1*}}{\Gamma_*}c_1 x - g_1(x) \quad (x < z_0), \\
&= \frac{\Phi_{1*}}{\Gamma_*}c_1 z_0 - g_1(x) \quad (x \geq z_0), \\
\zeta_2(x) - \Phi_{2*} &= \frac{\Phi_{2*}}{\Gamma_*}c_2 x - g_2(x).
\end{aligned} \tag{82}$$

The expressions (42),(53) change only in the regions $x \geq z_0$ and $z \geq z_0$. In these regions now

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[cz_0 - \frac{\Gamma_*}{\Phi_{1*}}g_1(x) + \frac{\Gamma_2}{\Gamma_*}c_2(x - z_0)\right] \quad (x \geq z_0), \tag{83}$$

$$\begin{aligned}
g_1(z) &= \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \left\{\int_{-\infty}^{z_0} dx\,(z-x)^3 e^{cx} + \right. \\
&\left. + \int_{z_0}^{z} dx\,(z-x)^3 \exp\left[cz_0 + \frac{\Gamma_2}{\Gamma_*}c_2(x - z_0)\right]\right\} \quad (z \geq z_0).
\end{aligned} \tag{84}$$

Taking eq.(54) into account and carrying out integration in eq.(84), we obtain

$$\begin{aligned}
g_1(z) &= \frac{\Phi_{1*}}{\Gamma_*}e^{cz_0}\left[1 + c(z - z_0) + \frac{1}{2}c^2(z - z_0)^2 + \frac{1}{6}c^3(z - z_0)^3 + \right. \\
&\left. + \frac{1}{24}c^4(z - z_0)^4 + \frac{1}{120}c^4\lambda(z - z_0)^5\right] \quad (z \geq z_0),
\end{aligned} \tag{85}$$

where $\lambda = c_2\Gamma_2/\Gamma_*$. Inserting eq.(85) in (83) and taking eq.(54) into account, we obtain

$$\begin{aligned}
f(x) &= \frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 \exp\left[cx - e^{cx}\right] \quad (x < z_0), \\
f(x) &= \frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 \exp\left\{cx - e^{cz_0}\left[1 + c(x - z_0) + \frac{1}{2}c^2(x - z_0)^2 + \right.\right. \\
&\left. + \frac{1}{6}c^3(x - z_0)^3 + \frac{1}{24}c^4(x - z_0)^4 + \frac{1}{120}c^4\lambda(x - z_0)^5\right] + \\
&\left. + \lambda(x - z_0)\right\} \qquad (x \geq z_0)
\end{aligned} \tag{86}$$

(obviously, the eq.(68) for $f(x)$ remains true as long as $x < z_0$).

In the case where both ideal supersaturations, Φ_1 and Φ_2, are stabilized simultaneously before the end of the stage of formation of the spectrum, we have

$$\Phi_{i*} < \Phi_{0i} <\sim \Phi_{i*}(1 + 1.15c_i/c\Gamma_*) \quad (i = 1,2). \tag{87}$$

In this case the changes in the iteration procedure do not lead to eqs.(80)-(86), but to the equations

$$\Phi_i(x) = \begin{cases} \Phi_{i*} + \frac{\Phi_{i*}}{\Gamma_*}c_i x & (x < z_0), \\ \Phi_{i*} + \frac{\Phi_{i*}}{\Gamma_*}c_i z_0 & (x \geq z_0) \end{cases} \quad (i = 1,2), \tag{88}$$

$$z_0 = \frac{\Gamma_*}{c_1}(\Phi_{01}/\Phi_{1*} - 1) = \frac{\Gamma_*}{c_2}(\Phi_{02}/\Phi_{2*} - 1), \tag{89}$$

$$\zeta_i(x) - \Phi_{i*} = \begin{cases} \frac{\Phi_{i*}}{\Gamma_*}c_i x - g_i(x) & (x < z_0), \\ \frac{\Phi_{i*}}{\Gamma_*}c_i z_0 - g_i(x) & (x \geq z_0) \end{cases} \quad (i = 1,2), \tag{90}$$

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[cz_0 - \frac{\Gamma_*}{\Phi_{1*}} g_1(x)\right] \quad (x \geq z_0), \tag{91}$$

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \left[\int_{-\infty}^{z_0} dx\,(z - x)^3 e^{cx} + + \int_{z_0}^{z} dx\,(z - x)^3 e^{cz_0}\right] \quad (x \geq z_0), \tag{92}$$

$$\begin{aligned} g_1(z) \quad = \quad & \frac{\Phi_{1*}}{\Gamma_*} e^{cz_0} \left[1 + c(z - z_0) + \frac{1}{2}c^2(z - z_0)^2 + \right. \\ & \left. \frac{1}{6}c^3(z - z_0)^3 + \frac{1}{24}c^4(z - z_0)^4\right] \quad (z \geq z_0), \end{aligned} \tag{93}$$

$$\begin{aligned} f(x) \quad &= \quad \frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}} c^4 \exp\left[cx - e^{cx}\right] \quad (x < z_0) \\ f(x) \quad &= \quad \frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}} c^4 \exp\left\{cx - e^{cz_0}\left[1 + c(x - z_0) + \frac{1}{2}c^2(x - z_0)^2 + \right.\right. \\ & \left.\left. + \frac{1}{6}c^3(x - z_0)^3 + \frac{1}{24}c^4(x - z_0)^4\right]\right\} \quad (x \geq z_0). \end{aligned} \tag{94}$$

Let us denote by N the total quantity of droplets per volume unit formed during the first stage of two-component condensation. This quantity, according to eqs.(14),(21) and (22), linearly depends on the spectrum by means of integral value

$$I = \int_{-\infty}^{\infty} dx\, f(x). \tag{95}$$

Therefore, the accuracy of determination of the value I has particular significance.

To estimate the accuracy of determination of the value I, let us change a little the above described iteration procedure by supposing that $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$ and $f_s(\Phi_{1*}, \Phi_{2*})$ (and with them Γ_* and c too) are the same in all the iteration steps and determined by insertion of the last of used approximations in eqs.(51),(52). Having chosen in this common way $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$ and $f_s(\Phi_{1*}, \Phi_{2*})$ one can guarantee that the less the function $g_1(x)$ in the RHS of eq.(44) is the more the RHS of eq.(44) is. This property makes it possible to construct, by means of an iteration procedure, the approximations $g_1^{(j)}(x) \quad (j = 0, 1, 2, ...)$ which monotonically approach the strict solution of eq.(44) with chosen $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$ and $f_s(\Phi_{1*}, \Phi_{2*})$. This property guarantees the uniqueness of strict solution.

Let us choose the $g_1^{(0)} = 0$ as the initial approximation in the iteration procedure. Such a choice ensures the inequality $g_1 > g_1^{(0)}$, where g_1 is the strict solution of eq.(44). Every next approximation is determined by inserting the precedent one in the RHS of eq.(44):

$$g_1^{(j+1)}(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} dx\, (z-x)^3 \exp\left[cx - \frac{\Gamma_*}{\Phi_{1*}} g_1^{(j)}(x)\right] \quad (j = 0, 1, 2, ...). \tag{96}$$

Using the indicated property of the RHS of eq.(44) and taking into account the obvious inequalities $g_1 > g_1^{(0)}, g_1^{(2)} > g_1^{(0)}$ and the fact that the calculation of the RHS with the help of strict solution g_1 leads to the same solution g_1, we conclude:

$$g_1 < g_1^{(1)},\ g_1 > g_1^{(2)},\ g_1 < g_1^{(3)},\ \dots, \tag{97}$$

$$g_1^{(3)} < g_1^{(1)},\ g_1^{(4)} > g_1^{(2)},\ g_1^{(5)} < g_1^{(3)},\ \dots. \tag{98}$$

According to eqs.(97),(98) the approximations $g_1^{(1)}, g_1^{(3)}, ...$ of odd order monotonically approach g_1 from superior, and the approximations $g_1^{(2)}, g_1^{(4)}, ...$ of even order monotonically approach g_1 from inferior.

The approximations of the spectrum $f^{(k)} \quad (k = 1, 2, 3, ...)$ are found by substituting $g_1^{(k)}(x)$ for $g_1(x)$ in the RHS of eq.(42):

$$f^{(k)}(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[cx - \frac{\Gamma_*}{\Phi_{1*}} g_1^{(k)}(x)\right] \quad (k = 1, 2, 3...) \tag{99}$$

In accordance with eqs.(97),(98) we have

$$f > f^{(1)},\ f < f^{(2)},\ f > f^{(3)},\ \ldots, \tag{100}$$

$$f^{(3)} > f^{(1)},\ f^{(4)} < f^{(2)},\ f^{(5)} > f^{(3)},\ \ldots . \tag{101}$$

The analogous inequalities take place for the iterations of the integral spectrum characteristic $I^{(k)}$ $(k = 1, 2, 3, ..)$ which are determined by substituting $f^{(k)}$ for $f(x)$ in the RHS of eq.(95):

$$I > I^{(1)},\ I < I^{(2)},\ I > I^{(3)},\ \ldots, \tag{102}$$

$$I^{(3)} > I^{(1)},\ I^{(4)} < I^{(2)},\ I^{(5)} > I^{(3)},\ \ldots . \tag{103}$$

Let us construct the iterations by described means. Introducing the value

$$h = 6\Gamma_* \chi_{0*} / \Phi_{1*} c^3 \tag{104}$$

and denoting $f_s(\Phi_{1*}, \Phi_{2*})$ by f_{s*}, we have in first approximation

$$g_1^{(1)}(z) = \frac{\Phi_{1*}}{\Gamma_*} \frac{h}{c} f_{s*} e^{cz}, \tag{105}$$

$$f^{(1)}(x) = f_{s*} \exp\left[cx - \frac{h}{c} f_{s*} e^{cx}\right], \tag{106}$$

$$I^{(1)} = \frac{1}{h} \int_{-\infty}^{\infty} d\xi \, \exp\left(\xi - e^{\xi}\right) = \frac{1}{h}. \tag{107}$$

In second approximation we obtain

$$g_1^{(2)}(z) = \chi_{0*} f_{s*} \int_{-\infty}^{z} dx \, (z - x)^3 \exp\left[cx - \frac{h}{c} f_{s*} e^{cx}\right], \tag{108}$$

$$f^{(2)}(x) = f_{s*} \exp\left\{cx - \frac{hc^3}{6} f_{s*} \int_{-\infty}^{x} dx' \, (x - x')^3 \exp\left[cx' - \frac{h}{c} f_{s*} e^{cx'}\right]\right\}, \tag{109}$$

$$I^{(2)} = \Psi / h, \tag{110}$$

where

$$\xi = cx + \ln\left(\frac{h}{c} f_{s*}\right), \tag{111}$$

$$\Psi = \int_{-\infty}^{\infty} d\xi \, \exp\left[\xi - \frac{1}{6}\int_{-\infty}^{\xi} d\xi' \, (\xi - \xi')^3 \exp\left(\xi' - e^{\xi'}\right)\right] = 1.15. \tag{112}$$

At the first step of iteration procedure (interrupted at first iteration) f_{s*} is found from eq.(52) with the help of eq.(105). That leads to the anterior formulas (54),(56),(68). At the second step of iteration procedure (interrupted at second iteration) f_{s*} is found from eq.(52) with the help of eq.(108). In this case both in first and in second iterations a small difference is observed with regard to the anterior results.

In accordance with eqs.(107),(110) and (112) it is true that

$$\frac{I^{(2)} - I^{(1)}}{I^{(1)}} = \Psi - 1 = 0.15. \tag{113}$$

Taking eq.(102) into account one can write

$$I^{(2)} > I > I^{(1)}, \tag{114}$$

where I corresponds to the strict solution of eq.(44) (with the same $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$ and f_{s*}). The relations (113),(114) guarantee the inequality

$$\frac{I - I^{(1)}}{I^{(1)}} < \Psi - 1 = 0.15 \tag{115}$$

which allows to conclude that the expression (107) approximates the integral characteristic I with the relative error less than 0.15.

Taking eqs.(25),(26) into account, it follows from eqs.(104),(31),(36),(39) and (43) that the value $1/h$ in the RHS of eq.(107) is a relatively "slow" function of $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$. A fairly accurate calculation of $1/h$ is attained in first iteration step. Therefore, in the same step we also find the integral characteristic I and total quantity of droplets N with the relative error less than 0.15.

5 Initial and final periods of two-component condensation

Omitting in the following the approximation superscript, for the spectrum in accordance with eq.(68) we have

$$f(x) = \frac{\Phi_{1*}}{6\Gamma_* \chi_{0*}} c^4 \exp\left[cx - e^{cx}\right]. \tag{116}$$

Inserting eq.(116) in eq.(28) we obtain

$$g_1 = \frac{\chi_0 n_{1s*} V_*}{\chi_{0*} n_{1s} V} \frac{\Phi_{1*}}{6\Gamma_*} c^4 \int_{-\infty}^{z} dx\, (z-x)^3 \exp\left[cx - e^{cx}\right]. \tag{117}$$

The expressions (117),(29) are already true not only during the stage of formation of spectrum (when $\chi_0 \simeq \chi_{0*}, V \simeq V_*$ and $n_{is} \simeq n_{is*}$ $(i = 1,2)$) but also during whole condensation process. The time dependence of the factor $n_{is*} V_*/n_{is} V$ $(i = 1,2)$ is assumed to be known, and the value χ_0 satisfies eq.(13).

The relations (27),(10),(13),(117),(29),(19),(20) form the consistent set of equations. Resolving this set we can obtain the function $z(t)$ of one independent variable t. Together with $z(t)$, the time dependences of ζ_i $(i = 1,2)$ are also determined.

For the total quantity of droplets formed per volume unit we have according to eq.(22):

$$N = n_{1s*} \frac{V_*}{V} \int_{-\infty}^{\infty} dx\, f(x). \tag{118}$$

Inserting eq.(116) in (118) and integrating, we obtain

$$N = n_{1s*} \frac{V_*}{V} \frac{\Phi_{1*} c^3}{6\Gamma_* \chi_{0*}}. \tag{119}$$

Let $\Delta_- \Phi_i$ $(i = 1,2)$ and $\Delta_- t$ be the changes of Φ_i and t corresponding to the change of z from $-\Delta_- x$ to 0, and let $\Delta_+ \Phi_i$ $(i = 1,2)$ and $\Delta_+ t$ be the changes of Φ_i and t corresponding to the change of z from 0 to $\Delta_+ x$. The values Φ_i and t have the magnitudes $\Phi_{i*} - \Delta_- \Phi_i$ and $t_* - \Delta_- t$ at moment of beginning of intensive nucleation and the magnitudes $\Phi_{i*} + \Delta_+\Phi_i$ and $t_* + \Delta_+ t$ at moment of end of intensive nucleation.

From eqs.(40),(76),(39) and (43) we have

$$\frac{\Delta_-\Phi_i}{\Phi_{i*}} = \frac{1.84c_i}{c_1\Gamma_1 + c_2\Gamma_2}, \quad \frac{\Delta_+\Phi_i}{\Phi_{i*}} = \frac{1.15c_i}{c_1\Gamma_1 + c_2\Gamma_2} \quad (i = 1, 2) \tag{120}$$

and, in view of eq.(10), also

$$\frac{\Delta_- t}{t_*} = \frac{1.84}{m_1\Gamma_1 + m_2\Gamma_2}, \quad \frac{\Delta_+ t}{t_*} = \frac{1.15}{m_1\Gamma_1 + m_2\Gamma_2}. \tag{121}$$

Supposing that the condition

$$m_1\Gamma_1 + m_2\Gamma_2 \gg 1 \tag{122}$$

is observed (this condition excludes from theory only very small m_1 and m_2), the smallness of the RHS of eqs.(120),(121) will be guaranteed what justifies the linearization of the upper of eqs.(10) in t and x during the first stage which has been used in eq.(40).

The full width of spectrum Δx and the full duration of first stage Δt are determined as follows

$$\Delta x = \Delta_- x + \Delta_+ x, \ \Delta t = \Delta_- t + \Delta_+ t. \tag{123}$$

From eqs.(76),(121) we have

$$\Delta x = 3/c, \ \Delta t = 3t_*/(m_1\Gamma_1 + m_2\Gamma_2) \tag{124}$$

The condition (122) leads to the smallness of intensive nucleation duration in comparison with the time of the beginning of nucleation.

In order to complete the description of the kinetics of two-component condensation under dynamic conditions, it is necessary to determine the time dependences of z, ζ_1 and ζ_2. The rate of increase of linear size of droplet is not so sensitive to supersaturations ζ_1 and ζ_2 as the nucleation intensity, hence the high accuracy of determination of the supersaturations ζ_1 and ζ_2 is no longer demanded.

Since, according to eq.(116), the spectrum is relatively symmetrical about the point $x = 0$, from eqs.(27),(117) and (29) one can obtain the approximations

$$\zeta_1 = \Phi_1 - \frac{\chi_0}{\chi_{0*}} \frac{n_{1s*} V_*}{n_{1s} V} \frac{\Phi_{1*}}{6\Gamma_*} c^3 z^3, \tag{125}$$

$$\zeta_2 = \Phi_2 - \frac{1-\chi_0}{\chi_{0*}} \frac{n_{1s*} V_*}{n_{2s} V} \frac{\Phi_{1*}}{6\Gamma_*} c^3 z^3, \tag{126}$$

corresponding to the approach of monodisperse droplets. The relative error of the second terms of sums in eqs.(125) and (126) becomes important if $z <\sim \Delta x = 3/c$. However, in this case these terms become small in comparison with the first terms attaining values near Φ_{1*} and Φ_{2*} as early as the beginning of first stage. Therefore, the RHS have a high relative accuracy from the first stage.

At first, let us consider the period when

$$|\Phi_i - \Phi_{i*}|/\Phi_{i*} \ll 1 \qquad (i = 1, 2). \tag{127}$$

With allowance for eqs.(13),(127) we obtain from eqs.(125),(126) and (19):

$$\zeta_1 = \Phi_{1*} \left[1 - \frac{1}{6\Gamma_*} c^3 z^3\right], \tag{128}$$

$$\zeta_2 = \Phi_{2*} \left[1 - P_* \frac{1}{6\Gamma_*} c^3 z^3\right], \tag{129}$$

$$\frac{dz}{dt} = \frac{\alpha_{c1}}{\tau_{1*}} \frac{a^3}{\chi_{0*}} \Phi_{1*} \left[1 - \frac{c^3}{6\Gamma_* a^3} z^3\right], \tag{130}$$

$$a^3 = 1 - \frac{\chi_{0*} f_1(\chi_{0*})}{\Phi_{1*}}. \tag{131}$$

Obviously, $a <\sim 1$.

Solving eq.(130) with initial condition (20), we obtain

$$\frac{t - t_*}{t_r} = \ln \frac{(1 + z/z_r + z^2/z_r^2)^{1/2}}{1 - z/z_r} + \sqrt{3} \arctan \frac{2z/z_r + 1}{\sqrt{3}} - \frac{\pi}{2\sqrt{3}}, \tag{132}$$

where

$$t_r = \frac{1}{9}(6\Gamma_*)^{1/3} a\Delta t = \frac{1}{3}\frac{(6\Gamma_*)^{1/3} a}{m_1\Gamma_1 + m_2\Gamma_2} t_*, \tag{133}$$

$$z_r = \frac{1}{3}(6\Gamma_*)^{1/3} a\Delta x = \frac{1}{c}(6\Gamma_*)^{1/3} a. \tag{134}$$

In virtue of eqs.(32),(38) it follows from eqs.(122),(133),(134) that $z_r >\sim 2\Delta x$, $3t_r >\sim 2\Delta t$ and $t_r \ll t_*$.

The relations (128),(129) and (132) determine the dependence of ζ_1, ζ_2 and t on z. To find the dependence of ζ_1, ζ_2 and z on t it is necessary to solve eq.(132) with respect to z. Particularly, we have

$$z = \frac{\Delta x}{\Delta t}(t - t_*) \quad (-\Delta_- t <\sim t - t_* <\sim 3t_r/2) \tag{135}$$

$$z = z_r \left[1 - \sqrt{3} e^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* >\sim 3t_r) \tag{136}$$

The expression (135) describes an initial period of condensation which, according to $3t_r/2 \geq \Delta t > \Delta_+ t$, ends a little later than the first stage. During this period $\zeta_i \simeq \Phi_i \simeq \Phi_{i*}$ $(i = 1, 2)$.

The expression (136) describes a final period of condensation. During this period the exponential term in the RHS of eq.(136) is already small so that z almost coincides with z_r. Then from eqs.(128),(129),(134) and (136) it follows that

$$\zeta_1 = \Phi_{1*} \left[1 - a^3 + 3\sqrt{3} a^3 e^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* >\sim 3t_r), \tag{137}$$

$$\zeta_2 = \Phi_{2*} \left[1 - P_* a^3 + 3\sqrt{3} P_* a^3 e^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* >\sim 3t_r). \tag{138}$$

According to these relations, t_r represents a relaxation time.

The region of validity of eqs.(135),(136) is also limited by inequalities (127) which can be broken when the ideal supersaturations continue to increase. According to eqs.(10),(122) and (133), the inequalities (127) are still observed at $t - t_* \simeq 3t_r$, but they are broken as the time increases. Thus, under the conditions when the ideal supersaturations increase the asymptotic relations (136)-(138) are valid only at $t - t_* \simeq 3t_r$. Then the eqs.(137),(138),(127) and (27) lead to the relations $\zeta_i/\Phi_i \ll 1$, $g_i/\Phi_i \simeq 1 \quad (i = 1,2)$ which mean that the droplets have absorbed practically all the condensing substance (provided earlier the metastability of vapor mixture).

As long as $t - t_* <\sim 3t_r$ (i.e. before the final period) the value g_i/Φ_i increases. According to eqs.(56),(29),(124) at t_* and at $t_* + \Delta_+ t$, we have, respectively:

$$\left.\frac{g_1}{\Phi_1}\right|_{t=t_*} = 1/\Gamma_*, \quad \left.\frac{g_2}{\Phi_2}\right|_{t=t_*} = P_*/\Gamma_*, \tag{139}$$

$$\left.\frac{g_1}{\Phi_1}\right|_{t=t_*+\Delta_+ t} = e^{1.15}/\Gamma_*, \quad \left.\frac{g_2}{\Phi_2}\right|_{t=t_*+\Delta_+ t} = P_* e^{1.15}/\Gamma_*. \tag{140}$$

From eqs.(139),(140) it follows that the values g_1/Φ_1 and g_2/Φ_2 increase the most rapidly after the end of final period of condensation, and in time $3t_r/2 <\sim t - t_* <\sim 3t_r$ they attain the magnitudes near 1, i.e. practically whole two-component vapor mixture is absorbed by droplets. During this period the evolution of ζ_1, ζ_2 and z is described by relations (132),(128),(129).

If the ideal supersaturations are stabilized then the relations (136)-(138) remain true during a final period as long as $t - t_* >\sim 3t_r$. Their validity will be limited only by restriction (30). From eqs.(22) and (128) it follows that during whole final period the distribution $p(\rho, t)$ practically does not change. The relative width of spectrum is characterized by value $\Delta x/2z_r$ which is equal to $(9/16\Gamma_* a^3)^{1/3}$ as it follows from eq.(134).

If the ideal supersaturations continue to increase, then the relations $g_i/\Phi_i \simeq 1 \quad (i = 1,2)$ attained by $t - t_* \simeq 3t_r$ can be assumed as initial conditions for following evolution.

First, let us consider the condensation in materially open system.

Since in this case $n_{is} = n_{is*}$ $(i = 1,2)$ and $V = V_*$, from eqs.(19), (13), (125),

(126) it follows that

$$\begin{aligned} z &= \frac{(6\Gamma_*)^{1/3}}{c}\left(\frac{\chi_{0*}}{\chi_0}\right)^{1/3}\left(\frac{\Phi_1-\zeta_1}{\Phi_{1*}}\right)^{1/3} = \\ &= \left(\frac{n_{2tot*}}{n_{1tot*}}\right)^{1/3}\frac{(6\Gamma_*)^{1/3}}{c}\left(\frac{\chi_{0*}}{1-\chi_0}\right)^{1/3}\left(\frac{\Phi_2-\zeta_2}{\Phi_{2*}}\right)^{1/3}, \end{aligned} \tag{141}$$

$$\zeta_1 - \chi_0 f_1(\chi_0) = \frac{\tau_{1*}}{\alpha_{c1}}\chi_0\frac{dz}{dt}, \tag{142}$$

$$\zeta_2 - (1-\chi_0) f_2(\chi_0) = \frac{\tau_{2*}}{\alpha_{c2}}(1-\chi_0)\frac{dz}{dt}. \tag{143}$$

Taking into account the initial conditions $g_i/\Phi_i \simeq 1$ at $t - t_* \simeq 3t_r$, let us assume that $\Phi_i - \zeta_i \simeq \Phi_i$ $(i = 1, 2)$ in eq.(141) and find z in first approximation:

$$\begin{aligned} z &= \frac{(6\Gamma_*)^{1/3}}{c}\left(\frac{\chi_{0*}}{\chi_0}\right)^{1/3}\left(\frac{\Phi_1}{\Phi_{1*}}\right)^{1/3} = \\ &= \left(\frac{n_{2tot*}}{n_{1tot*}}\right)^{1/3}\frac{(6\Gamma_*)^{1/3}}{c}\left(\frac{\chi_{0*}}{1-\chi_0}\right)^{1/3}\left(\frac{\Phi_2}{\Phi_{2*}}\right)^{1/3}. \end{aligned} \tag{144}$$

Inserting eq.(144) in (142),(143) and making allowance for eqs.(43), (10), (13), (19), we have in first approximation:

$$\frac{\zeta_1 - \chi_0 f_1(\chi_0)}{\Phi_{1*} - \chi_{0*} f_1(\chi_{0*})} = \frac{1}{3}\frac{(6\Gamma_*)^{1/3}}{\Gamma_1 + \Gamma_2 m_2/m_1}\left(\frac{\chi_0}{\chi_{0*}}\right)^{2/3}\left(\frac{\Phi_{1*}}{\Phi_1}\right)^{\frac{(3-m_1)}{m_1}}, \tag{145}$$

$$\frac{\zeta_2 - (1-\chi_0) f_2(\chi_0)}{\Phi_{2*} - (1-\chi_{0*}) f_2(\chi_{0*})} = \frac{1}{3}\frac{(6\Gamma_*)^{1/3}P_*^{1/3}}{\Gamma_1 m_1/m_2 + \Gamma_2}\left(\frac{1-\chi_0}{1-\chi_{0*}}\right)^{2/3}\left(\frac{\Phi_{2*}}{\Phi_2}\right)^{(3-m_2)/m_2}. \tag{146}$$

In order that the supersaturations ζ_1 and ζ_2 do not increase with time, the values m_1 and m_2 are to satisfy the restrictions

$$0 < m_i \leq 3 \qquad (i = 1, 2). \tag{147}$$

Taking eqs.(32),(38) into account, it follows from eqs.(145),(146) that

$$\frac{\zeta_1 - \chi_0 f_1(\chi_0)}{\Phi_{1*} - \chi_{0*} f_1(\chi_{0*})} \ll 1, \quad \frac{\zeta_2 - (1-\chi_0) f_2(\chi_0)}{\Phi_{2*} - (1-\chi_{0*}) f_2(\chi_{0*})} \ll 1 \tag{148}$$

These estimates together with usually observed conditions of slight dependence of activities on solution composition

$$\chi_0 f_1(\chi_0) \sim \chi_{0*} f_1(\chi_{0*}), \quad (1-\chi_0) f_2(\chi_0) \sim (1-\chi_{0*}) f_2(\chi_{0*}), \tag{149}$$

mean that the vapor mixture metastability (decreasing with time) at this stage is much less than its maximal magnitude, therefore a new intensive formation of embryos will no more occur.

From eqs.(148),(149) it also follows that $\zeta_i/\Phi_i \ll 1$ $(i = 1, 2)$ and all the more $\zeta_i/\Phi_{i*} \ll 1$ $(i = 1, 2)$. That confirms the approximate equalities $\Phi_i - \zeta_i \simeq \Phi_i$ $(i = 1, 2)$ used for final period and provides a high relative accuracy of expressions (144)-(146). According to eq.(144), the droplets grow so that they have time to accumulate in themselves practically all the condensing substance of both components.

Let us note that the time of validity of the expressions (144)-(146) can be limited not only by condition (141) but also by other causes such as breakdown of free molecular regime of material exchange between a droplet and a vapor mixture, non-isothermal effects of condensation, coagulation, stabilization of ideal supersaturations, etc.

According to eqs.(22),(144), the graph of one-dimension distribution of droplets $p(\rho, t)$ moves as a whole along the ρ-axis. The relative width of the spectrum is characterized by value $D = \Delta x/2z$ decreasing with time:

$$\begin{aligned} D &= \left(\frac{9}{16\Gamma_*}\right)^{1/3} \left(\frac{\chi_0}{\chi_{0*}}\right)^{1/3} \left(\frac{\Phi_{1*}}{\Phi_1}\right)^{1/3} = \\ &= \left(\frac{n_{1tot*}}{n_{2tot*}}\right)^{1/3} \left(\frac{9}{16\Gamma_*}\right)^{1/3} \left(\frac{1-\chi_0}{\chi_{0*}}\right)^{1/3} \left(\frac{\Phi_{2*}}{\Phi_2}\right)^{1/3}. \end{aligned} \tag{150}$$

In the case of materially closed system from eqs.(19), (13), (125), (126) with consideration of

$$n_{is}\Phi_i V = n_{is*}\Phi_{i*}V_* \quad (i = 1, 2) \tag{151}$$

we have

$$z = \chi_{0*}^{1/3}\frac{(6\Gamma_*)^{1/3}}{c}\left[\frac{\Phi_1+\Phi_2-\zeta_1-\zeta_2}{\chi_0\Phi_1+(1-\chi_0)\Phi_2 n_{1tot*}/n_{2tot*}}\right]^{1/3}, \tag{152}$$

$$\zeta_1-\chi_0 f_1(\chi_0) = \frac{\tau_{1*}}{\alpha_{c1}}\chi_0 S_1(\Phi_1)\frac{dz}{dt}, \tag{153}$$

$$\zeta_2-(1-\chi_0) f_2(\chi_0) = \frac{\tau_{2*}}{\alpha_{c2}}(1-\chi_0) S_2(\Phi_2)\frac{dz}{dt}. \tag{154}$$

Assuming $\Phi_i-\zeta_i\simeq\Phi_i$ $(i=1,2)$, from eq.(152) we obtain in first approximation

$$z = \chi_{0*}^{1/3}\frac{(6\Gamma_*)^{1/3}}{c}\left[\frac{\Phi_1+\Phi_2}{\chi_0\Phi_1+(1-\chi_0)\Phi_2 n_{1tot*}/n_{2tot*}}\right]^{1/3}. \tag{155}$$

The expression (155) leads to the equality

$$dz/dt = 0 \tag{156}$$

not only in virtue of evident equality for a materially closed system

$$m_1 = m_2 \tag{157}$$

but also because of relation observed in this approximation for such a system

$$\chi_0 = \frac{n_{1tot*}}{n_{1tot*}+n_{2tot*}}. \tag{158}$$

Thus, in first approximation we have

$$z = \left(\frac{\chi_{0*}}{\chi_0}\right)^{1/3}\frac{(6\Gamma_*)^{1/3}}{c}, \tag{159}$$

$$\zeta_1-\chi_0 f_1(\chi_0)=0,\quad \zeta_2-(1-\chi_0)f_2(\chi_0)=0. \tag{160}$$

In view of estimates (149) the equalities (160) justify the approximate relations $\Phi_i-\zeta_i\simeq\Phi_i$ $(i=1,2)$ used in eq.(159) at final period and provide a high relative accuracy of eqs.(159),(160).

According to eqs.(22) and (159), the one-dimensional distribution of droplets $p(\rho,t)$ practically does not change during a final period. The relative width of spectrum is characterized by value $D=\Delta x/2z$ which is equal to

$$D = \left(\frac{9}{16\Gamma_*}\right)^{1/3}\left(\frac{\chi_0}{\chi_{0*}}\right)^{1/3} \tag{161}$$

and practically does not change with time.

The validity time of eqs.(159),(160) is still limited by condition (30).

6 Attainment of the metastability maximum in consequence of stabilization of both ideal supersaturations

Now, let us consider the case where an attainment of metastability maximum is due to the simultaneous stabilization of both ideal supersaturations. For the moment t_* of attainment of metastability maximum and for the magnitudes Φ_{1*} and Φ_{2*} of ideal supersaturations of both components we have:

$$t_* = t_0; \; \Phi_{i*} = \Phi_{0i} = (t_0/t_i)^{m_i} \quad (i = 1, 2). \tag{162}$$

Approaching to the point $z = 0$ the real supersaturation ζ_i continues to increase and the rate of consumption of i-component of vapor mixture by the droplets still remains less than the rate of increasing of the corresponding ideal supersaturation. In view of eqs.(41) we obtain (instead of eq.(52)):

$$g_1'(0) < \frac{\Phi_{1*}}{\Gamma_*} c. \tag{163}$$

At the moment when the ideal supersaturation Φ_i is stabilized the real supersaturation ζ_i begins to decrease.

Taking eqs.(53),(163) into account, let us introduce the parameter ϵ by

$$\epsilon = \frac{6\Gamma_* \chi_{0*}}{\Phi_{1*} c^4} f_s(\Phi_{1*}, \Phi_{2*}), \tag{164}$$

where $f_s(\Phi_{1*}, \Phi_{2*})$ is given by relation (35) in which Φ_{1*} and Φ_{2*} are determined by external conditions.

Considering eq.(164), instead of eqs.(56),(93) we shall have in first approximation

$$g_1(z) = \epsilon \frac{\Phi_{1*}}{\Gamma_*} e^{cz} \qquad (z < 0), \tag{165}$$

$$g_1(z) = \epsilon \frac{\Phi_{1*}}{\Gamma_*} \left[1 + cz + \frac{1}{2} c^2 z^2 + \frac{1}{6} c^3 z^3 + \frac{1}{24} c^4 z^4 \right] \quad (z \geq 0). \tag{166}$$

It is evident that the fulfillment of relation (163) is provided by condition $\epsilon < 1$.

From eqs.(27),(29),(165),(166) it also follows that

$$\zeta_1(0) = \Phi_{1*}\left(1 - \frac{\epsilon}{\Gamma_*}\right), \tag{167}$$

$$\zeta_2(0) = \Phi_{2*}\left(1 - P_*\frac{\epsilon}{\Gamma_*}\right). \tag{168}$$

Instead of eq.(94) for the spectrum in first approximation we have

$$f(x) = \epsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 \exp\left[cx - \epsilon e^{cx}\right] \quad (x < 0),$$

$$f(x) = \epsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 \exp\left[-\epsilon\left(1 + cx + \frac{1}{2}c^2x^2 + \frac{1}{6}c^3x^3 + \frac{1}{24}c^4x^4\right)\right] \quad (x \geq 0). \tag{169}$$

The stabilization of Φ_1 and Φ_2, according to eqs.(4),(5), also means the stabilization of n_{1s}, n_{2s} and V. The equalities $n_{is} = n_{is*}$ $(i = 1,2)$ and $V = V_*$ are now observed with a high relative accuracy in a materially open system as well as in a materially closed one. Therefore, eq.(28) takes the form

$$g_1 = \chi_{0*}\int_{-\infty}^{z} dx\,(z - x)^3 f(x). \tag{170}$$

Inserting eq.(169) in (170), one could obtain the second approximation of g_1 correct during whole condensation process. This approximation together with eqs.(19),(27) and $\Phi_i = \Phi_{i*}$ $(i = 1,2)$ would allow to obtain a consistent differential equation of the first order in unknown function z of one independent variable t.

Supposing that

$$\epsilon <\sim 1/e^8, \tag{171}$$

one can replace (169) by

$$f(x) = \epsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 e^{cx} \quad (x < 0),$$

$$f(x) = \epsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4 \exp\left[-\frac{\epsilon}{24}c^4x^4\right] \quad (x \geq 0). \tag{172}$$

Figure 2 shows the behaviour of spectrum $f(x)$ in different cases of stabilization of ideal supersaturations, the parameters $m_1, m_2, t_1,$ and t_2 being fixed. Curve A corresponds to $f(x)$ given by eq.(68) (stabilization of both Φ_1 and Φ_2 after the formation of spectrum, $z_0 > 1.15/c$). Spectrum B is given by eq.(94) at $z_0 = 0$ (simultaneous stabilization of Φ_1 and Φ_2 at moment of attainment of metastability maximum). Both spectra C and D correspond to the case of simultaneous stabilization of Φ_1 and Φ_2 before the attainment of metastability maximum and are given, respectively, by eq.(169) with $\epsilon < 1$ and by eq.(172) with $\epsilon <\sim 1/e^8$.

According to eqs.(172), for the left and right half-widths of the spectrum we obtain

$$\Delta_- x = 1/c, \quad \Delta_+ x = \left(\frac{24}{\epsilon}\right)^{1/4} \frac{1}{c}. \tag{173}$$

Inserting eqs.(172) in (118), taking into account eqs.(170), $V = V_*$ and neglecting the small contribution from $x < 0$, we obtain

$$N = A n_{1s*} \left(\frac{\epsilon^3}{54}\right)^{1/4} \frac{\Phi_{1*}}{\Gamma_* \chi_{0*}} c^3, \tag{174}$$

where

$$A = \int_0^\infty d\xi \, e^{-\xi^4} = 0.91, \tag{175}$$

According to eqs.(173),(40),(170),(43), instead of eqs.(120),(121) we have

$$\frac{\Delta_- \Phi_i}{\Phi_{i*}} = \frac{c_i}{c_1 \Gamma_1 + c_2 \Gamma_2}, \quad \frac{\Delta_+ \Phi_i}{\Phi_{i*}} = 0, \tag{176}$$

$$\frac{\Delta_- t}{t_*} = \frac{1}{m_1 \Gamma_1 + m_2 \Gamma_2}, \quad \frac{\Delta_+ t}{t_*} = \left(\frac{24}{\epsilon}\right)^{1/4} \frac{1}{m_1 \Gamma_1 + m_2 \Gamma_2}. \tag{177}$$

As it follows from eqs.(177) and (171), the condition (122) guarantees the smallness (in comparison with t_*) only of time interval $\Delta_- t$ but not of time interval $\Delta_+ t$. From eqs.(173),(177) and (171) the strong inequalities

$$\Delta_- x \ll \Delta_+ x, \quad \Delta_- t \ll \Delta_+ t \tag{178}$$

also follow which allow to obtain the expressions

$$\Delta x = \left(\frac{24}{\epsilon}\right)^{1/4} \frac{1}{c}, \quad \Delta t = \left(\frac{24}{\epsilon}\right)^{1/4} \frac{t_*}{m_1 \Gamma_1 + m_2 \Gamma_2}. \tag{179}$$

Therefore, by neglecting the very inessential part of spectrum for $x < 0$, one can present eqs.(172) as

$$f(x) = 4\frac{\Phi_{1*}}{\Gamma_* \chi_{0*}} (\Delta x)^4 \exp\left[- \left(\frac{x}{\Delta x} \right)^4 \right] \theta(x). \tag{180}$$

Obviously, the condition (171) corresponds to the case of instantaneous creation of metastability.

In accordance with eq.(180) the spectrum has a relatively symmetrical (about the point $x = \Delta x/2$) form resembling regular polygon with the width Δx. Hence with the help of eqs.(27),(170),(180),(175) and $\Phi_i = \Phi_{i*}$ one can obtain the approximations

$$\zeta_1 = \Phi_{1*} - \frac{4A\Phi_{1*}}{\Gamma_*} \frac{1}{(\Delta x)^3} \left(z - \frac{\Delta x}{2} \right)^3, \tag{181}$$

$$\zeta_2 = \Phi_{2*} - P_* \frac{4A\Phi_{1*}}{\Gamma_*} \frac{1}{(\Delta x)^3} \left(z - \frac{\Delta x}{2} \right)^3, \tag{182}$$

corresponding to an approach of monodisperse droplets (relatively to the average size $z - \Delta x/2$). For $z <\sim 3\Delta x/2$ a relative error of second terms in the RHS of eqs.(181),(182) becomes important. However, the second terms themselves become negligible in comparison with the first ones. Thus, the RHS of eqs.(181),(182) have a high relative accuracy beginning from the first stage which in view of equation (178) begins as a matter of fact at moment t_* when $z = 0$.

Taking into account eqs.(13), $\chi_0 = \chi_{0*}, n_{is} = n_{is*}$ $(i = 1, 2)$ and inserting equations (181),(182) in (19), we obtain

$$\frac{dz}{dt} = \frac{\alpha_{c1}}{\tau_{1*}} \frac{a^3}{\chi_{0*}} \Phi_{1*} \left[1 - \frac{4A}{\Gamma_* a^3} \frac{1}{(\Delta x)^3} \left(z - \frac{\Delta x}{2} \right)^3 \right]. \tag{183}$$

Replacing the initial condition (20) for the eq.(183) by practically equivalent condition $z = \Delta x/2$ at $t = t_* + \Delta t/2$ and solving eq.(183), we have

$$\begin{aligned} \frac{t - t_* - \Delta t/2}{t_r} \quad = \quad & \ln \left\{ \frac{[(z - \Delta x/2)^2/z_r^2 + (z - \Delta x/2)/z_r + 1]^{1/2}}{1 - (z - \Delta x/2)/z_r} \right\} + \\ & \sqrt{3} \arctan \left[\frac{2(z - \Delta x/2)/z_r + 1}{\sqrt{3}} \right] - \frac{\pi}{2\sqrt{3}}, \end{aligned} \tag{184}$$

where

$$z_r = \left(\frac{\Gamma_*}{4A}\right)^{1/3} a\Delta x, \qquad t_r = \frac{1}{3}\left(\frac{\Gamma_*}{4A}\right)^{1/3} a\Delta t \tag{185}$$

(taken into account the equality $\Delta x/\Delta t = \alpha_{c1}a^3\Phi_{1*}/\tau_{1*}\chi - 0*$ following from eq.(19)). The estimates $z_r >\sim 2\Delta x, 3t_r >\sim 2\Delta t$ are fulfilled in virtue of $a \sim 1, \Gamma \gg 1$ and $A \simeq 0.9$

The expressions (181),(182) and (184) determine the dependence of ζ_1, ζ_2 and t on z. In order to find the time dependence of ζ_1, ζ_2 and z it is necessary to solve the equation (184) for z. In particular,

$$z = \frac{\Delta x}{\Delta t}(t - t_*) \qquad (0 <\sim t - t_* <\sim \frac{3}{2}t_r + \frac{\Delta t}{2}), \tag{186}$$

$$z = z_r\left[1 - \sqrt{3}\exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r}\right)\exp\left(-\frac{t - t_*}{t_r}\right)\right] + \frac{\Delta x}{2} \;\; (t - t_* >\sim 3t_r + \frac{\Delta t}{2}). \tag{187}$$

The expression (186) describes an initial period of condensation and expression (187) describes a final one. During a final period of condensation the exponential term in the RHS of eq.(187) is already negligible so that z practically does not change with time and has a magnitude near $z_r + \Delta x/2$.

Inserting eq.(187) in (181),(182) and taking eq.(184) into account we obtain

$$\zeta_1 = \Phi_{1*}\left[1 - a^3 + 3\sqrt{3}a^3\exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r}\right)\exp\left(-\frac{t - t_*}{t_r}\right)\right] \;\; (t - t_* >\sim 3t_r + \frac{\Delta t}{2}), \tag{188}$$

$$\begin{aligned}\zeta_2 \;=\; & \Phi_{2*}\left[1 - P_*a^3 + 3\sqrt{3}P_*a^3\exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r}\right)\exp\left(-\frac{t - t_*}{t_r}\right)\right] \\ & (t - t_* >\sim 3t_r + \frac{\Delta t}{2}).\end{aligned} \tag{189}$$

The validity of relations (188), is still limited by restriction (30).

With allowance for $P \sim 1, a \sim 1$ and$A \simeq 0.9$ from eqs.(188),(189) it follows that during a final period of condensation $\zeta_i/\Phi_{i*} \ll 1$ $(i = 1, 2)$. From eqs.(22),(187) it also follows that the one-dimensional distribution of droplets

$p(\rho, t)$ changes with time very feebly. The relative width of the spectrum of linear sizes is characterized by value $\Delta x/2z_r$ which is approximately equal to $(A/2\Gamma_* a^3)^{1/3}$.

7 Conclusions

By means of classical approach to the binary condensation we have derived the consistent set of equations of binary condensation under dynamical conditions. Supposing that both real supersaturations attain their maximums simultaneously ('synchronously') at the moment of attainment of metastability maximum, we have considered four different cases.

First, we studied the case where both ideal supersaturations are stabilized after the formation of the spectrum of linear sizes of droplets. With the help of iteration procedure we have obtained the spectrum of linear sizes of droplets $f(x)$ in first and second approximations. According to eq.(77), the first approximation of spectrum given by eq.(68) is fairly accurate. The spectrum $f(x)$ does not depend on time by definition (22), and the time dependence of the two-dimensional distribution of droplets $n(\rho, \chi, t)$ given by (14),(22) is determined by the time dependence of values χ_0 and z provided in this case by eqs.(13),(125), (126), (132). The equations (125),(126),(132) provide also the time dependence of both real supersaturations ζ_1 and ζ_2. The total quantity of droplets N formed per volume unit is given by eq.(119).

Then we considered the cases of stabilization of both ideal supersaturations Φ_1 and Φ_2 after the attainment of metastability maximum: either, a) both Φ_1 and Φ_2 are stabilized simultaneously before the end of stage of formation of spectrum, or, b) Φ_1 is stabilized before the end of this stage and Φ_2 is stabilized after the end of this stage. For both cases with the help of iteration procedure we have found the spectrum and shown that the first approximation allows us to find the total quantity of droplets N with the relative error less than 0.15.

We considered also the case where the attainment of metastability maximum is due to the simultaneous stabilization of both ideal supersaturations. In this case for the spectrum we have attained the general expression (169) which can be rewritten as (172) if $\epsilon <\sim e^{-8}$. The equations (187)-(189) represent the asymptotic behaviour of z, ζ_1, and ζ_2 with time.

In section 5 we have defined the terms "initial period" and "final period" because only for these periods we can obtain explicit expressions for the time dependence of z. The time dependence of z is very important for our theory because z is contained in the expression (22) for the one-dimensional distribution $p(\rho, t)$ and, therefore, in the two-dimensional distribution $n(\rho, \chi, t)$. The value z represents the coordinate of the maximum of spectrum which moves as a whole along the ρ-axis with the velocity equal to the rate of increase of linear size of droplet. As it follows from eqs.(135) and (186), the time dependence of z is linear during initial period. During a final period the time dependence of z is very slight and given by eqs. (136) and (187) if the ideal supersaturations are stabilized. If both ideal supersaturations Φ_1 and Φ_2 continue to increase, then time dependence of z is given by eq.(144) for the materially open system and by eq.(159) for the materially closed system (in the last case z doesn't depend on t if we assume $\chi_0 \simeq n_{1tot*}/(n_{1tot*} + n_{2tot*})$).

The relative width of spectrum can be characterized by value $D = \Delta x/z$ which generally slowly decreases with time or remains constant during final period.

To illustrate the developed theory we have carried out the numerical calculations for the condensation in the materially open system "ethanol (first component) - hexanol (second component)" at $T = 260$ K in the case of stabilization of ideal supersaturations after the formation of spectrum of linear sizes of droplets, the

Table 1.

Main values of theory for the condensation in the ethanol (1) - hexanol (2) open system at $m_1 = 1,\ t_1 = 0.05$ s, $m_2 = 1,\ t_2 = 0.05$ s, and $T = 260$ K

$\alpha_{c1} = 0.625\,,\quad \alpha_{c2} = 0.5$

χ_{c*}	χ_{0*}	Φ_{1*}	Φ_{2*}	t_*, s	Γ_1	Γ_2	Γ_*	c_1	c_2
0.765	0.996	2.146	2.146	0.1073	65.2	20.0	85.3	$2.3\text{x}10^{-4}$	$2.3\text{x}10^{-4}$

z_r	Δx	t_r, s	Δt, s	c
28372	13098	0.0027	0.0038	$2.3\text{x}10^{-4}$

$\alpha_{c1} = 0.0042\,,\quad \alpha_{c2} = 0.004$

χ_{c*}	χ_{0*}	Φ_{1*}	Φ_{2*}	t_*, s	Γ_1	Γ_2	Γ_*	c_1	c_2
0.801	0.996	2.712	2.712	0.1356	41.8	10.4	52.2	0.011	0.011

z_r	Δx	t_r, s	Δt, s	c
532	274	0.0050	0.0078	0.011

parameters in eq.(10) being as follows: $m_1 = 1,\ t_1 = 0.05$ s$, m_2 = 1,\ t_2 = 0.05$ s.

Without describing the procedure of numerical calculations, let us note that, unlike the theory of one-component condensation, a correctness of data about the sticking coefficients α_{c1}, α_{c2} influences not only a correctness of theoretical predictions but also their accuracy since we have to solve the system of four equations for $\chi_{c*}, \chi_{0*}, \Phi_{1*}, \Phi_{2*}$ with the supplementary condition $t_1\Phi_{1*}^{1/m_1} = t_2\Phi_{2*}^{1/m_2}$ following from (11). Our calculations were carried out for two couples of sticking coefficients: $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$ and $\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$, thermodynamic parameters for the ethanol-hexanol system being taken following Strey and Viisanen (1993). The results of calculations for main values of theory are summarized in Table 1.

The total quantity N of droplets formed per volume unit strongly depends on sticking coefficients: $N = 8.5\text{x}10^3$ cm^{-3} for $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$; and

$N = 1.91\text{x}10^9$ cm^{-3} for $\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$. Figures 3a and 3b show the corresponding spectra $f(x)$ of linear sizes of droplets (eq.(116)). The time dependences of the real supersaturations ζ_1 and ζ_2 for the time interval $0 \leq t - t_* \leq 3.5\ t_r$ are shown by Figures 4a and 4b (eqs.(128),(129), (132)). In both cases the difference between ζ_1 and ζ_2 is very small because $\zeta_{1*} = \zeta_{2*}$ and that P_* is nearly equal to 1 ($P_* = 0.99996$ at $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$ and $P_* = 0.9998$ at $\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$), but it increases with time and attains a value of the order of 10^{-5} ($\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$) or of 10^{-4} ($\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$) at $t \simeq t_* + 3t_r/2$.

It should be noted that we cannot obtain any analytical expression for the duration of all condensation process which is determined by the time t_{cond} at which the constraint (30) is broken and the binary condensation changes into the binary coalescence. Besides, we cannot obtain any explicit expression for the time dependence of ζ_1, ζ_2, z for the interval of time $3t_r/2 < t < 3t_r$. It's evident that numeric methods like the methods applied by Wilemski and Wyslouzil (1995) and by Wyslouzil and Wilemski (1995,1996) would make it possible to obtain the time dependence of ζ_1, ζ_2 and z for this interval as well as to estimate t_{cond} for any condensing system. This is an advantage of numeric methods. On the other hand, it will be necessary to draw a comparison between the results of presented theory and experimental data as soon as appropriate experiments are carried out. Particularly, it would be very interesting to compare our theoretical predictions with experimental data for the time dependences of real supersaturations ζ_1, ζ_2 and average concentration χ_0 of solution in droplets as well as for the total quantity N of nucleated droplets.

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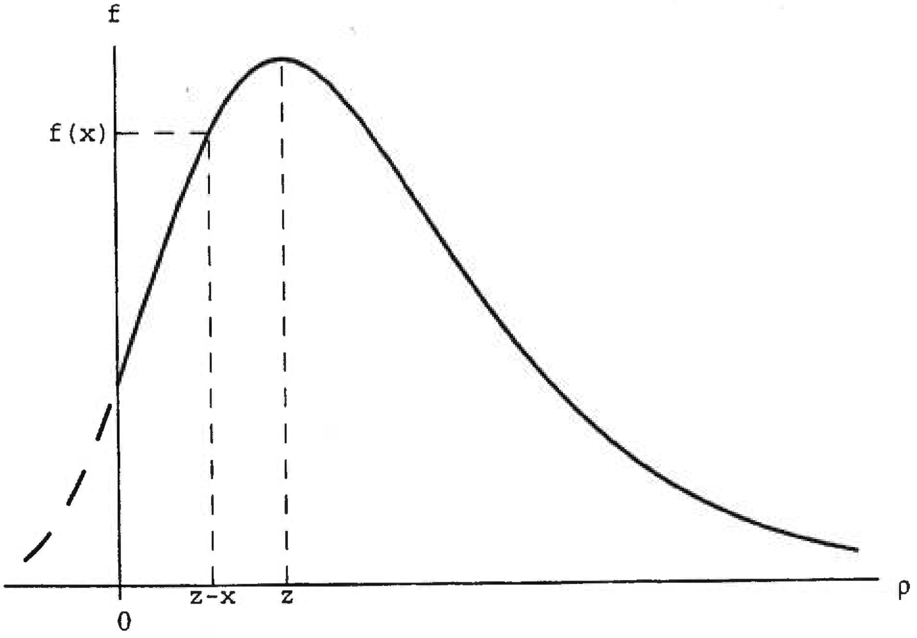

Figure 1. Spectrum of linear sizes of droplets f as a function of ρ.

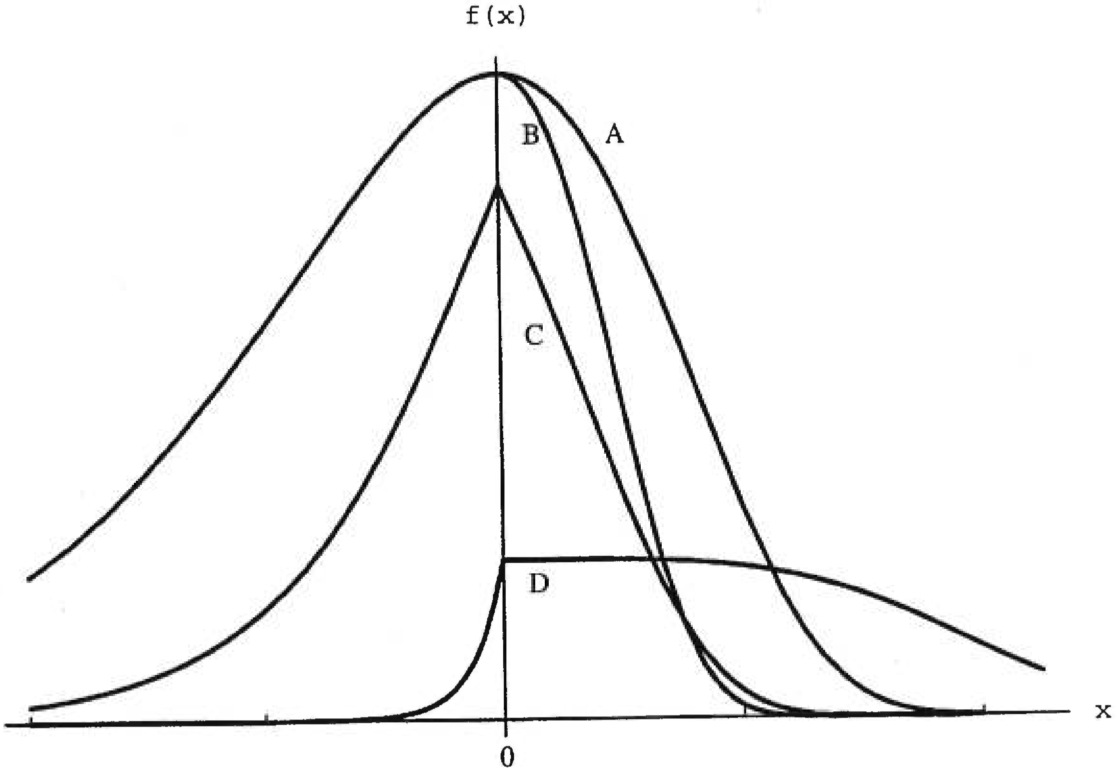

Figure 2. Spectrum of linear sizes of droplets f as a function of x for different cases of stabilization of ideal supersaturations at fixed m_1, m_2, t_1, t_2. The curves correspond to the following cases: (**A**) to $z_0 > 1.15/c$ [equation (68)]; (**B**) to $z_0 = 0$ [equation (94)]; (**C**) to $\varepsilon < 1$ [equation (172)]; (**D**) to $\varepsilon <\sim 1/e^8$ [equation (175)].

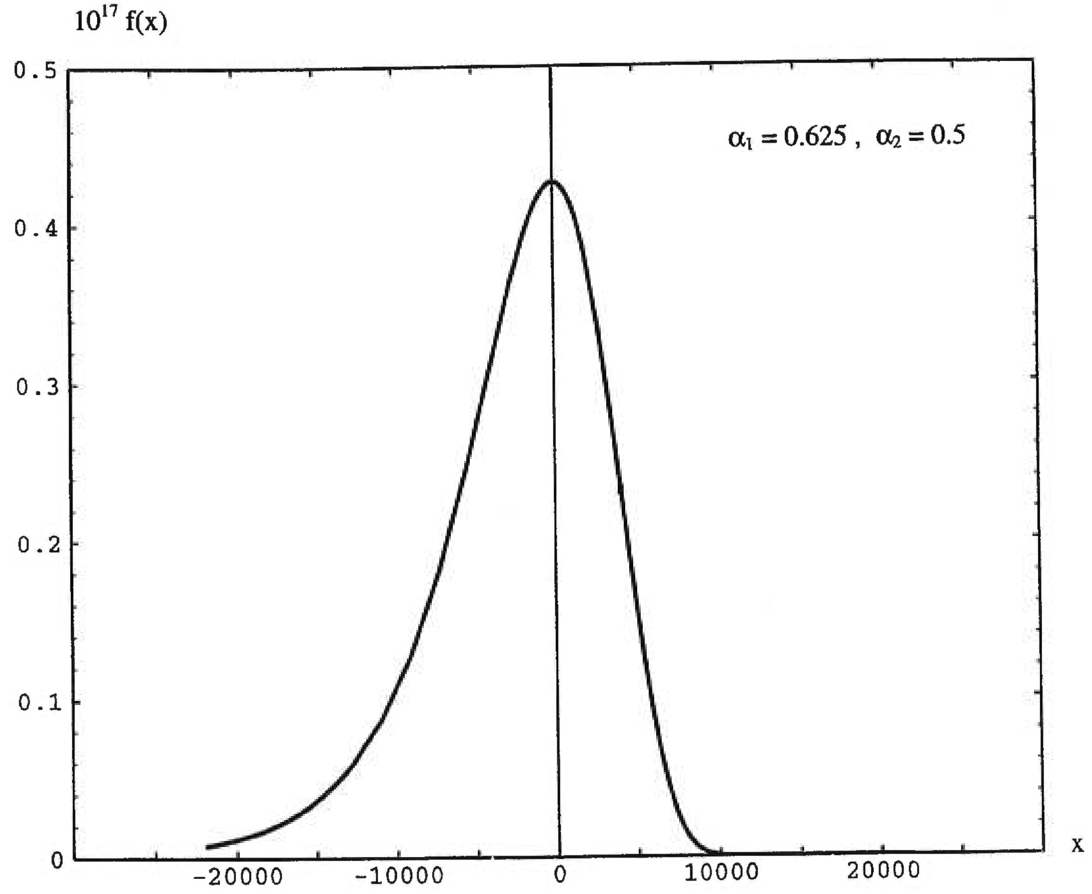

Figure 3a. Spectrum of linear sizes of droplets $f(x)$ (equation (116)) for the ethanol(1)-hexanol(2) open system at $T = 260$ K, $m_1 = 1, t_1 = 0.05$ s, $m_2 = 1, t_2 = 0.05$ s in the case of stabilization of ideal supersaturations after the formation of spectrum, the sticking coefficients being $\alpha_{c1} = 0.625, \alpha_{c2} = 0.5$.

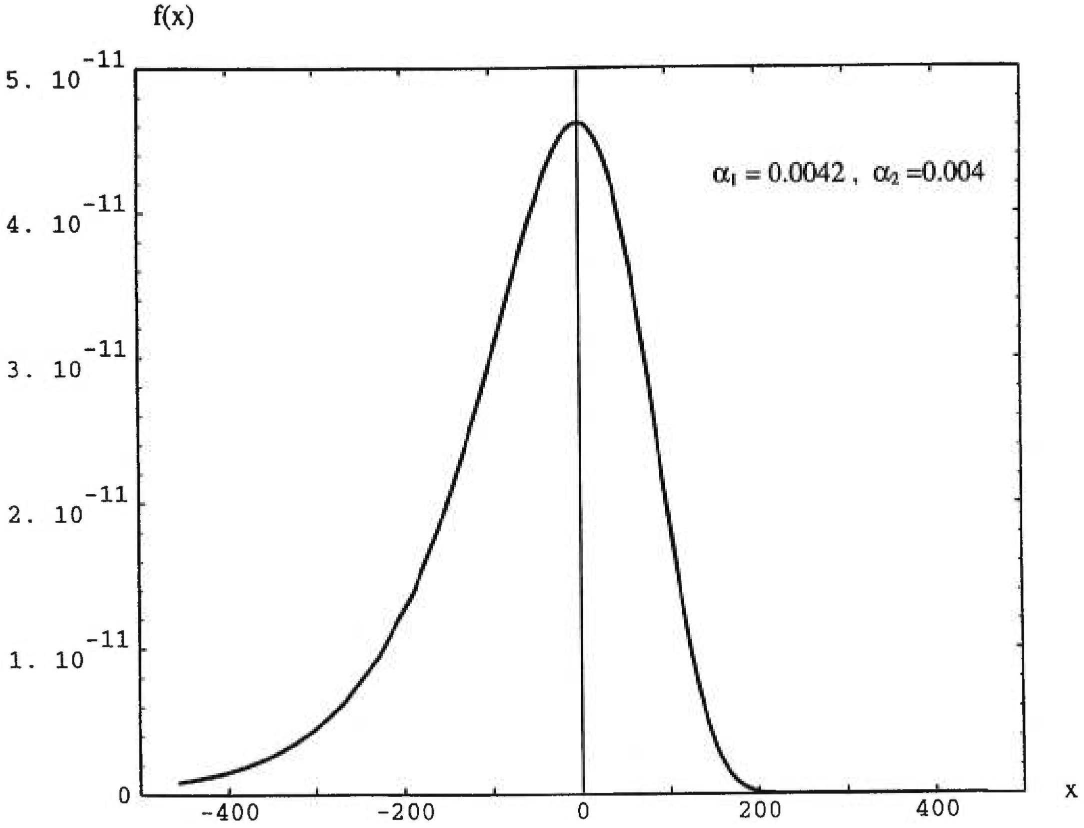

Figure 3b. Spectrum of linear sizes of droplets $f(x)$ (equation (116)) for the ethanol(1)-hexanol(2) open system at $T = 260$ K, $m_1 = 1, t_1 = 0.05$ s, $m_2 = 1, t_2 = 0.05$ s in the case of stabilization of ideal supersaturations after the formation of spectrum, the sticking coefficients being $\alpha_{c1} = 0.0042, \alpha_{c2} = 0.004$.

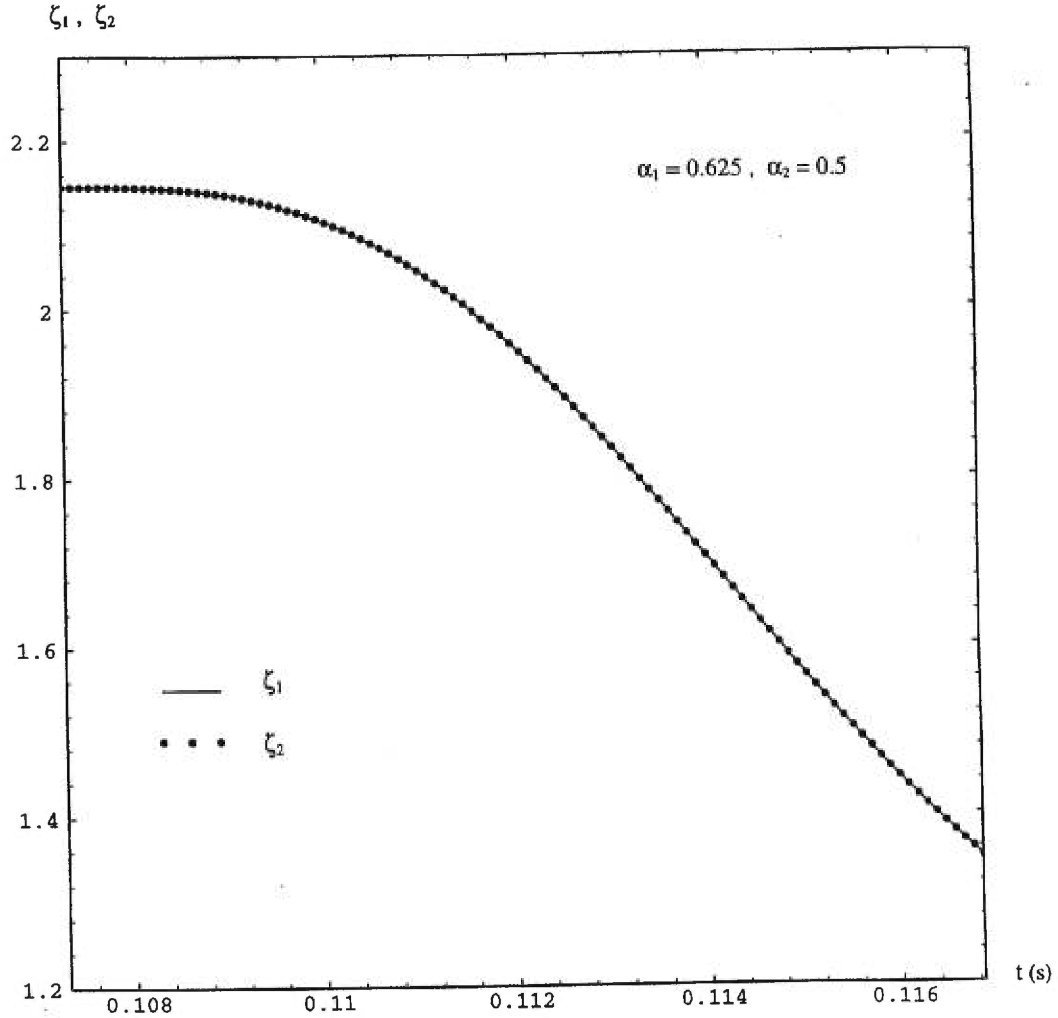

Figure 4a. Time dependence of real supersaturations ζ_1 (solid line) and ζ_2 (points) in the binary ethanol(1)-hexanol(2) open system at $T = 260$ K, $m_1 = 1, t_1 = 0.05$ s, $m_2 = 1, t_2 = 0.05$ s in the case of stabilization of Φ_1, Φ_2 after the formation of spectrum $f(x)$ plotted according to equations (128), (129) and (132), the sticking coefficients being $\alpha_{c1} = 0.625, \alpha_{c2} = 0.5$.

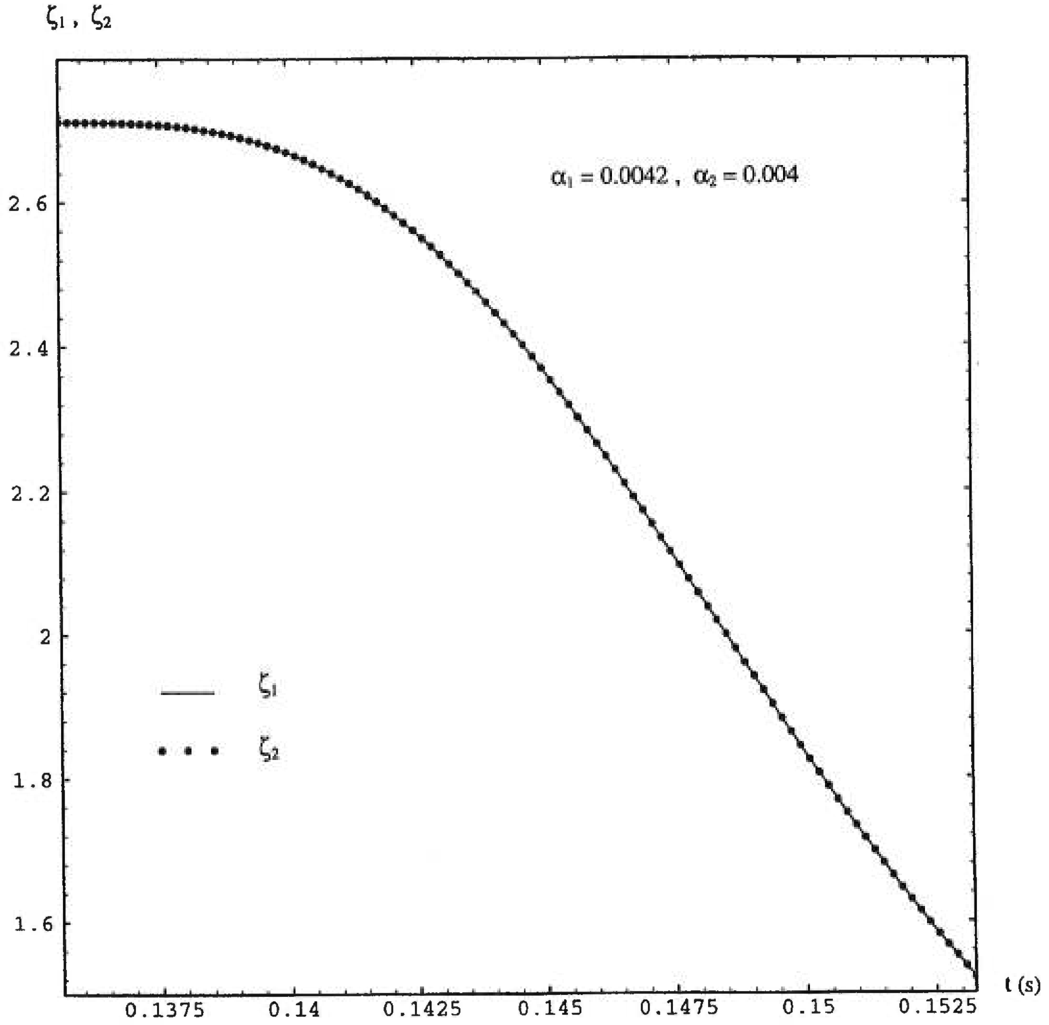

Figure 4b. Time dependence of real supersaturations ζ_1 (solid line) and ζ_2 (points) in the binary ethanol(1)-hexanol(2) open system at $T = 260$ K, $m_1 = 1, t_1 = 0.05$ s, $m_2 = 1, t_2 = 0.05$ s in the case of stabilization of Φ_1, Φ_2 after the formation of spectrum $f(x)$ plotted according to equations (128), (129) and (132), the sticking coefficients being $\alpha_{c1} = 0.0042, \alpha_{c2} = 0.004$.

CONCLUSION

Dans cette thèse nous avons étudié certains problèmes de la théorie de la condensation binaire homogène.

Premièrement, nous avons considéré la thermodynamique de la nucléation binaire, en nous concentrant en particulier sur l'énergie libre de formation d'une goutte, le choix de ses variables d'état indépendantes et la distribution d'équilibre des gouttes. Cette dernière joue un rôle essentiel dans la théorie de la nucléation binaire, car la vitesse de nucléation binaire (la plus importante caractéristique du processus) est proportionnelle à la distribution d'équilibre. Cela est une conséquence du fait que l'on suppose toujours que la distribution des gouttes dans la région précritique des variables d'état est celle d'équilibre et qu'elle a la forme de la distribution de Gibbs. Cependant, le problème de la détermination de son facteur de normalisation est aussi complexe qu'important: le facteur de normalisation de cette distribution d'équilibre ne peut pas être déterminé de façon unique. Il existe quelques approches de ce problèmes dont aucune ne peut être retenue comme la meilleure. Ici nous avons discuté de ce problème et nous avons présenté un nouveau facteur de normalisation qui a été obtenu à l'aide d'une approche unifiée de la condensation binaire homogène et de la condensation binaire hétérogène. Les résultats théoriques ont été illustrés avec des calculs numériques pour un système binaire "éthanol - hexanol" et un système monocomposante "eau". Ces calculs montrent que le nouveau facteur pourrait assurer, dans certains cas, un meilleur accord entre les prédictions théoriques et les données expérimentales concernant la vitesse de nucléation binaire.

Deuxièmement, nous avons développé la théorie cinétique de la nucléation binaire non-isotherme. Cette théorie permet de tenir compte de l'influence des effets thermiques sur le processus de la condensation binaire. Les effets thermiques de la condensation sont causés par la chaleur de condensation. Les molécules du mélange de vapeurs absorbées par une goutte de la solution binaire liquide lui transmettent de la chaleur de condensation, tandis que les molécules émises par la goutte de la solution liquide lui enlèvent de la chaleur de condensation. Comme la goutte croissante de la solution liquide absorbe plus de molécules qu'elle n'en émet, sa température moyenne augmente au fur et à mesure de sa croissance, la température du mélange de vapeurs étant constante. Cet échauffement de la goutte liquide augmente sa faculté d'émettre des molécules. Par conséquent, il cause la diminution de la vitesse de nucléation et l'augmentation de la durée de nucléation. En outre, cela influence la composition des gouttes liquides et d'autres caractéristiques du processus.

La théorie de la nucléation binaire non-isotherme a été développée à partir de l'équation discrète du bilan décrivant l'échange de substance et d'énergie entre le mélange de vapeurs et les gouttes de solution liquide. Cette équation tridimensionnelle décrit l'évolution temporelle de la distribution de ces gouttes selon trois variables indépendantes: les nombres de molécules des deux composantes dans une goutte liquide et sa température. En réduisant l'équation discrète du bilan à la forme différentielle, on obtient l'équation cinétique tridimensionnelle de la nucléation binaire non-isotherme. Dans le cas des chaleurs de condensation arbitraires, cette équation cinétique dépasse les bornes de l'approximation de Fokker et Planck. Seulement dans le cas où les chaleurs de condensation sont très petites par rapport à la fluctuation efficace de l'énergie d'une goutte liquide, l'équation cinétique peut être réduite à celle de Fokker et Planck. Dans la présente thèse, pourtant, aucune restriction n'est imposée sur les chaleurs de condensation et, par conséquent, l'équation cinétique à résoudre dépasse les bornes de l'approximation de Fokker et Planck.

L'analyse de l'équation cinétique permet de déterminer la hiérarchie des échelles de temps de la nucléation binaire non-isotherme. Cela rend possible de séparer et de décrire analytiquement l'étape de relaxation thermique pendant laquelle la distribution des gouttes selon la température s'approche d'une gaussienne, alors que leur distribution selon les nombres de molécules ne change guère.

À l'étape suivant la relaxation thermique, l'équation cinétique tridimensionnelle peut être résolue en utilisant successivement la méthode de Chapman et Enskog et celle de séparation complète des variables. L'application successive de ces deux méthodes permet (dans le cas non-stationnaire aussi bien que dans le cas stationnaire) de réduire notre équation cinétique à l'équation monodimensionnelle de Fokker et Planck dont les coefficients contiennent toute l'information sur les effets thermiques. L'analyse d'une telle équation est bien connue. Ainsi, toutes les caractéristiques de la nucléation binaire non-isotherme peuvent être déterminées. Dans cette thèse, nous avons présenté les caractéristiques stationnaires: la distribution tridimensionnelle des gouttes, la vitesse de nucléation, la composition et la température moyennes des gouttes. Les résultats théoriques ont été illustrés avec des calculs numériques pour les systèmes "éthanol-eau" et "éthanol-hexanol". Ces calculs montrent que la théorie développée assure un meilleur accord, par rapport à la théorie classique, entre les prédictions théoriques et les données expérimentales pour la vitesse de nucléation.

Finalement, nous avons étudié la condensation binaire isotherme aux conditions dynamiques. Dans ce cas, la formation et la croissance des gouttes se passent en même temps que la métastabilité d'un mélange de vapeurs croît graduellement, atteint son maximum et décroît. C'est ainsi que la condensation binaire se passe le plus souvent dans la nature.

Nous avons développé la théorie cinétique de ces processus pour les systèmes ouverts ainsi que pour les systèmes fermés (du point de vue de l'échange de matière entre le système où la condensation se passe et son environnement). Les deux sursaturations idéales que les vapeurs du mélange auraient eues en absence d'absorption des molécules par les gouttes sont déterminées par les conditions extérieures. Par conséquent, la dépendance temporelle des sursaturations idéales est considérée comme donnée.

Nous avons considéré le cas où les sursaturations réelles des deux vapeurs atteignent leurs maximums simultanément au moment du maximum de la métastabilité du mélange de vapeurs. Nous avons obtenu le système d'équations intégrales pour les processus considérés. Il est démontré que la méthode itérative permet de construire le spectre des dimensions linéaires des gouttes et la distribution des gouttes selon leurs deux variables d'état indépendantes, la précision relative étant assez élevée dès la première itération. De même, cette méthode permet de trouver la dépendance temporelle des sursaturations réelles des deux composantes du mélange de vapeurs aussi bien que le nombre total de gouttes par unité de volume. Les résultats théoriques ont été illustrés avec des calculs numériques pour un système ouvert "éthanol - hexanol".

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KINETIC THEORY OF NONISOTHERMAL BINARY NUCLEATION: THE STAGE OF THERMAL RELAXATION

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Abstract—A generalization of the method used in the kinetics of nonisothermal unary nucleation is proposed to construct the kinetic theory of nonisothermal binary nucleation allowing one to take account of the release of the latent heat of condensation. The three-dimensional balance equation describing the material and heat exchange of liquid solution particles with the surrounding vapor–gas medium is obtained. Independent variables in this equation are the numbers of molecules of each component in a liquid solution nucleus and its temperature. Going beyond the framework of the Fokker–Planck approximation is proposed for the corresponding kinetic equation. A hierarchy of time scales of nonisothermal binary nucleation is established and an analytical description of the thermal relaxation of the nuclei is given. Theoretical results are illustrated by numerical calculations for the nucleation in a water–ethanol system. © 1999 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

inary condensation is a very widespread first-order phase transition and hence is of great terest in many fields. They usually distinguish three stages of any first-order phase ansition. During the first of them nuclei of a new phase are formed (this stage is also called e stage of nucleation) which play the role of condensation centers afterwards. It is during e second stage that the phase transition takes place properly—the bulk of a metastable hase passes to a liquid phase. During the third stage the growth of large drops occurs to e detriment of small ones.

It is well known that nonisothermal effects can strongly influence a process of first-order hase transition, particularly a vapor-to-liquid transition. There exist different kinds of onisothermal effects in the condensation.

First, the heating of the growing nuclei by the latent heat of condensation. This causes reduction of the nucleation rate in two ways: (1) increasing the ability of the nuclei to emit olecules; (2) decreasing the metastability of vapor phase (owing to the increase in the mperature of condensing system).

Second, temperature fluctuations of nuclei exist even in the absence of matter exchange etween the nuclei and the medium. They also influence the emissivity of nuclei.

Third, the nuclei as particles of condensed matter are thermally quasi-isolate from one nother being surrounded by the rarefied vapor–gas medium. Consequently, the temperaure of a nucleus decreases gradually during each event of emission of a molecule, while the olecule passes from the nucleus through its surface layer to the vapor. Therefore, the missivity of the nucleus must be determined by some intermediate value of its temperature ut neither by the initial one (before the emission event) nor by the final one (after the mission event).

At present, there exists a complete enough and adequate theoretical description of onisothermal unary nucleation and condensation. Taking account of the release of latent eat, Kantrowitz (1951) obtained the differences between isothermal and nonisothermal

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2. BALANCE EQUATION

First, let us construct a three-dimensional balance equation of nonisothermal binary ucleation. Let us assume that the metastability of the vapor mixture is created instanneously and does not change during the whole nucleation process. The temperature T_0 of e vapor mixture and the number density of passive gas molecules are also fixed. We also ssume that there are not chemical reactions nor heterogeneous nucleating centers in the ondensing system.

It is evident that there are three types of elementary interactions of a nucleus with the apor–gas medium: (1) absorption of a molecule of 1st or 2nd components of the vapor ixture; (2) emission of a molecule of 1st or 2nd components of the vapor mixture; (3) eflection of a molecule of the vapor–gas medium.

The nuclei formed have so small sizes that the times of their internal relaxation processes re very small in comparison with the time between successive interactions of a nucleus with e vapor–gas medium, and the interactions themselves take place under a free-molecular egime. This allows us to assume that the nucleus attains its internal thermodynamical quilibrium before each successive interaction with the vapor–gas medium.

Let us choose the numbers ν_1 and ν_2 of molecules of 1st and 2nd component in a nucleus nd its thermal energy E as its independent characteristics. The thermal energy E of a ucleus is linear in the temperature and will be measured from its value at the temperature $_0$ of the vapor–gas medium. Expressing all the quantities which have the dimensions of nergy in units of $k_B T_0$ (k_B is Boltzmann's constant), we have

$$E = (c_1\nu_1 + c_2\nu_2)\,[T/T_0 - 1], \tag{1}$$

here c_i $(i = 1, 2)$ is the molecular specific heat of i-component in a nucleus (all the specific eats are expressed in units of k_B).

Let ε be the thermal energy of molecules striking a nucleus and let ε' be the thermal energy f molecules reflected or emitted by a nucleus. Since the times of internal relaxation rocesses of nucleus are small, the number W_i^- $(i = 1, 2)$ of molecules of component i which nucleus emits in unit time as well as the distribution w' of the emitted or reflected olecules with respect to their energy ε' are determined (in consideration of the thermal daptation of reflected molecules) by the energy of nucleus:

$$W_i^- \equiv W_i^-(\nu_1, \nu_2, E)\ (i = 1, 2), \qquad w' \equiv w'(\nu_1, \nu_2, E \,|\, \varepsilon'). \tag{2}$$

ere the variables ν_1, ν_2, and E correspond to the state of the nucleus before the interaction nd we have taken account that the temperature fluctuation effect and the effect of nucleus ermal quasi-isolationship compensate each other. Of course, the distribution $w(\varepsilon)$ of the olecules striking a nucleus with respect to their energy ε is determined by the temperature $_0$ of the vapor–gas medium. For the distributions $w(\varepsilon)$ and $w'(\nu_1, \nu_2, E \,|\, \varepsilon')$ (which we ssume being Maxwellian) we shall use the normalization relations

$$\int_0^\infty d\varepsilon\, w(\varepsilon) = 1, \qquad \int_0^\infty d\varepsilon'\, w'(\nu_1, \nu_2, E \,|\, \varepsilon') = 1. \tag{3}$$

Let us denote by $g(\nu_1, \nu_2, E)$ the distribution of nuclei with respect to the variables ν_1, ν_2, nd E at the time t (we shall not indicate the time dependence of values).

Denoting by $W_i(\nu_1, \nu_2)$ and β_i $(i = 1, 2)$ the number of molecules of component i being bsorbed by a nucleus per unit time and, respectively, the molecular heat of condensation of omponent i, let us write the discrete balance equation governing the evolution of the istribution $g(\nu_1, \nu_2, E)$:

$$\frac{\partial g(\nu_1, \nu_2, E)}{\partial t} = D_1^+ + D_1^- + D_2^+ + D_2^- + \tfrac{1}{2} D_{g1} + \tfrac{1}{2} D_{g2}, \tag{4}$$

$$I_E = -\left[\frac{\beta_1^2}{k_1} W_1 + \frac{\beta_2^2}{k_2} W_2\right]\left(\frac{E}{c_1 v_1 + c_2 v_2} + \frac{\partial}{\partial E}\right) g(v_1, v_2, E), \tag{14}$$

$$\frac{1}{k_i} = \frac{\tilde{c}_i}{\alpha_{ci}\beta_i^2}\left[\alpha_{ci} + \alpha_{ti}(1 - \alpha_{ci}) + \alpha_g p_i\right] \quad (i = 1, 2), \tag{15}$$

$$p_i = \left(\frac{m_i}{m_g}\right)^{1/2} \frac{n_g c_g}{2 n_i \tilde{c}_i} \quad (i = 1, 2), \tag{16}$$

$_i$, m_i, and n_i ($i = 1, 2$) are the effective (in the sense of energy transfer to the nucleus) specific eat, mass, and number density of molecules, respectively, of component i of the vapor ixture; c_g, m_g, and n_g are the analogous values of the passive gas.

The terms D_1 and D_2 in equation (11) describe the simultaneous transfer of both the ubstance and the condensation heat to the nuclei by the molecules of 1st and 2nd omponents, respectively.

The term $-\partial I_E/\partial E$ in equation (11) describes the transfer of the kinetic and internal nergies to the nuclei by all the molecules of the vapor–gas medium. Its form corresponds to e fulfillment of the condition

$$1/(c_1 v_1 + c_2 v_2)^{1/2} \ll 1 \tag{17}$$

hich means a smallness of the energy transfer by the molecules of the vapor–gas medium comparison with the rms fluctuation of the nucleus energy, since the value $(c_1 v_1 + c_2 v_2)^{1/2}$ epresents, according to the thermodynamic theory of fluctuations, the rms fluctuation of nucleus energy in the absence of substance exchange between the nucleus and the vapor ixture.

3. KINETIC EQUATION OF NONISOTHERMAL BINARY NUCLEATION

et us introduce the variable ξ instead of variable E as

$$\xi = \frac{E}{[2(c_1 v_1 + c_2 v_2)]^{1/2}} \tag{18}$$

nd present the distribution $g(v_1, v_2, E)$ in the form

$$g(v_1, v_2, E) = [2\pi(c_1 v_1 + c_2 v_2)]^{-1/2} e^{-\xi^2} P(v_1, v_2, \xi), \tag{19}$$

here $P(v_1, v_2, \xi)$ is some function of v_1, v_2, ξ (and of t, too).

Since usually $\beta_i \gg 1$ ($i = 1, 2$), the parameter

$$\tau_i = \frac{\beta_i}{[2(c_1 v_1 + c_2 v_2)]^{1/2}} \quad (i = 1, 2) \tag{20}$$

ill not be small despite inequality (17). The parameter τ_i represents the relative condensaion heat of component i per molecule, i.e. the condensation heat of component i per olecule expressed in units of rms fluctuation of the nucleus energy and divided by $\sqrt{2}$. lthough τ_i is always less than 1, in order of magnitude $\tau_i \sim 1$.

Let us introduce the operator

$$\hat{L}_i \equiv -W_i F_i' - W_i \frac{\partial}{\partial v_i} \quad (i = 1, 2), \tag{21}$$

cting on v_i-dependent functions (here $F_i' \equiv \partial F/\partial v_i$, and F is the free energy of formation of he nucleus with the characteristics v_1, v_2, and $E = 0$: $F \equiv F(v_1, v_2, E = 0)$). Let us define the alues v_{ic}, Δv_{ic} ($i = 1, 2$) by the relations

$$F_i'|_{v_1 = v_{1c}, v_2 = v_{2c}} = 0, \qquad \Delta v_{ic} = |2/F_{ii}''|\,|_{v_1 = v_{1c}, v_2 = v_{2c}} \quad (i = 1, 2). \tag{22}$$

ssumed to be much less than unity: $\Theta \ll 1$. Thus, we conclude that on the RHS of quation (25) the last term is the main one.

Equation (25) governs the time evolution of the three-dimensional distribution P. The ierarchy of terms established above corresponds to the hierarchy of time scales in the evelopment of the distribution P.

The eigenfunctions of the principal operator of the governing equation, i.e. of the perator of the dominant term on the RHS of equation (25), are the Hermite polynomials $_j \equiv H_j(\xi)$ ($H_0 = 1, H_1 = 2\xi, H_2 = 4\xi^2 - 2, \ldots$), satisfying the recursion relations

$$\frac{\partial}{\partial \xi} H_j = 2jH_{j-1}, \left(\frac{\partial}{\partial \xi} - 2\xi\right) H_j = -H_{j+1}. \tag{27}$$

ence,

$$\left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial \xi} - 2\xi\right)\frac{\partial}{\partial \xi} - \sum_{m=2}^{\infty} \frac{(-1)^m}{m!m!}(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)\left(\frac{\partial}{\partial \xi} - 2\xi\right)^m \frac{\partial^m}{\partial \xi^m}\right] H_j = -j\lambda_j H_j, \tag{28}$$

here $j = 0, 1, 2, \ldots$ and

$$\lambda_j = 2\,\frac{k_1+1}{k_1}\tau_1^2 W_1 + 2\,\frac{k_2+1}{k_2}\tau_2^2 W_2 + (j-1)! \sum_{m=2}^{j} \frac{2^m(\tau_1^{2m} W_1 + \tau_2^{2m} W_2)}{m!m!(j-m)!}. \tag{29}$$

We can conclude that $-j\lambda_j$ ($j = 0, 1, 2, \ldots$) are the eigenvalues of the principal operator. hey all are negative except that for $j = 0$ which is equal to 0. For $j = 0$ and $j = 1$ the sum ver m in equation (29) is absent. Obviously, $\lambda_1 < \lambda_2 < \cdots$.

The Hermite polynomials form a complete system of eigenfunctions satisfying the rthogonality and normalization relations

$$(H_j, H_k) = \delta_{jk} 2^j j! \quad (j, k = 0, 1, 2, \ldots), \tag{30}$$

here δ_{jk} is the Kronecker delta and the scalar product (Φ, Ψ) of function Φ and Ψ of ξ is efined as

$$(\Phi, \Psi) = \pi^{-1/2} \int_{-\infty}^{\infty} \mathrm{d}\xi\, \mathrm{e}^{-\xi^2} \Phi\Psi. \tag{31}$$

From equations (19), (31) and $H_0 = 1$ it follows that the two-dimensional distribution $\equiv f(\nu_1, \nu_2)$ of the nuclei with respect to variables ν_1 and ν_2 is given by the equation $= (H_0, P)$, i.e. the two-dimensional distribution f is the projection of the three-dimensional ne P on H_0.

Let us take the projection of governing equation (25) on H_0. According to equations (27) nd (30), only the first and second terms (which are the smallest ones, of order of $1/(\Delta\nu_{1c})^2$ or $/(\Delta\nu_{2c})^2$) make contributions to this projection. Since $f = (H_0, P)$, we obtain

$$\frac{\partial f}{\partial t} = -\frac{\partial J_1}{\partial \nu_1} - \frac{\partial J_2}{\partial \nu_2}, \tag{32}$$

here

$$J_i = \left(H_0, \left(\hat{L}_i - W_i \sum_{m=1}^{\infty} \frac{\tau_i^m}{m!}\frac{\partial^m}{\partial \xi^m}\right) P\right) \quad (i = 1, 2) \tag{33}$$

s the flux (averaged over ξ) of nuclei along the ν_i-axis.

5. NUMERICAL CALCULATIONS

To illustrate our theoretical results by numerical calculations we considered the binary ucleation in the vapor mixture of water (1st component) and ethanol (2nd component) at $_0 = 293.15$ K. Air at the normal atmospheric pressure was chosen as carrier gas. All the hysical properties of both components required for calculations are well determined for oth liquid and vapor phases. Besides, accurate fits of several thermodynamic properties vs omposition are required for water (1)– ethanol (2) liquid solution and they are fortunately lso available.

The specific heats of pure water and ethanol in liquid and vapor phases were determined ith the help of formulas given in *Thermophysical Properties of Matter* (1970). The latent eat of pure water was calculated from the formula given by Feder *et al.* (1966) and that of ure ethanol was obtained by linearly extrapolating data in *CRC Handbook of Chemistry nd Physics* (1992–1993). The equilibrium vapor pressure of pure water was taken from *RC Handbook of Chemistry and Physics* (1992–1993), and that of pure ethanol was alculated from the formula given by Mirabel and Katz (1977). The partial molar volumes $_1$ and v_2 of pure liquid water and ethanol, respectively, were computed from the density alues given by *CRC Handbook of Chemistry and Physics* (1992–1993) and the the volume of the nucleus was related to v_1 and v_2 as $V = \nu_1 v_1 + \nu_2 v_2$. As for the surface tension σ of ater–ethanol liquid solution, we, following Wilemski (1987), fitted ln σ with a third-order olynomial in the variable $4(1-\chi)/(4-3\chi)$, using data in Timmermans (1960). Following irabel and Katz (1977) and Wilemski (1987), the liquid-phase activity coefficients were etermined from the three-parameter Redlich–Kister equation of d'Avila and Silva (1970).

Since there exist no theoretical nor experimental data on the thermal accommodation nd sticking coefficients, calculations were carried out at various values of α_{ci}, α_{ti} ($i = 1, 2$), nd α_g in order to illustrate the influence of these parameters on theoretical predictions. o illustrate the dependence of theoretical predictions on the degree of vapor mixture etastability, calculations were performed for four couples of water and ethanol activities $_1, \zeta_2$ at each set of coefficients α_{ci}, α_{ti} ($i = 1, 2$), and α_g (activity ζ_i ($i = 1, 2$) is defined as $_i = n_i/n_{si}$, where n_i is the number density of i-component molecules in the vapor mixture, nd n_{si} is the equilibrium number density of i-component molecules in a vapor saturated ver the pure bulk liquid of this component). Results of calculations are presented in able 1.

Since the values τ_i ($i = 1, 2$) do not depend on α_{ci}, α_{ti} ($i = 1, 2$), and α_g and the time t_v does ot depend on α_{t1}, α_{t2}, α_g, we presented τ_i ($i = 1, 2$), and t_v only in the first part of Table 1.

Figure 1 shows the time dependence of the first mode of the deviation $P - f$ of the istribution of nuclei with respect to the temperature from a Gaussian equilibrium distribu-ion at the stage of thermal relaxation not only for the binary nucleation in the water–thanol system (using equation (35)) but also for the unary nucleation of pure water vapor according to Grinin and Kuni (1989)). According to equation (35) and to the analogous quation of the one-component theory (Grinin and Kuni, 1989), the first mode of the eviation $P - f$ corresponds to the greatest relaxation time (t_ξ) and, therefore, is the slowest the most "long-lived") mode of $P - f$. The second mode decreases with time about three imes as fast as the first one. Air at the normal atmospheric pressure was a carrier gas in oth system and the thermal accommodation coefficients of both water and ethanol were qual to 1. Figure 1a corresponds to the binary system and Fig. 1b represents the nucleation f pure water. The curves of series A were obtained for the case where the sticking oefficients α_{c1} and α_{c2} of water and ethanol were both equal to 0.5; series B corresponds to he case where α_{c1} and α_{c2} were both equal to 0.1. In each series, the values of the thermal ccommodation coefficient of air were taken as follows: $\alpha_g = 1$ for the boldest (lower) curve; $_g = 0.5$ for the dashed (medium) curve; $\alpha_g = 1$ for the thinnest (upper) curve. According to ig. 1, the supersaturation (activity) of pure water vapor has to be equal to about 3.5 so that he time of thermal relaxation of the unary nucleation should be the same as (or close to) the ime of thermal relaxation of the binary nucleation of water and ethanol at the activities $_1 = 1.5$ and $\zeta_2 = 1.0$.

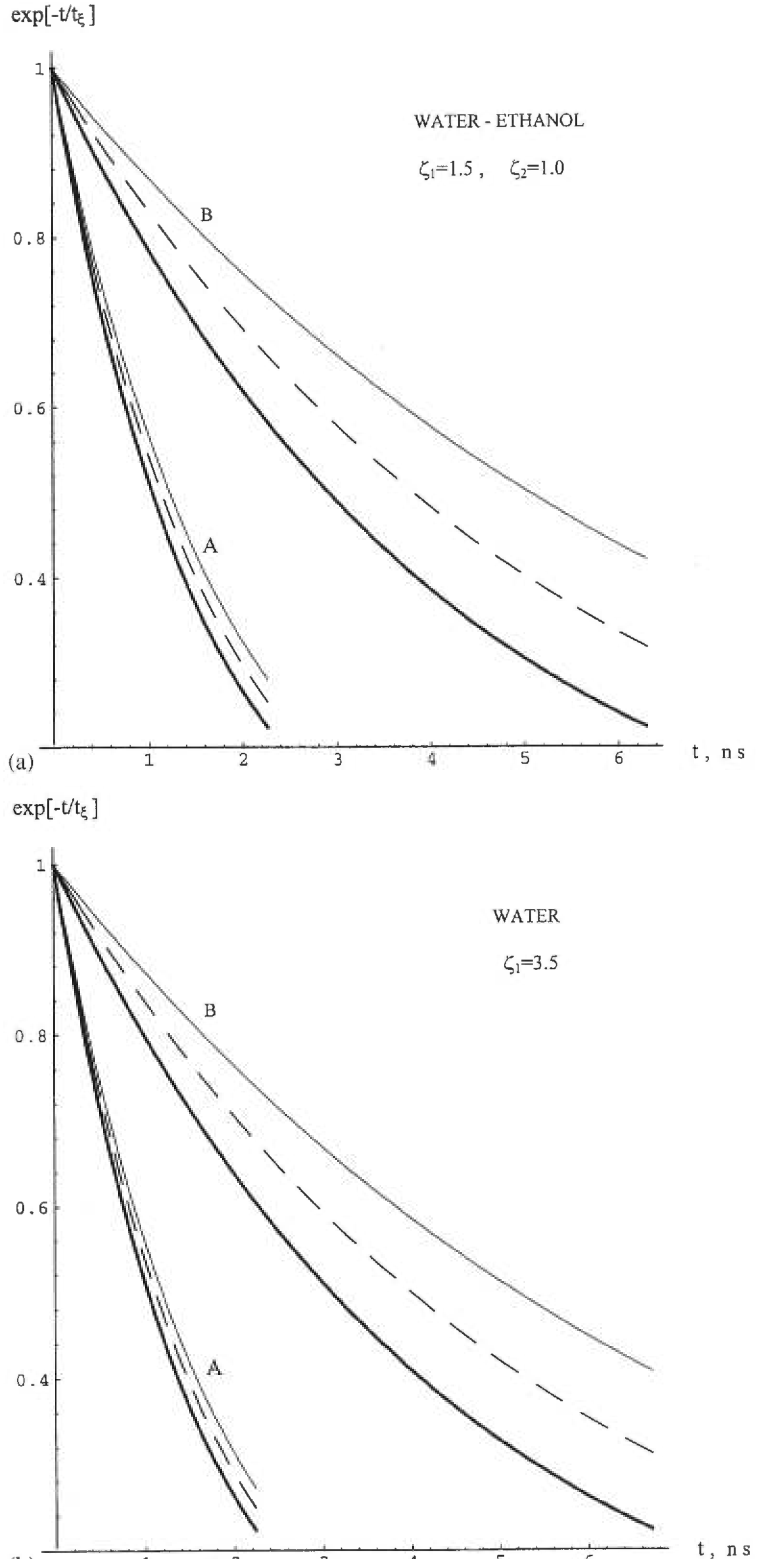

Fig. 1. Thermal relaxation stage of (a) the binary nucleation in the water(1)–ethanol(2) system (the activities being $\zeta_1 = 1.5$ and $\zeta_2 = 1.0$) and (b) the unary nucleation of pure water (at $\zeta_1 = 3.5$), at $T_0 = 293.15$ K with air as a carrier gas. The curves show the time dependence of the slowest (first) mode of the deviation $P - f$ of the distribution of nuclei with respect to temperature from a quasiequilibrium Gaussian distribution (equation (38)). Series A corresponds to the sticking coefficients $\alpha_{c1} = 0.5$ and $\alpha_{c2} = 0.5$; series B corresponds to $\alpha_{c1} = 0.1$ and $\alpha_{c2} = 0.1$. In each series, the values of the thermal accomodation coefficient of air are: $\alpha_g = 1$ for the boldest (lower) curve; $\alpha_g = 0.5$ for the dashed (medium) curve; $\alpha_g = 0.1$ for the thinnest (upper) curve.

ucleation with the help of relation (33), we have to solve the equation (25) taking account of ll the terms on its RHS. These problems will be objects of our further research. Of course, s long as there are no experimental nor theoretical data about sticking and thermal ccommodation coefficients α_{ci}, α_{ti} $(i = 1, 2)$, α_g, theoretical predictions will remain unertain enough. Nevertheless, we will be able to get approximative magnitudes of these oefficients by making a comparison between theoretical predictions and experimental data n nucleation rates.

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KINETICS OF TWO-COMPONENT CONDENSATION UNDER DYNAMIC REGIME WITH "SYNCHRONOUS" ATTAINMENT OF THE METASTABILITY MAXIMUM

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Abstract—A kinetic theory is presented for isothermal homogeneous two-component condensation under dynamic regime with synchronous attainment of the metastability maximum. It is shown that extending the iteration method of treating of one-component condensation under dynamic conditions to the case of two-component theory makes it possible to construct the spectrum of linear sizes and two-dimensional distribution of two-component droplets, a relative degree of accuracy being high enough even at the first iteration step. This method also allows one to find the time dependence of both real supersaturations as well as the total number of droplets formed per unit volume during two-component condensation. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

Two-component condensation, i.e. formation and growth of drops of a liquid solution of two substances in a metastable vapor mixture of these substances, is a process widespread in the nature and important for technical applications (we shall use the term "metastable" instead of less general terms "supersaturated", "supercooled", etc.). The theory of two-component condensation is an important part of the theory of first-order phase transitions. At the same time a development of two-component condensation theory is extremely important for various applications, for example, in order to construct the quantitative methodology of forecasting of acid rains.

We usually distinguish three stages of first-order phase transition. During the first of them the embryos of a new phase are formed (this stage is also called the stage of nucleation) which are condensation centers afterwards. It is during the second stage that the phase transition properly takes place—the bulk of a metastable phase passes to a liquid phase. During the third stage, the growth of large drops occurs to the detriment of small ones.

At present there exists the complete and adequate theoretical description of all three stages of the one-component condensation. At the same time, the kinetic theory of two-component condensation has been developed almost exclusively for the simplest case where the metastability of two-component vapor mixture is created instantaneously (in neglecting both the thermal effects of condensation and presence of heterogeneous nucleation centers). The bases of such binary nucleation theory have been founded by Reiss (1950) who based his argument on the results of Flood (1934) and on the classical one-component nucleation theory of Becker and Döring (1935), Volmer (1939), Kramers (1940), Zeldovitch (1942) and Frenkel (1946). Very important contribution to the theory of binary nucleation has been made by Stauffer (1976), and that work has corrected the rate of binary nucleation obtained earlier by Reiss (1950). The consistent kinetic theory of binary nucleation has been constructed with the help of the method of complete separation of variables by Kuni *et al.* (1990) and Melikhov *et al.* (1990, 1991) who have also found the new normalization factor of equilibrium distribution. Important contributions to the development of stationary theory of binary nucleation have been made by Mirabel and Katz (1974), Hirschfelder (1974),

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The applicability of the theory is limited only by the conditions of validity of the classical capillarity approximations. It means that the droplets must be large enough, they hold at least some tens of molecules. The formation of droplets demands their passage through a high activation barrier, i.e. has a pure fluctuation character.

It is supposed that the condensing system and its environment do not exchange droplets. At the same time, we shall consider both materially open systems, in which the condensing substances sources exist homogeneously distributed, as well as materially closed systems. The absolute temperature T and volume V of materially open system are assumed fixed. In a materially closed system a vapor mixture metastability changes as a result of the changes of T and V, which we shall naturally take into account. It is also supposed that there are no heterogeneous nucleation centers in the vapor mixture, and that no chemical reaction occurs in considered system.

2. COMPLETE SET OF EQUATIONS OF THE KINETICS OF TWO-COMPONENT CONDENSATION

Let us denote by ζ_i $(i=1,2)$ the supersaturation of the vapor of i-component over the plane surface of its own liquid phase:

$$\zeta_i = n_i/n_{is} \quad (i=1,2), \tag{1}$$

where n_i is the number density of molecules of i-component in a vapor mixture; n_{is} is the number density of molecules of i-component vapor saturated over a plane surface of its own liquid phase (obviously, n_{is} depends on temperature T).

Let us introduce the value

$$\Phi_i = n_{i\text{tot}}/n_{is} \quad (i=1,2), \tag{2}$$

where $n_{i\text{tot}}$ is the total quantity (in the vapor mixture as in the droplets) of molecules of i-component in the system volume unit. Obviously, Φ_i represents the "ideal supersaturation" of i-component which could be observed in the system at the same external conditions if there was no consumption of this component by the droplets. In materially open system T, V, n_{1s} and n_{2s} are constant, and Φ_1 and Φ_2 change only as a result of injections of corresponding component by external sources. In materially closed system, the total quantities of molecules of both components remain constant, i.e. $Vn_{i\text{tot}} = \text{Const}$ $(i=1,2)$. Therefore, in materially closed system the following equations are observed:

$$n_{is*}V_*/n_{is}V = \Phi_i/\Phi_{i*} \quad (i=1,2), \tag{3}$$

where the subscript "$*$" marks the values at some moment t_*, when a nucleation rate is maximal. For the theory that is intended to be developed this moment coincides with the moment when a vapor mixture metastability is maximal, i.e. a critical embryo formation free energy is minimal.

Usually in addition to the droplets and binary vapor mixture participating in a material exchange with the droplets, in a condensing system there is some passive gas the molecules of which do not participate in a material exchange with the droplets. Let us suppose the passive gas concentration is high enough. Then non-isothermal effects of condensation will not be important, and the equation of state of the passive gas and character of thermal contact of the system with the environment will determine the unabmiguous relationship between n_{is} $(i=1,2)$ and V. Taking equation (3) into account, let us present this relationship as a parametric one:

$$n_{is*}/n_{is} = S_i(\Phi_i) \quad (i=1,2), \tag{4}$$

$$V_*/V = \Phi_i/\Phi_{i*}S_i(\Phi_i) \quad (i=1,2), \tag{5}$$

where $S_i(\Phi_i)$ is some function (we do not indicate its dependence on Φ_{i*}). With the help of Clapeyron–Clausius' formula one can rewrite equation (4) as

$$T/T_* = [S_i(\Phi_i)]^{1/\beta_{i*}} \quad (i=1,2), \tag{6}$$

Let us denote by ν_1 and ν_2 the numbers of molecules of the first and second components, respectively, in the droplet. Let us choose the values ρ and χ determined according to

$$\rho = (\nu_1 + \nu_2)^{1/3}, \qquad \chi = \nu_1/(\nu_1 + \nu_2) \tag{12}$$

as the droplet state variables. The variable ρ represents the linear size of droplet, and variable χ represents the composition of the solution in a droplet. Let us denote by $n(\rho, \chi, t)$ the distribution (corresponding to unit volume and expressed in units of n_{1s}) of droplets with respect to the variables ρ and χ at moment t. It has been shown (Kuni *et al.*, 1990; Melikhov *et al.*, 1990, 1991) that the variable χ is the stable one in near-critical region. According to Dzhikaev (1992), during the second stage of two-component condensation at the instantaneous creation of metastability, the distribution of droplets has a Gaussian dependence on the variable χ in supercritical region, and an average magnitude χ_0 of variable χ is determined by means of quasistationary condition on χ. Therefore, it is natural to assume that in the present theory the distribution of droplets with respect to the stable variable χ in the supercritical region also has a form of Gaussian distribution, and that an average magnitude χ_0 of variable χ in this region is determined by means of quasistationary condition $\dot{\chi} = \mathrm{d}\chi/\mathrm{d}t = 0$ leading to the transcendental equation

$$\alpha_{c1} v_{T1} n_{1is}(1 - \chi_0)[\zeta_1 - \chi_0 f_1(\chi_0)] = \alpha_{c2} v_{T2} n_{2s} \chi_0 [\zeta_2 - (1 - \chi_0) f_2(\chi_0)], \tag{13}$$

where α_{ci} and v_{Ti} $(i = 1, 2)$ are, respectively, the condensation coefficient and average thermal velocity of molecule of i-component in vapor mixture; $f_1(\chi)$ and $f_2(\chi)$ are the activity coefficients of the first and second components in a liquid solution with composition χ. Therefore, the distribution $n(\rho, \chi, t)$ has the form

$$n(\rho, \chi, t) = p(\rho, t)[2\pi(\Delta\chi)^2]^{-1/2} \exp\left[-\frac{(\chi - \chi_0)^2}{2(\Delta\chi)^2}\right], \tag{14}$$

where $\Delta\chi$ is an equilibrium value of the r.m.s. fluctuation of solution concentration in a droplet. The function $p(\rho, t)$ represents obviously the one-dimensional distribution (corresponding to unit volume and expressed in units of n_{1s}) of droplets with respect to variable ρ at moment t.

It has been shown (Dzhikaev, 1992) that a linear size of droplet, practically immediately after its formation, increases with time with the rate independent of linear size:

$$\dot{\rho} = \frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{n_{1s}}{n_{1s*}} \frac{\alpha_{c1}}{\tau_{1*}} [\zeta_1 - \chi_0 f_1(\chi_0)] + \frac{n_{2s}}{n_{2s*}} \frac{\alpha_{c2}}{\tau_{2*}} [\zeta_2 - (1 - \chi_0) f_2(\chi_0)], \tag{15}$$

$$\tau_i = [v_{Ti} n_{is} (\pi v^2/48)^{1/3}]^{-1} \quad (i = 1, 2). \tag{16}$$

Here $v \equiv v(\chi)$ is the droplet volume per molecule (it is supposed that it depends only on χ). In equations (15) and (16) the temperature dependence of α_{ci}, v_{Ti} and v is much slighter than hat of n_{is}, and one can neglect it.

Under the conditions of validity of macroscopic theory of condensation, the characterstic size of droplets is much greater than their sizes at moment of formation. Therefore, the solution of equation (15) has to satisfy the initial condition

$$\rho(t)|_{t=0} = 0. \tag{17}$$

Taking into account that for all the droplets $\dot{\rho}$ does not depend on ρ and there is no droplet exchange between the system and environment, one can (Kuni, 1984, 1988) present he distribution $p(\rho, t)$ in the form

$$p(\rho, t) = \frac{n_{1s*} V_*}{n_{1s} V} \theta(\rho) f(z - \rho). \tag{18}$$

Here

$$\theta(u) = \begin{cases} 1 & (u \geqslant 0), \\ 0 & (u < 0), \end{cases}$$

one-dimensional distribution $f_s(\zeta_1, \zeta_2)$ independent of ρ. Thus, one can use $f_s(\zeta_1, \zeta_2)$ as a boundary condition to $p(\rho, t)$. Taking into account that during the first stage $n_{is}V \approx n_{is*}V_*$, we obtain from equation (22)

$$f(x) = f_s(\zeta_1(x), \zeta_2(x)), \tag{23}$$

where $\zeta_i(x)$ $(i = 1, 2)$ is the magnitude of the supersaturation ζ_i at time $t(x)$ when the droplets with given x were formed.

According to Kuni *et al.* (1990), Melikhov *et al.* (1991) and Dzhikaev (1992), the distribution f_s expressed in units of n_{1s} has the form

$$f_s(\zeta_1, \zeta_2) = K(\zeta_1, \zeta_2)\exp[-F(\zeta_1, \zeta_2)], \tag{24}$$

where the dependence of the pre-exponential factor $K(\zeta_1, \zeta_2)$ on ζ_1, ζ_2 is a power one; $F(\zeta_1, \zeta_2)$ is the height of activation barrier of two-component nucleation at saddle point, i.e. critical embryo formation free energy, expressed in units of $k_B T_*$, at the current magnitudes of supersaturations ζ_1, ζ_2. For $F(\zeta_1, \zeta_2)$, in accordance with Kuni *et al.* (1990) and Melikhov *et al.* (1990), one can obtain the expression

$$F(\zeta_1, \zeta_2) = 16\pi\gamma_*^3 v^2(\chi_c)/3[\chi_c \ln \zeta_1 + (1 - \chi_c)\ln \zeta_2 - G(\chi_c)]^2, \tag{25}$$

where

$$G(\chi_c) = \chi_c \ln[\chi_c f_1(\chi_c)] + (1 - \chi_c)\ln(1 - \chi_c) f_2(\chi_c)], \tag{26}$$

χ_c is the composition of solution in a critical embryo; γ_* is the surface tension of embryo in units of $k_B T_*$ (assumed independent of the composition of solution in an embryo).

The expressions (14), (13), (19), (22)–(24) represent the solution of the kinetic equation of two-component condensation (obtained first by Reiss, 1950) for the considered supercritical droplets. In order that this set of equations comprising the unknown functions $\zeta_1(x)$ and $\zeta_2(x)$ becomes consistent it is necessary to add to them the material balance equations for both components:

$$\Phi_i = \zeta_i + g_i \quad (i = 1, 2), \tag{27}$$

where g_i, according to equations (1) and (2), represents the total quantity (corresponding to unit volume and expressed in units of n_{1s}) of molecules of i-component condensed in all the droplets. Taking into account the facts that ρ^3 is the total number of molecules in a droplet of linear size ρ and that χ_0 does not depend on ρ, we obtain in view of relations (14), (21) and (22)

$$g_1 = \chi_0 \frac{n_{1s*}V_*}{n_{1s}V} \int_{-\infty}^{z} dx(z - x)^3 f(x), \tag{28}$$

$$g_2 = \frac{1 - \chi_0}{\chi_0} \frac{n_{1s}}{n_{2s}} g_1 . \tag{29}$$

The relations (14), (13), (22)–(24) together with (10) and (27)–(29) compose the consistent set of equations of the two-component condensation. The unknowns in this set are the spectrum $f(x)$, coordinate z and composition χ_0.

Let $\rho_{\min}(t)$ be the coordinate of the left bound of the region in which the values of the distribution $p(\rho, t)$ are relatively important at time t. Obviously, during a nucleation stage $\rho_{\min}(t) = 0$. However, after its end the coordinate $\rho_{\min}(t)$ begins moving along the ρ-axis with the rate $\dot{\rho}$ of the increase of linear size of droplet. The decrease of the supersaturations ζ_1 and ζ_2 (on account of the consumption of vapor mixture substances by the ensemble of supercritical droplets) slows the velocity of movement of the coordinate $\rho_{\min}(t)$ down, according to equation (15). The decrease of the supersaturations ζ_1 and ζ_2 (causing the decrease of the metastability of condensing vapor mixture) induces simultaneously the increase of the critical droplet size $\rho_c(\zeta_1, \zeta_2)$ at the current magnitudes of supersaturations.

where the $\Phi_i(x)$ is the ideal supersaturation Φ_i at time $t(x)$ when the droplets with given x were formed. According to equation (39), the value $1/c_i$ represents the length on the x-axis on which the relative change of supersaturation Φ_i is $1/\Gamma_*$.

Linearizing $\Phi_i(x)$ in x near $x=0$ and using equation (39), we have

$$\Phi_i(x) = \Phi_{i*} + \frac{\Phi_{i*}}{\Gamma_*} c_i x \quad (i=1, 2), \tag{40}$$

and expression (21) takes the form

$$\zeta_i(x) - \Phi_{i*} = \frac{\Phi_{i*}}{\Gamma_*} c_i x - g_i(x) \quad (i=1, 2), \tag{41}$$

Inserting equation (41) in equation (34) and taking equations (29) and (36) into account, we obtain

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*}) \exp\left[cx - \frac{\Gamma}{\Phi_{1*}} g_1(x) \right], \tag{42}$$

where

$$c = \frac{\Gamma_1}{\Gamma_*} c_1 + \frac{\Gamma_2}{\Gamma_*} c_2. \tag{43}$$

During the nucleation stage on account of its relative shortness one can assume $n_{is} = n_{is*}$ $(i=1, 2)$, $V = V_*$ and $\chi_0 = \chi_{0*}$. Taking equation (42) into account, we rewrite equation (28) as

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} \mathrm{d}x (z-x)^3 \exp\left[cx - \frac{\Gamma}{\Phi_{1*}} g_1(x) \right]. \tag{44}$$

According to the definition of t_* as a time moment of attainment of the metastability maximum, we have

$$\left.\frac{\mathrm{d}F}{\mathrm{d}t}\right|_{t=t_*} = 0, \tag{45}$$

$$\left.\frac{\mathrm{d}^2F}{\mathrm{d}t^2}\right|_{t=t_*} > 0. \tag{46}$$

Using equations (25) and (26), from equations (45) and (46) we obtain, respectively, equation

$$\left.\frac{\chi_c}{\zeta_1}\frac{\mathrm{d}\zeta_1}{\mathrm{d}t}\right|_{t=t_*} + \left.\frac{1-\chi_c}{\zeta_2}\frac{\mathrm{d}\zeta_2}{\mathrm{d}t}\right|_{t=t_*} = 0 \tag{47}$$

and the inequality

$$\left.\left[\frac{\chi_c}{1-\chi_c}\frac{1}{\zeta_1^2}\left(\frac{\mathrm{d}\zeta_1}{\mathrm{d}t}\right)^2 - \frac{\chi_c}{\zeta_1}\frac{\mathrm{d}^2\zeta_1}{\mathrm{d}t^2} - \frac{1-\chi_c}{\zeta_2}\frac{\mathrm{d}^2\zeta_2}{\mathrm{d}t^2} \right]\right|_{t=t_*} > 0 \tag{48}$$

(it is assumed that the condition of metastability of two-component vapor mixture (Kuni *et al.*, 1990; Melikhov *et al.*, 1990) is observed). From equation (47) it follows that the alternative possibilities exist for the behavior of supersaturations ζ_1 and ζ_2 at the moment t_*: either

$$\left.\frac{\mathrm{d}\zeta_1}{\mathrm{d}t}\right|_{t=t_*} = \left.\frac{\mathrm{d}\zeta_2}{\mathrm{d}t}\right|_{t=t_*} = 0 \tag{49}$$

or

$$\left.\frac{\mathrm{d}\zeta_1}{\mathrm{d}t}\right|_{t=t_*} = -\left.\frac{1-\chi_c}{\chi_c}\frac{\zeta_1}{\zeta_2}\frac{\mathrm{d}\zeta_2}{\mathrm{d}t}\right|_{t=t_*} \neq 0. \tag{50}$$

Let us construct the second approximation corresponding to the insertion of equation (56) in the RHS of equation (44). In this approximation, the accumulation of substance by the droplets occurs more slowly than it occurs in reality.

We have

$$g_1(z) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*}) \int_{-\infty}^{z} \mathrm{d}x (z-x)^3 \exp[cx - \mathrm{e}^{cx}], \tag{58}$$

$$g_1'(0) = \chi_{0*} f_s(\Phi_{1*}, \Phi_{2*})\, 3b_2/c^3\,, \tag{59}$$

and also

$$f_s(\Phi_{1*}, \Phi_{2*}) = \frac{\Phi_{1*}}{3b_2\Gamma_*\chi_{0*}}\, c^4, \tag{60}$$

where

$$b_q = \int_0^{\infty} \mathrm{d}\xi\, \xi^q \exp[-\xi - \mathrm{e}^{-\xi}] \quad (q = 0, 1, 2, \ldots). \tag{61}$$

Numeric calculations show that

$$b_0 = 1 - 1/\mathrm{e} = 0.632, \quad b_1 = 0.797, \quad b_2 = 1.78, \quad b_3 = 5.66. \tag{62}$$

Denoting by symbol δ the difference between the magnitudes of value in the first and second approximations, one can, with the use of equation (10), establish

$$\frac{\delta\Phi_{1*}}{\Phi_{1*}} = \left(\frac{2}{b_2} - 1\right)\Bigg/\left[\Gamma_1 + \frac{m_2}{m_1}\Gamma_2\right] = 0.12\Bigg/\left[\Gamma_1 + \frac{m_2}{m_1}\Gamma_2\right],$$

$$\frac{\delta\Phi_{2*}}{\Phi_{2*}} = \left(\frac{2}{b_2} - 1\right)\Bigg/\left[\frac{m_1}{m_2}\Gamma_1 + \Gamma_2\right] = 0.12\Bigg/\left[\frac{m_1}{m_2}\Gamma_1 + \Gamma_2\right]. \tag{63}$$

Inserting equation (60) in equation (58) and using equation (61), we obtain

$$g_1(z) = \frac{\Phi_{1*}}{3b_2\Gamma_*} c^4 \int_{-\infty}^{z} \mathrm{d}x (z-x)^3 \exp[cx - \mathrm{e}^{cx}], \tag{64}$$

$$g_1(0) = \frac{b_3}{3b_2}\frac{\Phi_{1*}}{\Gamma_*}. \tag{65}$$

With the help of equation (27) at $x = 0$ and equations (65) and (29), one can obtain the relations

$$\zeta_{1*} = \Phi_{1*}\left[1 - \frac{b_3}{3b_2}\frac{1}{\Gamma_*}\right], \qquad \zeta_{2*} = \Phi_{2*}\left[1 - P_*\frac{b_3}{3b_2}\frac{1}{\Gamma_*}\right] \tag{66}$$

which, by virtue of equations (32), (36)–(38) and (62), justify the estimates (33) at the second step of iteration procedure.

Marking with superscripts 0, 1, 2, . . . the values at the corresponding iteration step, let us compare the first approximation with the second one.

From equations (10) and (63) it follows that

$$\frac{\delta t_*}{t_*} = \left(\frac{2}{b_2} - 1\right)\Big/(m_1\Gamma_1 + m_2\Gamma_2) = \frac{0.12}{m_1\Gamma_1 + m_2\Gamma_2}, \tag{67}$$

i.e. the moment $t_*^{(2)}$ has become a little more than the moment $t_*^{(1)}$ (we exclude from consideration very small m_1 and m_2, assuming $m_1\Gamma_1 + m_2\Gamma_2 \gg 1$) owing to the more slow accumulation of substance by the droplets in second approximation. The increase of the duration of droplet growth clears the result $g_1^{(2)}(0) > g_1^{(1)}(0)$ following from equations (56), (65) and (62).

and the estimate

$$\frac{f^{(2)}(x)}{f^{(2)}(0)} < \exp\left[-\frac{b_1}{b_2}c^2x^2 - \frac{b_0}{3b_2}c^3x^3\right] \quad (x > 0), \tag{78}$$

the analysis of which allows to conclude that already first approximation of spectrum given by equation (68) is fairly accurate. By this approximation we shall be satisfied afterwards.

4. SIMULTANEOUS AND NON-SIMULTANEOUS STABILIZATIONS OF IDEAL SUPERSATURATIONS AFTER THE ATTAINMENT OF THE METASTABILITY MAXIMUM

Above, in the developed iteration procedure, it was supposed that the stabilization of ideal supersaturations Φ_1 and Φ_2 occurs after the end of formation of the most important part of spectrum. In the cases where the stabilization of either Φ_1 or Φ_2 or the stabilization of both Φ_1 and Φ_2 occurs before the end of the stage of formation of the most important part of the spectrum, the presented iteration procedure will change a little.

Let us consider at first the case where

$$\Phi_{1*} < \Phi_{01} \lesssim \Phi_{1*}(1 + 1.15c_1/c\Gamma_*), \qquad \Phi_{02} > \Phi_{2*}(1 + 1.15c_2/c\Gamma_*), \tag{79}$$

i.e. where one of the ideal supersaturations (Φ_1) is stabilized before the end of the stage of formation of the spectrum, and other ideal supersaturation (Φ_2) is stabilized after the end of that stage.

Relations (40) will take the form

$$\begin{aligned} \Phi_1(x) &= \Phi_{1*} + \frac{\Phi_{1*}}{\Gamma_*}c_1x \quad (x < z_0), \\ &= \Phi_{1*} + \frac{\Phi_{1*}}{\Gamma_*}c_1z_0 \quad (z \geqslant z_0), \\ \Phi_{2*} &= \Phi_{2*} + \frac{\Phi_{2*}}{\Gamma_*}c_2x, \end{aligned} \tag{80}$$

where

$$z_0 = \frac{\Gamma_*}{c_1}(\Phi_{01}/\Phi_{1*} - 1). \tag{81}$$

Respectively instead of equation (41) we have

$$\begin{aligned} \zeta_1(x) - \Phi_{1*} &= \frac{\Phi_{1*}}{\Gamma_*}c_1x - g_1(x) \quad (x < z_0), \\ &= \frac{\Phi_{1*}}{\Gamma_*}c_1z_0 - g_1(x) \quad (x \geqslant z_0), \\ \zeta_2(x) - \Phi_{2*} &= \frac{\Phi_{2*}}{\Gamma_*}c_2x - g_2(x). \end{aligned} \tag{82}$$

Expressions (42) and (53) change only in the regions $x \geqslant z_0$ and $z \geqslant z_0$. In these regions now

$$f(x) = f_s(\Phi_{1*}, \Phi_{2*})\exp\left[cz_0 - \frac{\Gamma_*}{\Phi_{1*}}g_1(x) + \frac{\Gamma_1}{\Gamma_*}c_2(x - z_0)\right] \quad (x \geqslant z_0), \tag{83}$$

$$g_1(z) = \chi_{0*}f_s(\Phi_{1*}, \Phi_{2*})\left\{\int_{-\infty}^{z_0} \mathrm{d}x(z - x)^3 \mathrm{e}^{cx} + \int_{z_0}^{z} \mathrm{d}x(z - x)^3 \exp\left[cz_0 + \frac{\Gamma_2}{\Gamma_*}c_2(x - z_0)\right]\right\} \quad (z \geqslant z_0). \tag{84}$$

$$f(x)=\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}\,c^4\exp\left\{cx-e^{cz_0}\left[1+c(x-z_0)+\frac{1}{2}c^2(x-z_0)^2\right.\right.$$

$$\left.\left.+\frac{1}{6}c^3(x-z_0)^3+\frac{1}{24}c^4(x-z_0)^4\right]\right\}\quad(x\geqslant z_0). \tag{94}$$

Let us denote by N the total quantity of droplets per volume unit formed during the first stage of two-component condensation. This quantity, according to equations (14), (21) and (22), linearly depends on the spectrum by means of integral value

$$I=\int_{-\infty}^{\infty}\mathrm{d}x\,f(x). \tag{95}$$

Therefore, the accuracy of determination of the value I has particular significance.

To estimate the accuracy of determination of the value I, let us change a little the above-described iteration procedure by supposing that χ_{0*}, Φ_{1*}, Φ_{2*} and $f_s(\Phi_{1*},\Phi_{2*})$ (and with them Γ_* and c too) are the same in all the iteration steps and are determined by insertion of the last of used approximations in equations (51) and (52). Having chosen in this common way χ_{0*}, Φ_{1*}, Φ_{2*} and $f_s(\Phi_{1*},\Phi_{2*})$ one can guarantee that the less the function $g_1(x)$ in the RHS of equation (44) is, the more the RHS of equation (44) is. This property makes it possible to construct, by means of an iteration procedure, the approximations $g_1^{(j)}(x)$ ($j=0,1,2,\ldots$) which monotonically approach the strict solution of equation (44) with chosen χ_{0*}, Φ_{1*}, Φ_{2*} and $f_s(\Phi_{1*},\Phi_{2*})$. This property guarantees the uniqueness of strict solution.

Let us choose the $g_1^{(0)}=0$ as the initial approximation in the iteration procedure. Such a choice ensures the inequality $g_1>g_1^{(0)}$, where g_1 is the strict solution of equation (44). Every next approximation is determined by inserting the preceding one in the RHS of equation (44):

$$g_1^{(j+1)}(z)=\chi_{0*}f_s(\Phi_{1*},\Phi_{2*})\int_{-\infty}^{z}\mathrm{d}x(z-x)^3\exp\left[cx-\frac{\Gamma_*}{\Phi_{1*}}g_1^{(j)}(x)\right]$$

$$(j=0,1,2,\ldots). \tag{96}$$

Using the indicated property of the RHS of equation (44) and taking into account the obvious inequalities $g_1>g_1^{(0)}$, $g_1^{(2)}>g_1^{(0)}$ and the fact that the calculation of the RHS with the help of strict solution g_1 leads to the same solution g_1, we conclude:

$$g_1<g_1^{(1)},\quad g_1>g_1^{(2)},\quad g_1<g_1^{(3)},\ldots, \tag{97}$$

$$g_1^{(3)}<g_1^{(1)},\quad g_1^{(4)}>g_1^{(2)},\quad g_1^{(5)}<g_1^{(3)},\ldots. \tag{98}$$

According to equations (97) and (98) the approximations $g_1^{(1)}, g_1^{(3)},\ldots$ of odd order monotonically approach g_1 from above, and the approximations $g_1^{(2)}, g_1^{(4)},\ldots$ of even order monotonically approach g_1 from below.

The approximations of the spectrum $f^{(k)}$ ($k=1,2,3,\ldots$) are found by substituting $g_1^{(k)}(x)$ for $g_1(x)$ in the RHS of equation (42):

$$f^{(k)}(x)=f_s(\Phi_{1*},\Phi_{2*})\exp\left[cx-\frac{\Gamma_*}{\Phi_{1*}}g_1^{(k)}(x)\right]\quad(k=1,2,3,\ldots) \tag{99}$$

In accordance with equations (97) and (98), we have

$$f>f^{(1)},\quad f<f^{(2)},\quad f>f^{(3)},\ldots, \tag{100}$$

$$f^{(3)}>f^{(1)},\quad f^{(4)}<f^{(2)},\quad f^{(5)}>f^{(3)},\ldots. \tag{101}$$

Taking equations (25) and (26) into account, it follows from equations (104), (31), (36), (39) and (43) that the value $1/h$ in the RHS of equation (107) is a relatively "slow" function of $\chi_{0*}, \Phi_{1*}, \Phi_{2*}$. A fairly accurate calculation of $1/h$ is attained in first iteration step. Therefore, in the same step we also find the integral characteristic I and total quantity of droplets N with the relative error less than 0.15.

5. INITIAL AND FINAL PERIODS OF TWO-COMPONENT CONDENSATION

Omitting in the following the approximation superscript, for the spectrum in accordance with equation (68) we have

$$f(x) = \frac{\Phi_{1*}}{6\Gamma_* \chi_{0*}} c^4 \exp[cx - \mathrm{e}^{cx}]. \tag{116}$$

Inserting equation (116) in equation (28) we obtain

$$g_1 = \frac{\chi_0 n_{1s*} V_*}{\chi_{0*} n_{1s} V} \frac{\Phi_{1*}}{6\Gamma_*} c^4 \int_{-\infty}^{z} \mathrm{d}x (z-x)^3 \exp[cx - \mathrm{e}^{cx}]. \tag{117}$$

The expressions (117) and (29) are already true not only during the stage of formation of spectrum (when $\chi_0 \simeq \chi_{0*}$, $V \simeq V_*$ and $n_{is} \simeq n_{is*}$ $(i=1,2)$) but also during whole condensation process. The time dependence of the factor $n_{is*} V_*/n_{is} V$ $(i=1,2)$ is assumed to be known, and the value χ_0 satisfies equation (13).

Relations (27), (10), (13), (117), (29), (19) and (20) form the consistent set of equations. Resolving this set we can obtain the function $z(t)$ of one independent variable t. Together with $z(t)$, the time dependences of ζ_i $(i=1,2)$ are also determined.

For the total quantity of droplets formed per volume unit we have according to equation (22):

$$N = n_{is*} \frac{V_*}{V} \int_{-\infty}^{\infty} \mathrm{d}x f(x). \tag{118}$$

Inserting equation (116) in equation (118) and integrating, we obtain

$$N = n_{is*} \frac{V_*}{V} \frac{\Phi_{1*} c^3}{6\Gamma_* \chi_{0*}}. \tag{119}$$

Let $\Delta_- \Phi_i$ $(i=1,2)$ and $\Delta_- t$ be the changes of Φ_i and t corresponding to the change of z from $-\Delta_- x$ to 0, let $\Delta_+ \Phi_i$ $(i=1,2)$ and $\Delta_+ t$ be the changes of Φ_i and t corresponding to the change of z from 0 to $\Delta_+ x$. The values Φ_i and t have the magnitudes $\Phi_{i*} - \Delta_- \Phi_i$ and $t_* - \Delta_- t$ at moment of beginning of intensive nucleation and the magnitudes $\Phi_{i*} + \Delta_+ \Phi_i$ and $t_* + \Delta_+ t$ at moment of end of intensive nucleation.

From equations (40), (76), (39) and (43) we have

$$\frac{\Delta_- \Phi_i}{\Phi_{i*}} = \frac{1.84 c_i}{c_1 \Gamma_1 + c_2 \Gamma_2}, \qquad \frac{\Delta_+ \Phi_i}{\Phi_{i*}} = \frac{1.15 c_i}{c_1 \Gamma_1 + c_2 \Gamma_2} \quad (i=1,2) \tag{120}$$

and, in view of equation (10), also

$$\frac{\Delta_- t}{t_*} = \frac{1.84}{m_1 \Gamma_1 + m_2 \Gamma_2}, \qquad \frac{\Delta_+ t}{t_*} = \frac{1.15}{m_1 \Gamma_1 + m_2 \Gamma_2}. \tag{121}$$

Supposing that the condition

$$m_1 \Gamma_1 + m_2 \Gamma_2 \gg 1 \tag{122}$$

s observed (this condition excludes from theory only very small m_1 and m_2), the smallness of he RHS of equations (120) and (121) will be guaranteed and this is what justifies the

where

$$t_r = \frac{1}{9}(6\Gamma_*)^{1/3} a\, \Delta t = \frac{1}{3}\frac{(6\Gamma_*)^{1/3} a}{m_1\Gamma_1 + m_2\Gamma_2} t_*, \tag{133}$$

$$z_r = \frac{1}{3}(6\Gamma_*)^{1/3} a\, \Delta x = \frac{1}{c}(6\Gamma_*)^{1/3} a. \tag{134}$$

In virtue of equations (32) and (38) it follows from equations (122), (133) and (134) that $z_r \gtrsim 2\Delta x$, $3t_r \gtrsim 2\Delta t$ and $t_r \ll t_*$.

Relations (128), (129) and (132) determine the dependence of ζ_1, ζ_2 and t on z. To find the dependence of ζ_1, ζ_2 and z on t it is necessary to solve equation (132) with respect to z. Particularly, we have

$$z = \frac{\Delta x}{\Delta t}(t - t_*) \quad (-\Delta_- t \lesssim t - t_* \lesssim 3t_r/2), \tag{135}$$

$$z = z_r\left[1 - \sqrt{3}\mathrm{e}^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* \gtrsim 3t_r). \tag{136}$$

Expression (135) describes an initial period of condensation which, according to $3t_r/2 \geqslant \Delta t > \Delta_+ t$, ends a little later than the first stage. During this period $\zeta_i \simeq \Phi_i \simeq \Phi_{i*}$ $i = 1, 2$).

Expression (136) describes a final period of condensation. During this period the exponential term in the RHS of equation (136) is already small so that z almost coincides with z_r. Then from equations (128), (129), (134) and (136) it follows that

$$\zeta_1 = \Phi_{1*}\left[1 - a^3 + 3\sqrt{3}a^3\mathrm{e}^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* \gtrsim 3t_r), \tag{137}$$

$$\zeta_2 = \Phi_{2*}\left[1 - P_* a^3 + 3\sqrt{3P_*}a^3\mathrm{e}^{\pi/2\sqrt{3}} \exp\left(-\frac{t - t_*}{t_r}\right)\right] \quad (t - t_* \gtrsim 3t_r). \tag{138}$$

According to these relations, t_r represents a relaxation time.

The region of validity of equations (135) and (136) is also limited by inequalities (127) which can be broken when the ideal supersaturations continue to increase. According to equations (10), (122) and (133), inequalities (127) are still observed at $t - t_* \simeq 3t_r$, but they are broken as the time increases. Thus, under the conditions when the ideal supersaturaions increase, the asymptotic relations (136)–(138) are valid only at $t - t_* \simeq 3t_r$. Then equations (137), (138), (127) and (27) lead to the relations $\zeta_i/\Phi_i \ll 1$, $g_i/\Phi_i \simeq 1$ $(i = 1, 2)$, which mean that the droplets have absorbed practically all the condensing substance (provided earlier the metastability of vapor mixture).

As long as $t - t_* \lesssim 3t_r$ (i.e. before the final period) the value g_i/Φ_i increases. According to equations (56), (29) and (124) at t_* and at $t_* + \Delta_+ t$, we have, respectively:

$$\left.\frac{g_1}{\Phi_1}\right|_{t=t_*} = 1/\Gamma_*, \quad \left.\frac{g_2}{\Phi_2}\right|_{t=t_*} = P_*/\Gamma_*, \tag{139}$$

$$\left.\frac{g_1}{\Phi_1}\right|_{t=t_*+\Delta_+ t} = \mathrm{e}^{1.15}/\Gamma_*, \quad \left.\frac{g_2}{\Phi_2}\right|_{t=t_*+\Delta_+ t} = P_*\mathrm{e}^{1.15}/\Gamma_*. \tag{140}$$

From equations (139) and (140), it follows that the values g_1/Φ_1 and g_2/Φ_2 increase the most rapidly after the end of final period of condensation, and in time $3t_r/2 \lesssim t - t_* \lesssim 3t_r$ they attain the magnitudes near 1, i.e. practically whole two-component vapor mixture is absorbed by droplets. During this period the evolution of ζ_1, ζ_2 and z is described by relations (132), (128) and (129).

If the ideal supersaturations are stabilized then relations (136)–(138) remain true during a final period as long as $t - t_* \gtrsim 3t_r$. Their validity will be limited only by restriction (30).

From equations (148) and (149) it also follows that $\zeta_i/\Phi_i \ll 1$ $(i=1, 2)$ and all the more $\zeta_i/\Phi_{i*} \ll 1$ $(i=1, 2)$. That confirms the approximate equalities $\Phi_i - \zeta_i \simeq \Phi_i$ $(i=1, 2)$ used for final period and provides a high relative accuracy of expressions (144)–(146). According to equation (144), the droplets grow so that they have time to accumulate in themselves practically all the condensing substance of both components.

Let us note that the time of validity of the expressions (144)–(146) can be limited not only by condition (141) but also by other causes such as breakdown of free molecular regime of material exchange between a droplet and a vapor mixture, non-isothermal effects of condensation, coagulation, stabilization of ideal supersaturations, etc.

According to equations (22) and (144), the graph of one-dimension distribution of droplets $p(\rho, t)$ moves as a whole along the ρ-axis. The relative width of the spectrum is characterized by value $D = \Delta x/2z$ decreasing with time:

$$\begin{aligned} D &= \left(\frac{9}{16\Gamma_*}\right)^{1/3} \left(\frac{\chi_0}{\chi_{0*}}\right)^{1/3} \left(\frac{\Phi_{1*}}{\Phi_1}\right)^{1/3} \\ &= \left(\frac{n_{1\mathrm{tot}*}}{n_{2\mathrm{tot}*}}\right)^{1/3} \left(\frac{9}{16\Gamma_*}\right)^{1/3} \left(\frac{1-\chi_0}{\chi_{0*}}\right)^{1/3} \left(\frac{\Phi_{2*}}{\Phi_2}\right)^{1/3}. \end{aligned} \tag{150}$$

In the case of materially closed system, from equations (19), (13), (125) and (126) with consideration of

$$n_{is}\Phi_i V = n_{is*}\Phi_{i*}V_* \quad (i=1, 2) \tag{151}$$

ve have

$$z = \chi_{0*}^{1/3} \frac{(6\Gamma_*)^{1/3}}{c} \left[\frac{\Phi_1 + \Phi_2 - \zeta_1 - \zeta_2}{\chi_0\Phi_1 + (1-\chi_0)\Phi_2 n_{1\mathrm{tot}*}/n_{2\mathrm{tot}*}}\right]^{1/3}, \tag{152}$$

$$\zeta_1 - \chi_0 f_1(\chi_0) = \frac{\tau_{1*}}{\alpha_{c1}} \chi_0 S_1(\Phi_1) \frac{\mathrm{d}z}{\mathrm{d}t}, \tag{153}$$

$$\zeta_2 - (1-\chi_0) f_2(\chi_0) = \frac{\tau_{2*}}{\alpha_{c2}} (1-\chi_0) S_2(\Phi_2) \frac{\mathrm{d}z}{\mathrm{d}t}. \tag{154}$$

Assuming $\Phi_i - \zeta_i \simeq \Phi_i$ $(i=1, 2)$, from equation (152) we obtain in first approximation

$$z = \chi_{0*}^{1/3} \frac{(6\Gamma_*)^{1/3}}{c} \left[\frac{\Phi_1 + \Phi_2}{\chi_0\Phi_1 + (1-\chi_0)\Phi_2 n_{1\mathrm{tot}*}/n_{2\mathrm{tot}*}}\right]^{1/3}. \tag{155}$$

Expression (155) leads to the equality

$$\mathrm{d}z/\mathrm{d}t = 0 \tag{156}$$

not only in virtue of evident equality for a materially closed system

$$m_1 = m_2 \tag{157}$$

but also because of relation observed in this approximation for such a system

$$\chi_0 = \frac{n_{1\mathrm{tot}*}}{n_{1\mathrm{tot}*} + n_{2\mathrm{tot}*}}. \tag{158}$$

Thus, in first approximation we have

$$z = \left(\frac{\chi_{0*}}{\chi_0}\right)^{1/3} \frac{(6\Gamma_*)^{1/3}}{c}, \tag{159}$$

$$\zeta_1 - \chi_0 f_1(\chi_0) = 0, \qquad \zeta_2 - (1-\chi_0) f_2(\chi_0) = 0. \tag{160}$$

Instead of equation (94) for the spectrum in first approximation we have

$$f(x)=\varepsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4\exp[cx-\varepsilon e^{cx}]\quad(x<0),$$

$$f(x)=\varepsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4\exp\left[-\varepsilon\left(1+cx+\frac{1}{2}c^2x^2+\frac{1}{6}c^3x^3+\frac{1}{24}c^4x^4\right)\right]\quad(x\geqslant 0).\quad(169)$$

The stabilization of Φ_1 and Φ_2, according to equations (4) and (5), also means the tabilization of n_{1s}, n_{2s} and V. The equalities $n_{is}=n_{is*}$ $(i=1,2)$ and $V=V_*$ are now bserved with a high relative accuracy in a materially open system as well as in a materially losed one. Therefore, equation (28) takes the form

$$g_1=\chi_{0*}\int_{-\infty}^{z}\mathrm{d}x(z-x)^3f(x).\quad(170)$$

Inserting equation (169) in equation (170), one could obtain the second approximation of $_1$ correct during whole condensation process. This approximation together with equations 9), (27) and $\Phi_i=\Phi_{i*}$ $(i=1,2)$ would allow to obtain a consistent differential equation of ıe first order in unknown function z of one independent variable t.

Supposing that

$$\varepsilon\lesssim 1/e^8,\quad(171)$$

ne can replace equation (169) by

$$f(x)=\varepsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4e^{cx}\quad(x<0),$$

$$f(x)=\varepsilon\frac{\Phi_{1*}}{6\Gamma_*\chi_{0*}}c^4\exp\left[-\frac{\varepsilon}{24}c^4x^4\right]\quad(x\geqslant 0).\quad(172)$$

Figure 2 shows the behavior of spectrum $f(x)$ in different cases of stabilization of ideal ıpersaturations, the parameters m_1, m_2, t_1, and t_2 being fixed. Curve A corresponds to $f(x)$ ıven by equation (68) (stabilization of both Φ_1 and Φ_2 after the formation of spectrum, $_0>1.15/c$). Spectrum B is given by equation (94) at $z_0=0$ (simultaneous stabilization of $_1$ and Φ_2 at moment of attainment of metastability maximum). Both spectra C and

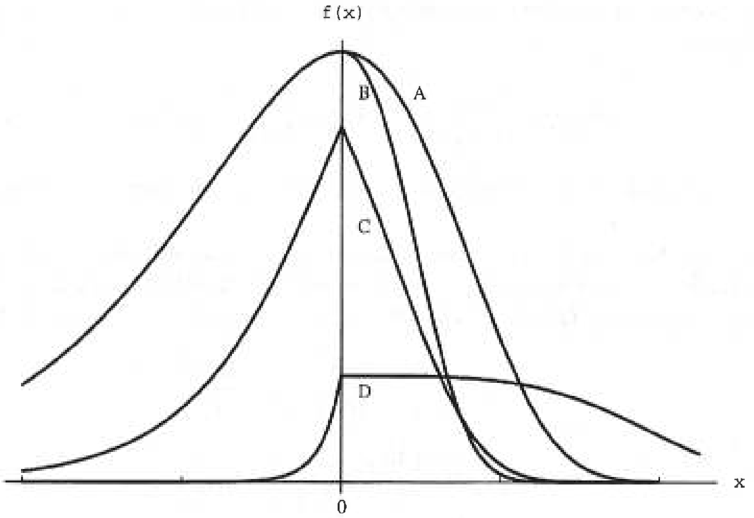

Fig. 2. Spectrum of linear sizes of droplets f as a function of x for different cases of stabilization of ideal supersaturations at fixed m_1, m_2, t_1, t_2. The curves correspond to the following cases: (A) to $z_0>1.15/c$ [equation (68)]; (B) to $z_0=0$ [equation (94)]; (C) to $\varepsilon<1$ [equation (172)]; (D) to $\varepsilon\lesssim 1/e^8$ [equation (175)].

omparison with the first ones. Thus, the RHS of equations (181) and (182) have a high elative accuracy beginning from the first stage which in view of equation (178) begins as . matter of fact at moment t_* when $z = 0$.

Taking into account equations (13), $\chi_0 = \chi_{0*}$, $n_{is} = n_{is*}$ $(i = 1, 2)$ and inserting equations 181) and (182) in equation (19), we obtain

$$\frac{dz}{dt} = \frac{\alpha_{c1}}{\tau_{1*}} \frac{a^3}{\chi_{0*}} \Phi_{1*} \left[1 - \frac{4A}{\Gamma_* a^3} \frac{1}{(\Delta x)^3} \left(z - \frac{\Delta x}{2} \right)^3 \right]. \tag{183}$$

ٍeplacing the initial condition (20) for equation (183) by practically equivalent condition $= \Delta x/2$ at $t = t_* + \Delta t/2$ and solving equation (183), we have

$$\frac{t - t_* - \Delta t/2}{t_r} = \ln \left\{ \frac{[(z - \Delta x)/2)^2/z_r^2 + (z - \Delta x/2)/z_r + 1]^{1/2}}{1 - (z - \Delta x/2)/z_r} \right\}$$

$$+ \sqrt{3}\arctan \left[\frac{2(z - \Delta x/2)/z_r + 1}{\sqrt{3}} \right] - \frac{\pi}{2\sqrt{3}}, \tag{184}$$

/here

$$z_r = \left(\frac{\Gamma_*}{4A} \right)^{1/3} a\, \Delta x, \qquad t_r = \frac{1}{3} \left(\frac{\Gamma_*}{4A} \right)^{1/3} a\, \Delta t \tag{185}$$

aking into account the equality $\Delta x/\Delta t = \alpha_{c1} a^3 \Phi_{1*}/\tau_{1*}\chi_{0*}$ following from equation (19)). 'he estimates $z_r \gtrsim 2\Delta x$, $3t_r \gtrsim 2\Delta t$ are fulfilled in virtue of $a \sim 1$, $\Gamma \gg 1$ and $A \simeq 0.9$.

Expressions (181), (182) and (184) determine the dependence of ζ_1, ζ_2 and t on z. In order) find the time dependence of ζ_1, ζ_2 and z it is necessary to solve equation (184) for z. In articular,

$$z = \frac{\Delta x}{\Delta t} (t - t_*) \quad \left(0 \lesssim t - t_* \lesssim \frac{3}{2} t_r + \frac{\Delta t}{2} \right), \tag{186}$$

$$z = z_r \left[1 - \sqrt{3}\exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r} \right) \exp\left(-\frac{t - t_*}{t_r} \right) \right] + \frac{\Delta x}{2} \left(t - t_* \gtrsim 3t_r + \frac{\Delta t}{2} \right). \tag{187}$$

Expression (186) describes an initial period of condensation and expression (187) de- :ribes a final one. During a final period of condensation, the exponential term in the RHS f equation (187) is already negligible so that z practically does not change with time and as a magnitude near $z_r + \Delta x/2$.

Inserting equation (187) in equations (181) and (182) and taking equation (184) into :count we obtain

$$\zeta_1 = \Phi_{1*} \left[1 - a^3 + 3\sqrt{3}a^3 \exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r} \right) \right.$$

$$\left. \times \exp\left(-\frac{t - t_*}{t_r} \right) \right] \quad \left(t - t_* \gtrsim 3t_r + \frac{\Delta t}{2} \right), \tag{188}$$

$$\zeta_2 = \Phi_{2*} \left[1 - P_* a^3 + 3\sqrt{3} P_* a^3 \exp\left(\frac{\pi}{2\sqrt{3}} + \frac{\Delta t}{2t_r} \right) \right.$$

$$\left. \times \exp\left(-\frac{t - t_*}{t_r} \right) \right] \quad \left(t - t_* \gtrsim 3t_r + \frac{\Delta t}{2} \right). \tag{189}$$

he validity of relations (188), (189) is still limited by restriction (30).

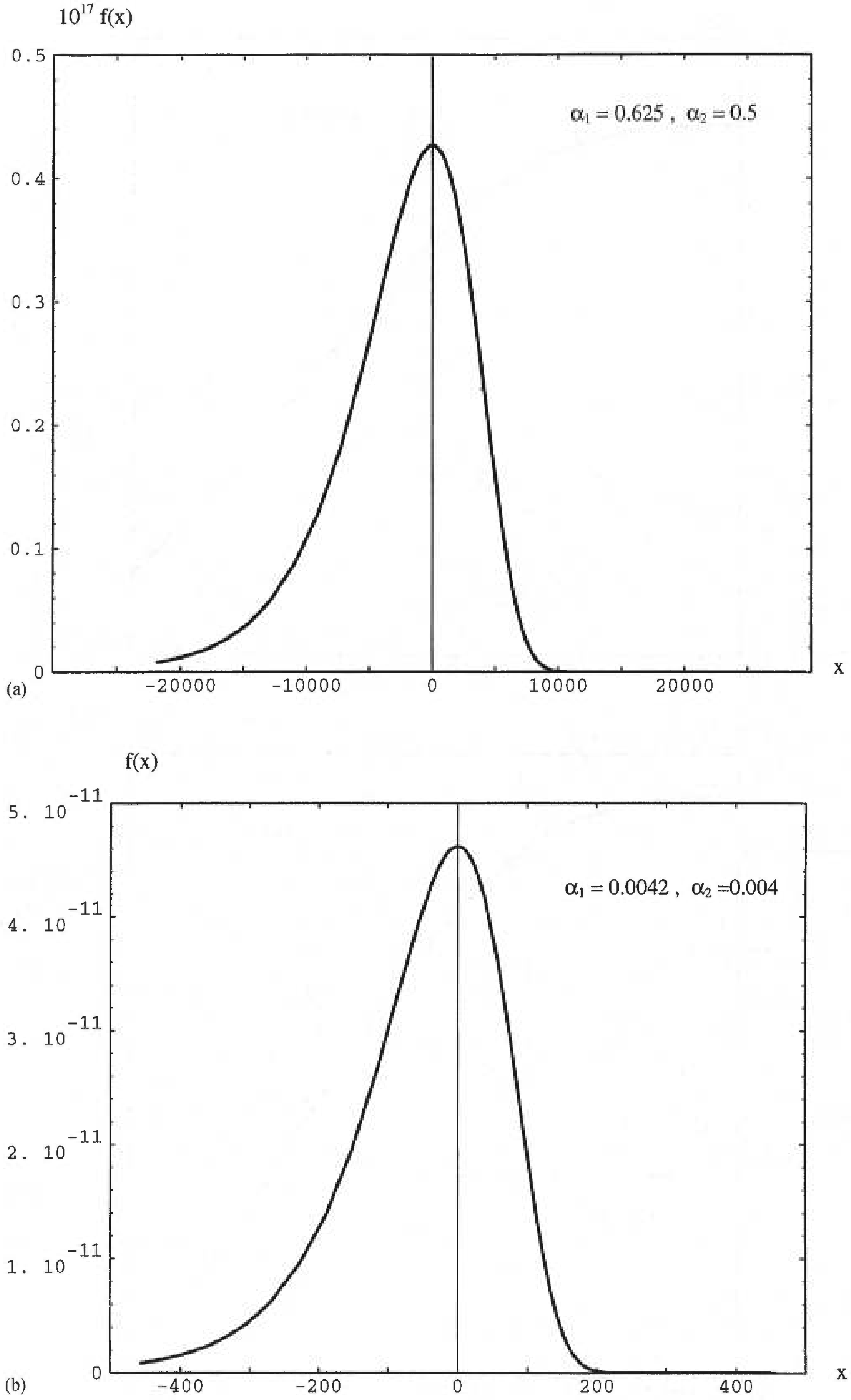

Fig. 3. Spectrum of linear sizes of droplets $f(x)$ (equation (116)) for the ethanol (1)–hexanol (2) open system at $T = 260$ K, $m_1 = 1$, $t_1 = 0.05$ s, $m_2 = 1$, $t_2 = 0.05$ s in the case of stabilization of ideal supersaturations after the formation of spectrum, the sticking coefficients being: (a) $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$; (b) $\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$.

s a whole along the ρ-axis with the velocity equal to the rate of increase of linear size of roplet. As it follows from equations (135) and (186), the time dependence of z is linear uring initial period. During a final period the time dependence of z is very slight and is iven by equations (136) and (187) if the ideal supersaturations are stabilized. If both ideal ıpersaturations Φ_1 and Φ_2 continue to increase, then time dependence of z is given by quation (144) for the materially open system and by equation (159) for the materially closed ystem (in the last case z does not depend on t if we assume $\chi_0 \simeq n_{1\mathrm{tot}*}/(n_{1\mathrm{tot}*} + n_{2\mathrm{tot}*})$).

The relative width of spectrum can be characterized by value $D = \Delta x/z$ which generally owly decreases with time or remains constant during final period.

To illustrate the developed theory we have carried out the numerical calculations for the ondensation in the materially open system "ethanol (first component)–hexanol (second omponent)" at $T = 260$ K in the case of stabilization of ideal supersaturations after the rmation of spectrum of linear sizes of droplets, the parameters in equation (10) being as llows: $m_1 = 1$, $t_1 = 0.05$ s, $m_2 = 1$, $t_2 = 0.05$ s.

Without describing the procedure of numerical calculations, let us note that, unlike the ieory of one-component condensation, a correctness of data about the sticking coefficients $_{1}$, α_{c2} influences not only a correctness of theoretical predictions but also their accuracy nce we have to solve the system of four equations for $\chi_{c*}, \chi_{0*}, \Phi_{1*}, \Phi_{2*}$ with the ıpplementary condition $t_1\Phi_{1*}^{1/m_1} = t_2\Phi_{2*}^{1/m_2}$ following from equation (11). Our calculations 'ere carried out for two couples of sticking coefficients: $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$ and $_{1} = 0.0042$, $\alpha_{c2} = 0.004$, thermodynamic parameters for the ethanol–hexanol system being ıken following Strey and Viisanen (1993). The results of calculations for main values of ieory are summarized in Table 1.

The total quantity N of droplets formed per volume unit strongly depends on sticking oefficients: $N = 8.5 \times 10^3$ cm^{-3} for $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$; and $N = 1.91 \times 10^9$ cm^{-3} for $_{1} = 0.0042$, $\alpha_{c2} = 0.004$. Figure 3a and b shows the corresponding spectra $f(x)$ of linear zes of droplets (equation (116)). The time dependences of the real supersaturations ζ_1 and $_{2}$ for the time interval $0 \leqslant t - t_* \leqslant 3.5t_r$ are shown by Fig. 4a and b (equations (128), (129) nd (132)). In both cases the difference between ζ_1 and ζ_2 is very small because $\zeta_{1*} = \zeta_{2*}$ nd P_* is nearly equal to 1 ($P_* = 0.99996$ at $\alpha_{c1} = 0.625$, $\alpha_{c2} = 0.5$ and $P_* = 0.9998$ at $_{1} = 0.0042$, $\alpha_{c2} = 0.004$), but it increases with time and attains a value of the order of 10^{-5} $_{c1} = 0.625$, $\alpha_{c2} = 0.5$) or of 10^{-4} ($\alpha_{c1} = 0.0042$, $\alpha_{c2} = 0.004$) at $t \simeq t_* + 3t_r/2$.

It should be noted that we cannot obtain any analytical expression for the duration of all ondensation process which is determined by the time t_{cond} at which constraint (30) is roken and the binary condensation changes into the binary coalescence. Besides, we ınnot obtain any explicit expression for the time dependence of ζ_1, ζ_2, z for the interval of me $3t_r/2 < t < 3t_r$. It is evident that numeric methods like the methods applied by ilemski and Wyslouzil (1995) and by Wyslouzil and Wilemski (1995, 1996) would make it ossible to obtain the time dependence of ζ_1, ζ_2 and z for this interval as well as to estimate $_{\mathrm{ond}}$ for any condensing system. This is an advantage of numerical methods. On the other ınd, it will be necessary to draw a comparison between the results of presented theory and cperimental data as soon as appropriate experiments are carried out. Particularly, it would e very interesting to compare our theoretical predictions with experimental data for the me dependences of real supersaturations ζ_1, ζ_2 and average concentration χ_0 of solution in oplets as well as for the total quantity N of nucleated droplets.

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ON THE EQUILIBRIUM DISTRIBUTION IN THE BINARY NUCLEATION THEORY

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Abstract—In considering a binary nucleation theory, it is shown that the unified approach to the homogeneous and heterogeneous nucleation theories makes it possible to obtain the equilibrium binary distribution satisfying both the mass action law and type II limiting consistency. Theoretical rates of binary nucleation are calculated by using the new equilibrium distribution, the distribution of Reiss, and that of Wilemski and Wyslouzil for the ethanol–hexanol system. Possible causes of the irregularity of discrepancies between theoretical predictions and experimental data are discussed. © 1999 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

ately, a significant progress has been attained in developing different aspects of kinetic eory of binary nucleation and condensation. As there exist some different approaches to this eory in the frameworks of capillarity approximation there appears the need to assess the ccuracy of competing approaches as well as to compare their predictions with experimental ata. The latter is not always possible because of absence of appropriate experimental results, ut for a wide range of situations high-quality experimental data are available.

Recently, Wilemski and Wyslouzil (1995) and Wyslouzil and Wilemski (1995, 1996) have btained a series of very interesting and important results concerning both kinetic and quilibrium aspects of the theory. In particular, they resolved several inconsistencies involving e binary equilibrium distribution. They proposed (Wilemski and Wyslouzil, 1995) a new rm of the binary equilibrium distribution which obeys the mass action law, reduces to ppropriate forms for the unary distributions and yields unique and physically well-behaved vaporation rate coefficients satisfying the new product rule. In this paper we will treat the inary equilibrium distribution proposed by Kuni *et al.* (1990) and Melikhov *et al.* (1990), who eneralized ideas developed by Rusanov *et al.* (1987) to the two-component theory. We will ow that the distribution of Kuni *et al.* satisfies all principal conditions formulated by Vilemski and Wyslouzil (1995). Then we will calculate the binary nucleation rate using this quilibrium distribution in the kinetic theory of Kuni *et al.* (1990) and Melikhov *et al.* (1990, 991) (yielding the same nucleation rate as Stauffer's theory (1976)) at avarious values of icking coefficients. The results of calculations will be compared with each other as well as ith the experimental data of Strey and Viisanen (1993) for the ethanol–hexanol system.

2. BINARY EQUILIBRIUM DISTRIBUTION

Let us denote by $f(\nu_1, \nu_2)$ the equilibrium distribution of binary nuclei with respect to the ariables ν_1 and ν_2 representing numbers of molecules of first and second components, spectively, in a nucleus. In the capillarity approximation the distribution $f(\nu_1, \nu_2)$ can be resented (Reiss, 1950; Wilemski and Wyslouzil, 1995) as

$$f(\nu_1, \nu_2) = N\left(\frac{n_1}{n_{1\infty}(\chi)}\right)^{\nu_1}\left(\frac{n_2}{n_{2\infty}(\chi)}\right)^{\nu_2}\exp[-F_s(\nu_1, \nu_2)], \tag{1}$$

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eterogeneous centers but on molecules themselves of condensing vapor to the two-omponent theory . The reasoning of interest is as follows.

Taking into account that each of n_1 molecules of the first component of vapor mixture nd each of n_2 molecules of its second component can serve as a heterogeneous center of ormation for a nucleus, we have, according to principles of equilibrium statistical thermo-ynamics

$$f(\nu_1, \nu_2) = n_1 e^{-F_1} + n_2 e^{-F_2}, \tag{6}$$

here F_1 is the work necessary that $\nu_1 - 1$ molecules of the first component of vapor ixture and ν_2 molecules of its second component join a single molecule of first component; $_2$ is the work necessary that $\nu_2 - 1$ molecules of second component of vapor mixture and $_1$ molecules of its first component join a single molecule of second component. Though entical nuclei with the variables ν_1 and ν_2 are formed as a result of both works F_1 and F_2, hese works in general are not equal to each other. It is because corresponding nuclei are ormed on single molecules of different species.

The works F_1 and F_2 do not coincide with the thermodynamic work $F \equiv F(\nu_1, \nu_2)$ either, hich, according to its meaning, is required for simultaneous unification of ν_1 molecules of rst component of vapor mixture and of ν_2 molecules of its second component in a nucleus ituated in a fixed point of condensing system. Of course, the differences between F_1, F_2, nd F have only a statistico-thermodynamical character, but not a mechanical one.

It has been shown by Kuni *et al.* (1987) that

$$F_1 = F - \ln[n_{1s}/n_1], \qquad F_2 = F - \ln[n_{2s}/n_2], \tag{7}$$

here n_{1s} and n_{2s} are the number densities of molecules of first and second components, espectively, in a liquid solution of composition χ.

Substituting equation (7) in equation (6), we have

$$f(\nu_1, \nu_2) = \frac{\;}{v(\chi)} e^{-F}, \tag{8}$$

here $v(\chi) = 1/[n_{1s}(\chi) + n_{2s}(\chi)]$ is the nucleus volume per molecule. Denoting by v_1 and $_2$ the partial molecular volume of first and second component, respectively, in their pure quids, and taking into account that F can be expressed through $F_s \equiv F_s(\nu_1, \nu_2)$ as

$$F = F_s - \nu_1 \ln \frac{n_1}{n_{1\infty}(\chi)} - \nu_2 \ln \frac{n_2}{n_{2\infty}(\chi)}, \tag{9}$$

ne can rewrite equation (8) as

$$f(\nu_1, \nu_2) = \frac{\nu_1 + \nu_2}{\nu_1 v_1 + \nu_2 v_2} \left(\frac{n_1}{n_{1\infty}(\chi)}\right)^{\nu_1} \left(\frac{n_2}{n_{2\infty}(\chi)}\right)^{\nu_2} \exp[-F_s]. \tag{10}$$

ince here the normalization factor $(\nu_1 + \nu_2)/(\nu_1 v_1 + \nu_2 v_2)$ does not depend on n_1 nor n_2, his equilibrium distribution automatically satisfies the mass action law. As for the limiting onsistency, equilibrium distribution (10) evidently satisfies that of type II ($1/v_1$ and $1/v_2$ eing the normalization factors of respective unary distributions) but does not satisfy that of ype I. It also gives well-behaved evaporation coefficients in the framework of Kelvin model.

Comparing equation (8) with equations (1), (3), we see that the normalization factor f Kuni *et al.* is $q_{\mathrm{KR}} = v^{-1}(\chi)\,(n_1 + n_2)^{-1}$ times as large as that of Reiss (q_{KR} is of the order f 10^4). Comparing equation (10) with equation (5), we see that the normalization factor of uni *et al.* differs by a factor $q_{\mathrm{KW}} = v^{-1}(\chi)\, n_{1\infty}^{-\chi} n_{2\infty}^{-1+\chi} \exp[-\chi\Theta_1 - (1-\chi)\Theta_2]$ from that of Vilemski and Wyslouzil. This factor (q_{KW}) is rather a complex function of many parameters f condensing system.

It should be noted that in the unary nucleation theory, Reiss *et al.* (1968) and Kikuchi 1969) obtained the corrections to the nucleation free energy like that of Rusanov *et al.* 1987), but they did it by more artificial means. These corrections give the ratio of molecule umber density of condensed phase to that of vapor phase as a pre-exponential factor in the lassical unary nucleation rate. As shown by Schmitt *et al.* (1983), this factor allows one to

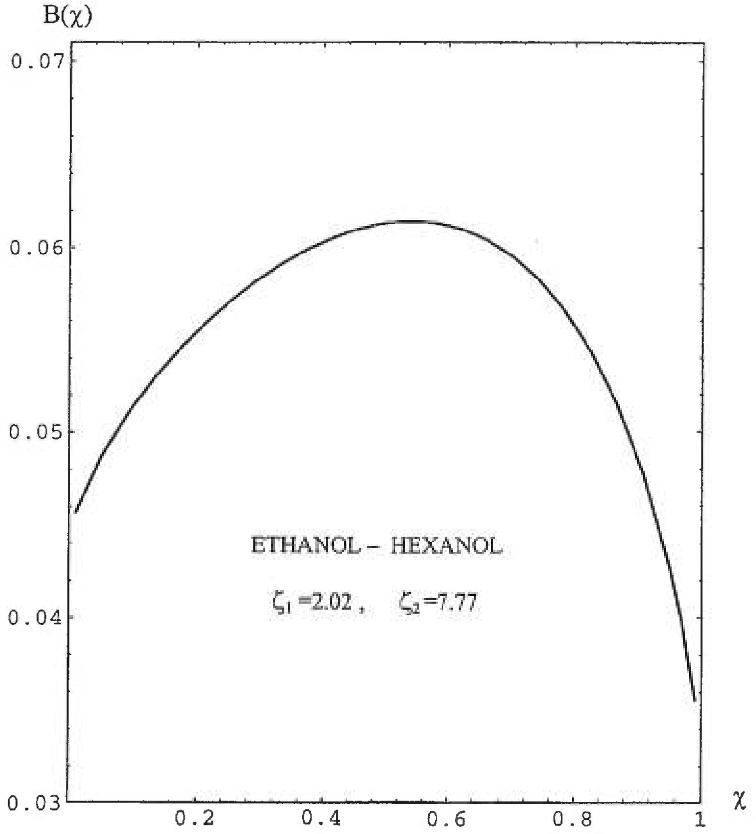

Fig. 1. Typical behavior of function $B(\chi)$ for a metastable binary system, presented by $B(\chi)$ for the ethanol (1)–hexanol (2) system at $\zeta_1 = 2.02$, $\zeta_2 = 7.77$, and $T = 260\,\mathrm{K}$. We have $\chi_c = 0.54$, $B(\chi_c) = 0.0619$, $B''(\chi_c) = -0.1239$.

$$A = \frac{a}{2\varepsilon^2}\{\varepsilon^2 - 1 - p + [(\varepsilon^2 + 1 + p)^2 - 4\varepsilon^2]^{1/2}\}, \tag{19}$$

$$C = \left[6\sqrt{\pi}\sqrt{-\tfrac{1}{2}F''_{\kappa\kappa}}\sqrt{\tfrac{1}{2}F''_{\chi\chi}}\;\frac{\gamma_c^{3/2}}{\nu_{1c} + \nu_{2c}}\,v_c^2\right]^{-1}, \tag{20}$$

vhere W_i ($i = 1, 2$) is the number of i-component molecules that the critical nucleus absorbs er unit time, the binary nucleation rate J can, finally, be presented as

$$J = AC\mathrm{e}^{-F_c}. \tag{21}$$

It is evident that, through W_1 and W_2, the condensation coefficients α_1 and α_2 strongly nfluence theoretical predictions for the nucleation rate J, which is proportional to a linear ombination of these coefficients. At the same time there exist no reliable theoretical nor xperimental data for them.

5. NUMERICAL CALCULATIONS AND CONCLUSIONS

Numerical calculations have been carried out with the help of *Mathematica* for the thanol (1)–hexanol (2) system at the same external conditions as the experiments of Strey nd Viisanen (1993). Results of calculations are presented by Fig. 2a and b in the form of the ependence of $\ln J$ on the mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$. The lines represent theoretical rates orresponding to the fixed values of activity fraction $y = \zeta_2/(\zeta_1 + \zeta_2)$, indicated on Fig. 2 ver the series. The corresponding experimental data are shown by circles. The theoretical

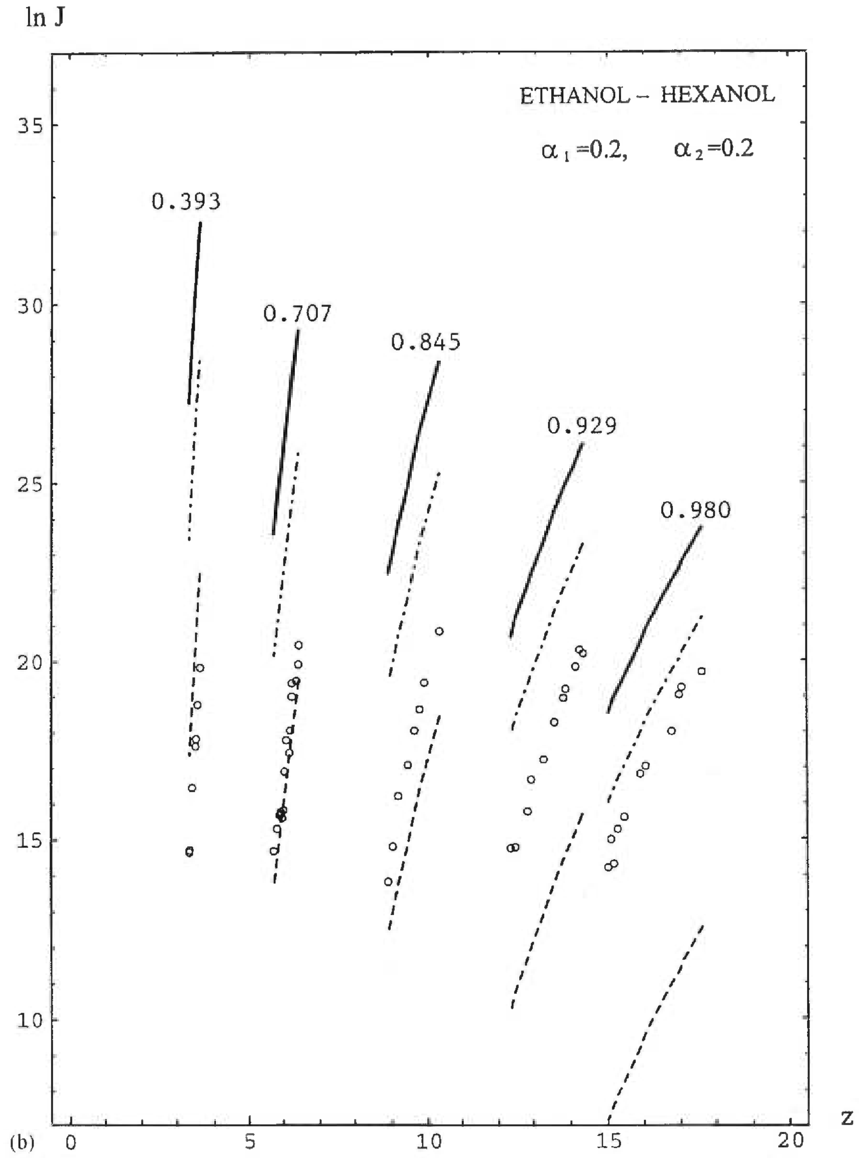

Fig. 2. *Continued.*

sed in Stauffer's rate formula (Wilemski and Wyslouzil, 1995). But theoretical rates of Vilemski and Wyslouzil better agree with experimental data than ours (obtained using quilibrium distribution (10) of Kuni *et al*., i.e. formula (21) for *J*), since for the considered ystem the normalization factor of Kuni *et al*., is approximately ten times as large as that of Vilemski and Wyslouzil, that is q_{KW} is of the order of 10. At the same time, q_{KR} is of the rder of 10^4 when y is small and tends to the value 10^5 when $y \to 1$ (e.g., $q_{\mathrm{KR}} \simeq 8 \times 10^4$ at $= 0.98$).

Since there exist no theoretical nor experimental data on the sticking coefficients α_1 and $_2$ for this system, we could, in principle, try to obtain a fine fit of theoretical rates to xperimental data by choosing appropriate values for α_1 and α_2. Magnitudes of α_1 and $_2$ must not depend, however, on metastability of a system, though they could be weak unctions of temperature. Therefore, within the framework of adequate theory we could btain a good fit of theoretical predictions to experimental data by means of unique choice f α_1 and α_2 (independent of vapor mixture metastability) for a given system. But for the onsidered system this does not work. Actually, the theoretical rates of nucleation in the

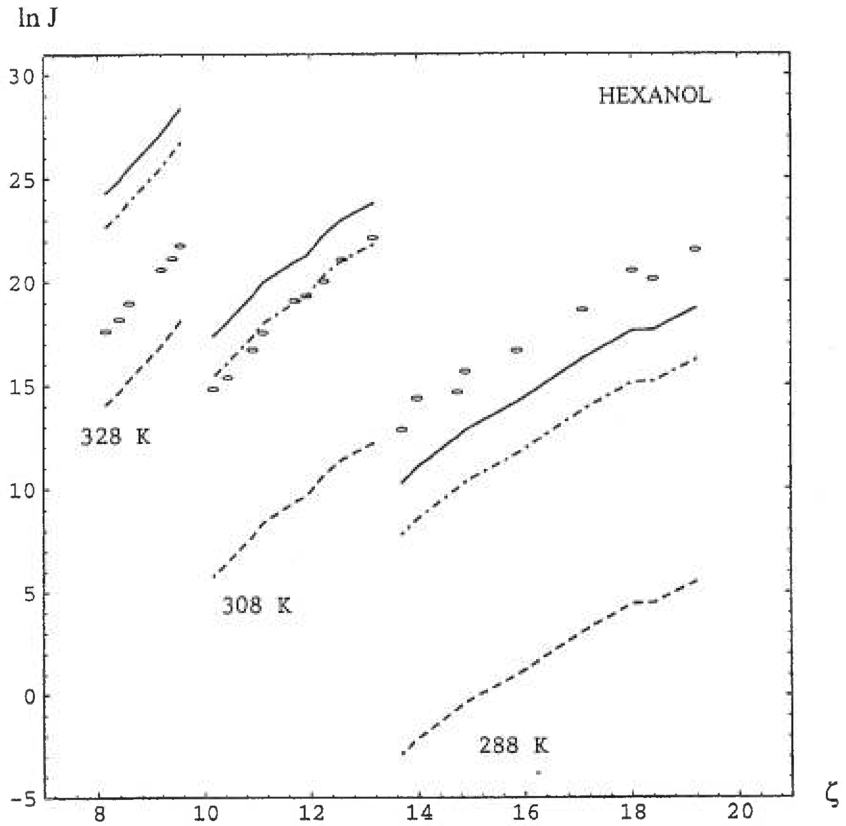

Fig. 3. Logarithm of nucleation rate J for pure hexanol vapor plotted vs a supersaturation (activity) $\zeta = \zeta_2$. The dimension of J is $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. The ellipses are the experimental data of Strey *et al.* (1986). The lines represent the nucleation rates calculated by using the classical nucleation rate expression (dashed lines, calculated by Strey *et al.* (1986)), The one-component analogue of the normalization factor of Kuni *et al.* (solid lines), and the normalization factor of Wilemski (dot–dashed lines). The initial (chamber) temperatures T_0 are indicated below the series. The corresponding nucleation temperatures are: about 258 K for $T_0 = 288$ K, about 276 K for $T_0 = 308$ K, and about 293 K for $T_0 = 328$ K.

emperatures are indicated below each series. Evidently, one can conclude that none of these hree normalization factors can be given an undeniable priority from the standpoint of the ıgreement between the theoretical and experimental rates for the considered systems. Iowever, for the homogeneous nucleation of toluene Schmitt *et al.* (1983) showed that the ıse of the one-component analogue of the normalization factor of Kuni *et al.*, brings the heoretical rates into considerably better agreement with the experimental data, the values ɔf the surface tension and the sticking coefficient being physically realistic.

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Kinetic theory of nonisothermal binary nucleation: the stage following thermal relaxation

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kinetic theory is constructed for a nonisothermal binary nucleation at the stage following the mal relaxation of nuclei. The three-dimensional kinetic equation to be solved reaches beyond framework of the Fokker–Planck approximation even if one of two components has a large e of condensation heat. It is shown that, by successively applying the method of Enskog–pman and the method of complete separation of variables to that kinetic equation, one can ce the problem of constructing the three-dimensional kinetic theory to the well-investigated lem of solving an one-dimensional kinetic equation of first-order phase transition, in the stationary case as well as in the stationary one. For the steady state, the main characteristics ucleation, including the nucleation rate, are found. Theoretical results are numerically eval-d for the nucleation in ethanol–hexanol system and compared with predictions of classical thermal) theory and experimental data. © 1999 Elsevier Science B.V. All rights reserved.

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words: Binary nucleation; Thermal effects; Latent heat; Binary aerosol

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Introduction

Binary nucleation is the first stage of any first-order phase transition in two-component tems, in particular, of the binary condensation consisting of the formation and growth drops of a liquid solution of two substances in a metastable mixture of vapors of se substances. During the nucleation the nuclei of a liquid phase are formed. They y the role of condensation centers afterwards.

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At present, there exists an adequate theoretical description of main aspects of one-component nucleation. At the same time the kinetic theory of binary nucleation has been developed almost exclusively for the case where the metastability of two-component vapor mixture is created instantaneously and both thermal effects of condensation and presence of heterogeneous nucleation centers are neglected [1–4]. However, it is well known, that heterogeneous nucleation can occur at much lower degrees of metastability than the homogeneous one. Besides, as follows from the nonisothermal one-component nucleation theory [5–9], nonisothermal effects can have a substantial influence on the kinetics of the process.

As discussed earlier [10] there exist several kinds of nonisothermal effects, but the most important of them is the effect due to the condensation heat transferred to a nucleus or extracted from it in all individual events of absorption or emission of a vapor molecule by a nucleus. As first pointed out by Feder et al. [6], in the case of one-component nucleation that effect can diminish the nucleation rate as many as hundreds of times relatively to the nucleation rate in the isothermal theory. Such a decrease is physically easily explained. Firstly, the temperature of a growing nucleus gradually increases with the growth of its size because of the release of the condensation heat. The increase in the temperature of nucleus causes an increase in its ability to emit molecules what naturally slows down its growth. Secondly, the increase in the temperature of nuclei causes an increase in the average temperature of vapor–gas medium and this is what decreases the metastability (supersaturation) of the condensing system.

Obviously, in the case of binary nucleation the thermal effect influences the nucleation rate in the same way as mentioned above. Therefore, the nonisothermal nucleation rate should be less than the isothermal (classical) one. Hence, it is not easy to explain the result of Lazaridis and Drossinos [11]: following the approach developed earlier by Langer [12] and extending the Barrett's [9] analysis of the one-component nucleation to the binary nucleation, they obtained an explicit analytical expression for the total rate of steady-state binary nonisothermal nucleation, but when applied to the water-ethanol system, their model predicts a nucleation rate that is higher than the classical (isothermal) nucleation rate.

As pointed out by many authors [13,4], the classical (isothermal) theory of binary nucleation predicts nucleation rates much higher than experimental results (including the water–alcohol systems, in the cluster models of Flageollet-Daniel et al. [14] and Laaksonen [15]). Although most of those authors agree that those discrepancies are the most probably accounted for by the effect of surface enrichment [14–18], taking account of thermal effects, nevertheless, can improve an agreement between theoretical predictions and experimental data on the nucleation rate. Evidently, such an improvement will be noticeable only if the quantity of the carrier gas in the system during experiments is not sufficient to ensure the constancy of nucleus mean temperature (an extensive treatment of carrier-gas effects is given by Ford [19] and Barrett et al. [20]).

In this paper we continue to develop the approach to the kinetic theory of non-isothermal binary nucleation proposed by Djikaev et al. [10] on the basis of the method developed by Grinin and Kuni [7] in constructing a kinetic theory of nonisothermal

$$+\left[\left(\frac{k_1+1}{k_1}\tau_1^2 W_1 + \frac{k_2+1}{k_2}\tau_2^2 W_2\right)\left(\frac{\partial}{\partial\xi} - 2\xi\right)\frac{\partial}{\partial\xi}\right.$$

$$\left. - \sum_{m=2}^{\infty}\frac{(-1)^m}{m!m!}(\tau_1^{2m}W_1 + \tau_2^{2m}W_2)\left(\frac{\partial}{\partial\xi} - 2\xi\right)^m \frac{\partial^m}{\partial\xi^m}\right] P\,, \tag{4}$$

where, for simplicity of the notation, the independent arguments v_1, v_2, ξ, and t are omitted and

$$\hat{L}_i \equiv -W_i F_i' - W_i \frac{\partial}{\partial v_i} \quad (i=1,2)\,, \tag{5}$$

$$\tau_i = \frac{\beta_i}{[2(c_1 v_1 + c_2 v_2)]^{1/2}} \quad (i=1,2)\,, \tag{6}$$

$$\frac{1}{k_i} = \frac{\tilde{c}_i}{\alpha_{ci}\beta_i^2}[\alpha_{ci} + \hat{\alpha}_i(1-\alpha_{ci}) + \alpha_g p_i], \quad p_i = \left(\frac{m_i}{m_g}\right)^{1/2}\frac{n_g c_g}{2n_i\tilde{c}_i} \quad (i-1,2)\,. \tag{7}$$

Here W_i and β_i $(i=1,2)$ are the number of i-component molecules being absorbed by a nucleus per unit time and the condensation heat of component i per molecule, respectively; α_{ci} and α_{ti} $(i=1,2)$ are the condensation (sticking) coefficient and the coefficient of thermal adaptation in a reflection event of i-component molecules, respectively; α_g is the coefficient of thermal adaptation in a reflection event of passive gas molecules; $\tilde{c}_i, m_i$, and n_i $(i=1,2)$ are the effective (in the sense of energy transfer to the nucleus) specific heat, mass and number density of molecules of component i of the vapor mixture, respectively; c_g, m_g, and n_g are the analogous quantities for the passive gas; $F_i' \equiv \partial F/\partial v_i$, F being the free energy of formation of a nucleus in the thermal equilibrium with the medium, i.e. with the characteristic $E=0$.

Retaining all terms of the series in the RHS of Eq. (4) means extending the theory to values $\tau_i \sim 1$ $(i=1,2)$ and thus going beyond the framework of the Fokker–Planck approximation. If both τ_1 and τ_2 are much smaller than 1, the Fokker–Planck approximation becomes acceptable and Eq. (4) can be reduced to the kinetic equation of Lazaridis and Drossinos [11].

In the case of one-component nucleation where either $\hat{L}_2=0$, $\tau_2=0$ or $\hat{L}_1=0$, $\tau_1=0$ (i.e. only the component is present in the system), Eq. (4) transforms itself into the kinetic equation of nonisothermal one-component nucleation of Kuni and Grinin [7].

In the variables v_1 and v_2, we are interested only in the near-critical region $|v_i - v_{ic}| \lesssim \Delta v_{ic}$ $(i=1,2)$, which is the most important one for the nucleation kinetics; the parameters v_{ic} and Δv_{ic} are defined as

$$F_i'\,|_{v_1=v_{1c},\, v_2=v_{2c}} = 0, \quad \Delta v_{ic} = |2/F_{ii}''|\,|_{v_1=v_{1c},\, v_2=v_{2c}} \quad (i=1,2)\,. \tag{8}$$

The values v_{1c}, v_{2c} would determine the coordinates of the saddle point of the surface of free energy of nucleation in the isothermal theory. Within the framework of the capillarity approximation

$$\Delta v_{ic}/v_{ic} \ll 1, \quad 1/\Delta v_{ic} \ll 1 \quad (i=1,2)\,. \tag{9}$$

The Hermite polynomials H_j $(j=0,1,2,\ldots)$ are eigenfunctions of the principal operator in the governing equation, i.e. of the operator in the leading (fifth) term on the RHS of Eq. (4). They satisfy the recursion relations

$$\frac{\partial}{\partial\xi}H_j = 2jH_{j-1}, \qquad \left(\frac{\partial}{\partial\xi} - 2\xi\right)H_j = -H_{j+1} \tag{17}$$

and form a complete system of eigenfunctions satisfying also the orthogonality and normalization conditions

$$(H_j, H_k) = \delta_{jk}2^j j! \quad (j,k=0,1,2,\ldots)\,, \tag{18}$$

where δ_{jk} is Kronecker's delta. Obviously, $-j\lambda'_j$ $(j=0,1,2,\ldots)$ represents the eigenvalue corresponding to H_j. All the eigenvalues are negative except that for $j=0$ which is equal to 0.

The function $f \equiv f(v_1,v_2,t)$ in Eq. (12) represents the two-dimensional distribution of nuclei with respect to v_1, v_2. Its time evolution is given by the equation

$$\frac{\partial f}{\partial t} = -\frac{\partial J_1}{\partial v_1} - \frac{\partial J_2}{\partial v_2}\,, \tag{19}$$

where

$$J_i = \left(H_0, \left(\hat{L}_i - W_i\sum_{m=1}^{\infty}\frac{\tau_i^m}{m!}\frac{\partial^m}{\partial\xi^m}\right)P\right) \quad (i=1,2) \tag{20}$$

is the flux (averaged on ξ) of nuclei along the v_i-axis. As can be seen during the stage of thermal relaxation $t \lesssim t_\xi$ the distribution of nuclei with respect to v_1 and v_2 does not change while the distribution with respect to the variable ξ approaches a quasiequilibrium Gaussian distribution by the end of that stage, and

$$P \simeq f \quad (t \gtrsim t_\xi) \tag{21}$$

as follows from Eq. (12) (t_ξ represents the principal relaxation time).

4. Evolution of nuclei after the stage of thermal relaxation

The quasiequilibrium distribution is an eigenfunction of the main operator of the governing equation (4), the corresponding eigenvalue being zero. Therefore, as follows from Eq. (21), the operators of the first four terms on the RHS of Eq. (4) also become important at the end of thermal relaxation stage. However, the operator of the last term is still the main one when acting on the deviation of P from f: according to Eq. (15), this deviation is orthogonal to the eigenfunction H_0 with the zero eigenvalue. This makes it possible to construct a solution of governing Eq. (4) for $t \gtrsim t_\xi$ with the help of the Enskog–Chapman method.

(the prime in the sum over m in Eq. (25) eliminates the term with $j=m$ which means $\Gamma_{mm}=0$ for any m).

Rewriting Eqs. (25) in the form

$$z_j^{(l)}(f)=a_j^{(l)}\hat{L}_1 f+b_j^{(l)}\hat{L}_2 f\,, \tag{28}$$

$$a_j^{(1)}=\frac{(2\tau_1^2)^{j-1}}{j!j\lambda_j},\qquad a_j^{(l)}=\sum_{m=1}^{\infty}{}'\Gamma_{jm}a_m^{(l-1)}\quad(l\geqslant 2)\,, \tag{29}$$

$$b_j^{(1)}=\frac{(2\tau_1^2)^{j-1}}{j!j\lambda_j}\tau_{21}^{j},\quad b_j^{(l)}=\sum_{m=1}^{\infty}{}'\Gamma_{jm}b_m^{(l-1)}\quad(l\geqslant 2)\,, \tag{30}$$

and substituting $z_j^{(l)}$ in Eq. (23), we have

$$z_j(f)=a_j\hat{L}_1 f+b_j\hat{L}_2 f\,, \tag{31}$$

$$a_j=\sum_{l=1}^{\infty}a_j^{(l)},\qquad b_j=\sum_{l=1}^{\infty}b_j^{(l)}\,. \tag{32}$$

Eqs. (31), (24) and (19) result in the equation governing the time evolution of two-dimensional distribution f:

$$\frac{\partial f}{\partial t}=-\Theta_1\frac{\partial}{\partial v_1}\hat{L}_1 f-\Theta_2\frac{\partial}{\partial v_2}\hat{L}_2 f+\delta_1\frac{\partial}{\partial v_1}\hat{L}_2 f+\delta_2\frac{\partial}{\partial v_2}\hat{L}_1 f\,, \tag{33}$$

with

$$\Theta_1=1-W_1\sum_{j=1}^{\infty}a_j,\quad \Theta_2=1-W_2\sum_{j=1}^{\infty}b_j\tau_{21}^{j},\quad \delta_1=\sum_{j=1}^{\infty}b_j,\quad \delta_2=\sum_{j=1}^{\infty}a_j\tau_{21}^{j}\,. \tag{34}$$

Thus, according to Eqs. (3), (22), (31), and(33), the problem of finding the three-dimensional distribution $g(v_1,v_2,E,t)$ in the nonisothermal theory is reduced to the well-investigated problem of finding the two-dimensional distribution $f(v_1,v_2,t)$. However, Eq. (33) for f significantly differs from the Reiss' kinetic equation of isothermal binary nucleation: both the difference of Θ_1 and Θ_2 from 1 and the presence of the third and fourth terms on the RHS of Eq. (33) are exclusively due to thermal effects. Nevertheless, Eq. (33) is still an equation of the Fokker–Planck type. Therefore, to solve this equation, one can apply the method of complete separation of variables used earlier in a kinetic theory of isothermal binary nucleation by Kuni et al. [21] and by Melikhov et al. [22]. The following section is based on those two works. (The most general form of that method for a two-dimensional kinetic theory of first-order phase transition is given by Kuni and Melikhov [23], and its covariant formulation for a multidimensional theory is provided by Kuni et al. [24].)

In the near-critical region the free energy F can be approximated by the bilinear form which in the variables x and y becomes a quadratic one:

$$F = F_c - x^2 + y^2 \,. \tag{42}$$

Let us denote by $n(x, y, t)$ the distribution of nuclei with respect to the variables x and y at the moment t and turn to the variables x and y in Eq. (33). Replacing v by v_c in the vicinity of the saddle point and taking Eq. (42) into account, we obtain

$$n(x, y, t) = v_c C f(\nu_1, \nu_2, t) \,, \tag{43}$$

$$C = \left[6\pi^{1/2} \sqrt{-\frac{1}{2}\left(\frac{\partial^2 F}{\partial \kappa^2}\right)_c} \sqrt{\frac{1}{2}\left(\frac{\partial^2 F}{\partial \chi^2}\right)_c} \frac{\gamma^{3/2}}{\nu_{1c} + \nu_{2c}} v_c^2 \right]^{-1} \,, \tag{44}$$

$$\begin{aligned} \partial_t n(x, y, t) = a\{&\partial_x(\partial_x - 2x) - \varphi^{-1}\partial_x(\partial_y + 2y) \\ &- \varepsilon^{-1}\partial_y(\partial_x - 2x) + (\varphi\varepsilon)^{-1}(1 + p)\partial_y(\partial_y + 2y)\} n(x, y, t) \,, \end{aligned} \tag{45}$$

where

$$a = W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1 W_2(\delta_1 + \delta_2)c_{11}c_{12} \,, \tag{46}$$

$$\begin{aligned} \varphi &= -\frac{W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1 W_2(\delta_1 + \delta_2)c_{11}c_{12}}{W_1\Theta_1 c_{11}c_{21} + W_2\Theta_2 c_{12}c_{22} - W_1 W_2(\delta_1 c_{11}c_{22} + \delta_2 c_{12}c_{21})} \,, \\ \varepsilon &= -\frac{W_1\Theta_1 c_{11}^2 + W_2\Theta_2 c_{12}^2 - W_1 W_2(\delta_1 + \delta_2)c_{11}c_{12}}{W_1\Theta_1 c_{11}c_{21} + W_2\Theta_2 c_{12}c_{22} - W_1 W_2(\delta_1 c_{12}c_{21} + \delta_2 c_{11}c_{22})} \,, \end{aligned} \tag{47}$$

$$p = W_1 W_2(\Theta_1\Theta_2 - W_1 W_2\delta_1\delta_2)(c_{11}c_{22} - c_{12}c_{21})^2\varphi\varepsilon/a^2 \,, \tag{48}$$

and abbreviated notations $\partial_t \equiv \partial/\partial t, \ldots$ have been introduced for differentiation operators.

As the two-dimensional equilibrium distribution of nuclei $f_e(\nu_1, \nu_2)$ with respect to the variables ν_1 and ν_2 is [21,25]

$$f_e(\nu_1, \nu_2) = v^{-1} \mathrm{e}^{-F(\nu_1, \nu_2)} \,, \tag{49}$$

the two-dimensional equilibrium distribution $n_e(x, y)$ with respect to x and y takes the form

$$n_e(x, y) = C\mathrm{e}^{-F_c}\mathrm{e}^{x^2}\mathrm{e}^{-y^2} \tag{50}$$

(we again replaced v by v_c). Thus, the variables x and y have been separated in the equilibrium distribution. This allows one to conclude that the variable x is unstable and the variable y is stable. Therefore, the ordinary boundary conditions are applied to Eq. (45):

$$n(x, y, t)/n_e(x, y) = \begin{cases} 1 & (x \to -\infty) \,, \\ 0 & (x \to \infty) \end{cases} \tag{51}$$

(for arbitrary y).

As shown by Kuni and Melikhov [7], the solution of Eq. (57) with boundary conditions (59) is given by

$$n(u,\eta,t) = \pi^{-1/2}\rho(u,t)\mathrm{e}^{-\xi^2}\,, \tag{60}$$

where the time evolution of the function $\rho(u,t)$ is governed by the one-dimensional equation

$$\partial_t\rho(u,t) = A\partial_u(\partial_u - 2u)\rho(u,t) \tag{61}$$

with the boundary conditions

$$\rho(u,t)/\rho_e(u) = \begin{cases} 1 & (u \to -\infty)\,, \\ 0 & (u \to \infty) \end{cases} \tag{62}$$

the function ρ_e being defined as

$$\rho_e(u) = C\pi^{1/2}\mathrm{e}^{-F_c}\mathrm{e}^{u^2}\,. \tag{63}$$

According to Eq. (60),

$$\rho(u,t) = \int_{-\infty}^{\infty} \mathrm{d}\eta\, n(u,\eta,t)\,. \tag{64}$$

This shows that $\rho(u,t)$ represents the one-dimensional distribution of nuclei with respect to the unstable variable u. Eq. (57) can be presented in the form of two-dimensional continuity equation

$$\partial_t n(u,\eta,t) = -\partial_u j_u - \partial_\eta j_\eta\,, \tag{65}$$

where j_u and j_η are the flux densities of nuclei along the u- and η-axis. Evidently, distribution (60) makes the flow j_η vanish, what means that in the variables u, η the two-dimensional flow of nuclei is parallel to the u-axis.

Let us present Eq. (61) in the form

$$\partial_t\rho(u,t) = -\partial_u J_u, \quad J_u = -A(\partial_u - 2u)\rho(u,t)\,, \tag{66}$$

where J_u (function of u and t) is the one-dimensional flow of nuclei along the u-axis integrated over the stable variable.

In the near-critical region $|u| \lesssim 1$, we have the estimates $\partial/\partial u \sim u \sim 1$ (without paying attention to signs) which, with the help of Eqs. (60) and (61), allow us to conclude that the characteristic time t_u of the change of the distribution of nuclei with respect to unstable variable in that region can be estimated as

$$t_u \sim A^{-1}\,. \tag{67}$$

Obviously, t_u will also represent the time in which the steady state is established in the entire near-critical region $|u| \lesssim 1$.

In the steady state J_u is independent of u and t. Therefore, according to Eqs. (66) and (62), for the one-dimensional steady-state nucleation flux $(J_u)_s$ and distribution $\rho_s(u)$ we have

$$(J_u)_s = \pi^{-1/2}A\rho_e(u)|_{u=0}, \qquad \rho_s(u) = \pi^{-1/2}\rho_e(u)\int_u^{\infty} \mathrm{d}u'\,\mathrm{e}^{-u'^2} \tag{68}$$

(subscript “s” marks steady-state values).

$$p_s(x) = \pi^{-1/2} p_e(x) \int_x^{\infty} \mathrm{d}x' \, \mathrm{e}^{-x'^2} . \tag{77}$$

Comparing Eqs. (63) and (73), we conclude that the dependence of the one-dimensional equilibrium distributions $p_e(x)$ and $\rho_e(u)$ on the unstable variable is identical. In addition, the comparison of Eqs. (68) and (77) shows that the one-dimensional steady-state distributions $p_s(x)$ and $\rho_s(u)$ also have an identical dependence on the unstable variable. Besides, as follows from Eqs. (66) and (74),

$$(J_x)_s = (J_u)_s . \tag{78}$$

Therefore, the one-dimensional flux density $(J_u)_s$ given by Eq. (68), determines the steady-state rate of binary nonisothermal nucleation J_s which can be presented as

$$J_s = AC\mathrm{e}^{-F_c} . \tag{79}$$

Using results of the one-dimensional theory and taking account of Eq. (66), one can obtain the estimate

$$\partial_u - 2u \simeq -2u \quad (u \gtrsim 1) , \tag{80}$$

and the relation

$$J_u \simeq \dot{u}\rho(u,t), \qquad \dot{u} = 2Au \ (u \gtrsim 1) . \tag{81}$$

The value $\dot{u}$ represents the rate of regular growth in time of the unstable variable u. Obviously, for the unstable variable x one could write the identical estimate and relation, as follows from (74). Eq. (81) allows one to conclude that the fluctuation-induced nucleation is completed in the region $|u| \lesssim 1$ of the variables u, η (in the variables x, y it is completed in the region $|x| \lesssim 1$). To the left of the region $|u| \lesssim 1$ (or $|x| \lesssim 1$) the nuclei are still in equilibrium, while to the right of it they already grow irreversibly.

5. Mean values of composition and temperature of the nucleus

Eq. (66) with boundary conditions (62) (or Eq. (74) with boundary conditions (72)) is well known and investigated in the one-dimensional theory of first-order phase transitions. Accordingly, we can use the results of one-dimensional theory for the one-dimensional distribution $\rho(u,t)$ (or $p(x,t)$) and the nucleation rate J_u (or J_x). Thus, Eqs. (69), (43), (22), and (3) determine the three-dimensional distribution of nuclei with respect to the variables v_1, v_2 and E in the nonisothermal binary nucleation. The rate of nucleation is given by Eq. (66) (or (74)). In the particular case of steady-state nucleation the one-dimensional distribution $\rho_s(u)$ is given by the second of Eq. (68) and the expression for $n(x,y,t)$ is reduced to Eq. (76); the nucleation rate is then determined by Eq. (79).

For example, using Eq. (26), neglecting the terms of order $\tau_1^6, \tau_1^8, \ldots$ and solving Eqs. (87) and (88), one can find

$$a_1 = \frac{1}{\lambda_1} + \tau_1^2 K_1 + \tau_1^4 Q_1, \quad a_2 = \tau_1^2 K_2 + \tau_1^4 Q_2, \quad a_3 = \tau_1^4 Q_3 , \tag{89}$$

$$K_1 = -\frac{1}{2\lambda_1\lambda_2} U_3 + \frac{1}{2\lambda_1^2\lambda_2} U_3^2, \qquad K_2 = \frac{1}{2\lambda_2} - \frac{1}{2\lambda_1\lambda_2} U_3 ,$$

$$\begin{aligned} Q_1 = &-\frac{2}{9\lambda_1\lambda_3} U_4 + \frac{1}{3\lambda_1\lambda_2\lambda_3} U_3(U_3 + U_4) + \frac{2}{9\lambda_1^2\lambda_3} U_4^2 - \frac{1}{4\lambda_1^2\lambda_2^2} U_3^3 \\ &- \frac{2}{3\lambda_1^2\lambda_2\lambda_3} U_3^2 U_4 - \frac{1}{2\lambda_1\lambda_2^2\lambda_3} U_3^3 - \frac{1}{2\lambda_1^2\lambda_2^2\lambda_3} U_3^4 - \frac{1}{\lambda_1\lambda_2^2\lambda_3^2} U_3^4 , \end{aligned}$$

$$\begin{aligned} Q_2 = &-\frac{1}{3\lambda_2\lambda_3} U_3 + \frac{1}{4\lambda_1\lambda_2^2} U_3^2 + \frac{1}{3\lambda_1\lambda_2\lambda_3} U_3 U_4 + \frac{1}{2\lambda_2^2\lambda_3} U_3^2 \\ &- \frac{1}{4\lambda_1^2\lambda_2^2} U_3^2 - \frac{1}{\lambda_1\lambda_2^2\lambda_3} U_3^2 , \end{aligned}$$

$$Q_3 = \frac{2}{9\lambda_3} - \frac{2}{9\lambda_1\lambda_3} U_4 - \frac{1}{3\lambda_2\lambda_3} U_3 + \frac{1}{3\lambda_1\lambda_2\lambda_3} U_3^2 ,$$

$$b_1 = \frac{\tau_{21}}{\lambda_1} + \tau_1^2 R_1 + \tau_1^4 S_1, \quad b_2 = \tau_1^2 R_2 + \tau_1^4 S_2, \quad b_3 = \tau_1^4 S_3 , \tag{90}$$

$$R_1 = -\frac{\tau_{21}^2}{2\lambda_1\lambda_2} U_3 + \frac{\tau_{21}}{2\lambda_1^2\lambda_2} U_3^2, \qquad R_2 = \frac{\tau_{21}^2}{2\lambda_2} - \frac{\tau_{21}}{2\lambda_1\lambda_2} U_3 ,$$

$$\begin{aligned} S_1 = &-\frac{2\tau_{21}^3}{9\lambda_1\lambda_3} U_4 + \frac{\tau_{21}^2}{3\lambda_1\lambda_2\lambda_3} U_3(\tau_{21} U_3 + U_4) + \frac{2\tau_{21}}{9\lambda_1^2\lambda_3} U_4^2 - \frac{\tau_{21}^2}{4\lambda_1^2\lambda_2^2} U_3^3 \\ &- \frac{2\tau_{21}}{3\lambda_1^2\lambda_2\lambda_3} U_3^2 U_4 - \frac{\tau_{21}^2}{2\lambda_1\lambda_2^2\lambda_3} U_3^3 - \frac{\tau_{21}}{2\lambda_1^2\lambda_2^2\lambda_3} U_3^4 - \frac{\tau_{21}}{\lambda_1\lambda_2^2\lambda_3^2} U_3^4 , \end{aligned}$$

$$\begin{aligned} S_2 = &-\frac{\tau_{21}^3}{3\lambda_2\lambda_3} U_3 + \frac{\tau_{21}^2}{4\lambda_1\lambda_2^2} U_3^2 + \frac{\tau_{21}}{3\lambda_1\lambda_2\lambda_3} U_3 U_4 + \frac{\tau_{21}^2}{2\lambda_2^2\lambda_3} U_3^2 \\ &- \frac{\tau_{21}}{4\lambda_1^2\lambda_2^2} U_3^2 - \frac{\tau_{21}}{\lambda_1\lambda_2^2\lambda_3} U_3^2 , \end{aligned}$$

$$S_3 = -\frac{2\tau_{21}^3}{9\lambda_3} - \frac{2\tau_{21}}{9\lambda_1\lambda_3} U_4 - \frac{\tau_{21}^2}{3\lambda_2\lambda_3} U_3 + \frac{\tau_{21}}{3\lambda_1\lambda_2\lambda_3} U_3^2$$

($U_m \equiv W_1 + \tau_{21}^m W_2$ with arbitrary m). As follows from Eqs. (29), (30), and (26), the values $a_4, a_5, \ldots$ and $b_4, b_5, \ldots$ are of order $\tau_1^6, \tau_1^8, \ldots$ and hence they are not taken into account in solving Eqs. (87) and (88).

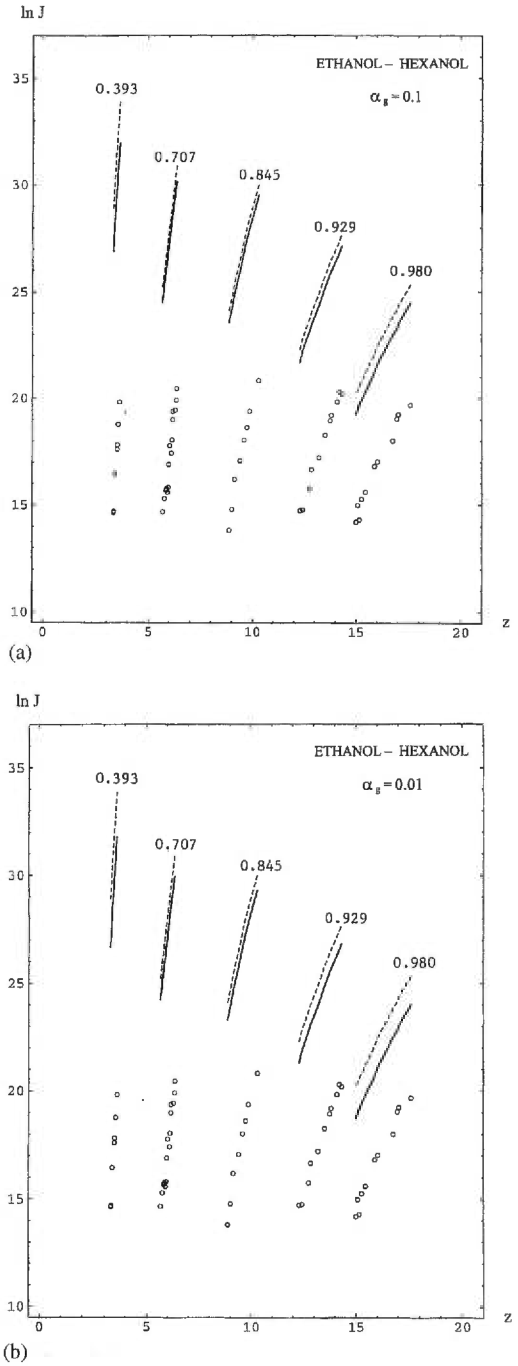

Fig. 1. Natural logarithm of nucleation rate J in the ethanol (1) – hexanol (2) system plotted vs. a mean activity $z = (\zeta_1^2 + \zeta_2^2)^{1/2}$, at $T_0 + 260$ K. The dimension of J is $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. The circles are the experimental data of Strey and Viisanen [26]. The solid lines are the nonisothermal nucleation rates (Eq. (79)) calculated at the indicated activity fraction $q = \zeta_2/(\zeta_1 + \zeta_2)$; the dashed lines represent the isothermal nucleation rates. The thermal accommodation coefficient of carrier gas (argon) is: (a) $\alpha_g = 0.1$; (b) $\alpha_g = 0.01$.

nucleation). In particular, the steady-state nucleation rate is given by Eq. (79), and the steady-state three-dimensional distribution with respect to v_1, v_2, and E is given by Eqs. (76), (43), (22), and (3). The average values of the temperature of the nucleus and solution concentration in it are given by Eqs. (86) and (83). Finally, numerical calculations were carried out for the nucleation rate in the system "ethanol–hexanol" to illustrate the theory developed. The results were compared with the predictions of the isothermal nucleation theory [21,22] and experimental data [26]. As expected, rates predicted by the nonisothermal theory are substantially lower than rates in the isothermal theory. Consequently, the nonisothermal theory improves the fit of theoretical results and experimental data. The model of Lazaridis and Drossinos [11] predicts nucleation rates that are slightly higher than classical nucleation rates and this is not easy to explain from the physical standpoint.

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