On the Fokker-Planck approximation in the kinetic equation of multicomponent classical nucleation theory

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Abstract

We examine the validity of the Fokker-Planck equation with linear force coefficients as an approximation to the kinetic equation of nucleation in homogeneous isothermal multicomponent condensation. Starting with a discrete equation of balance governing the temporal evolution of the distribution function of an ensemble of multicomponent droplets and reducing it (by means of Taylor series expansions) to the differential form in the vicinity of the saddle point of the free energy surface, we have identified the parameters whereof the smallness is necessary for the resulting kinetic equation to have the form of the Fokker-Planck equation with linear (in droplet variables) force coefficients. The “non-smallness” of these parameters results either in the appearance of the third or higher order partial derivatives of the distribution function in the kinetic equation or in its force coefficients becoming non-linear functions of droplet variables, or both; this would render the conventional kinetic equation of multicomponent nucleation and its predictions inaccurate. As a numerical illustration, we carried out calculations for isothermal condensation in five binary systems of various non-ideality at $T = 293.15$ K: 1-butanol–1-hexanol, water–methanol, water–ethanol, water–1-propanol, water–1-butanol. Our results suggest that under typical experimental conditions the kinetic equation of binary nucleation of classical nucleation theory may require a two-fold modification and, hence, the conventional expression for the steady-state binary nucleation rate may not be adequate for the consistent comparison of theoretical predictions with experimental data.

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1 Introduction

Nucleation is the initial stage of any homogeneous first order phase transition\(^1\)\(^-\)\(^3\) that does not occur as spinodal decomposition. At the nucleation stage of condensation, hereinafter the sole subject of consideration for the sake of concreteness, the initial growth of nascent particles (droplets) of the liquid phase is due exclusively to fluctuations; the association of two molecules and the subsequent association of the third, fourth, and additional molecules is thermodynamically unfavorable (i.e., is accompanied by an increase in the free energy of the system), but does occur owing to fluctuations. However, after a droplet attains some critical size (and composition, in the case of multicomponent condensation), the incorporation of each additional molecule becomes thermodynamically favorable (i.e., is accompanied by a decrease in the free energy of the system), and the droplet grows irreversibly. The free energy of formation of the critical droplet (often referred to as a “nucleus”) determines the height of the activation, or nucleation, barrier.

The distribution function of an ensemble of droplets with respect to the independent variables of state of a droplet represents the main object of interest in any theory of homogeneous condensation. In particular, such a distribution of near-critical droplets determines the nucleation rate. The temporal evolution of the distribution of near-critical droplets is governed by the equation whereof the finite-differences form is often referred to as a “balance equation” whereas its differential form is called a “kinetic equation” of nucleation.

In the case of isothermal nucleation (in which the temperature of any single droplet is constant and equal to the temperature of the surrounding vapor-gas medium), the kinetic equation of nucleation is assumed to be well approximated by the Fokker-Planck equation. In the case of non-isothermal nucleation, where the possibility of the deviation of the droplet temperature from that of the surrounding medium is taken into account, the Fokker-Planck approximation has been shown to be
inadequate to describe the evolution of the distribution function with respect to the droplet temperature. Hereinafter, we do not consider the nonisothermal case, but focus on the applicability of the Fokker-Planck approximation to the kinetic equation of isothermal multicomponent nucleation.

2 The Fokker-Planck approximation in the kinetic equation of homogeneous isothermal nucleation

In the kinetic theory of homogeneous isothermal condensation, the equation governing the temporal evolution of the distribution of near-critical droplets with respect to the number of molecules in a droplet (or with respect to numbers of molecules of different components in a droplet) is conventionally considered to have the Fokker-Planck form. The accuracy of such an assumption for unary nucleation has been thoroughly examined by Kuni and Grinin.

On the other hand, its accuracy in the case of multicomponent nucleation has been studied very little. We are aware of only two relevant papers; one by Kuni et al., who qualitatively outlined the general principles of the Fokker-Planck approximation in a kinetic equation of nucleation, and the other by Kurasov, who qualitatively discussed this issue in the case of nonisothermal binary nucleation. In this section, we will first briefly outline the results of Kuni and co-workers concerning this issue in unary nucleation (subsection 2.1) and then attempt to shed some light on the validity of the Fokker-Planck approximation in the kinetic equation of homogeneous isothermal multicomponent nucleation (subsection 2.2).

2.1 Unary nucleation

Consider an ensemble of one-component droplets within the metastable vapor (of the same component) at temperature $T$, and denote the number of molecules in a droplet by $\nu$; this will be the only variable of state if nucleation is isothermal (i.e., the droplet temperature is constant and equal
to $T$). The capillarity approximation,\textsuperscript{7} whereon the thermodynamics of classical nucleation theory (CNT) is based, requires the liquid droplets to be sufficiently large, with $\nu \gg 1$, and of spherical shape, with sharp boundaries, and uniform density inside. The metastability of the one-component vapor is usually characterized by the saturation ratio $\zeta = n / n_{1\infty}$, where $n$ is the number density of vapor molecules and $n_{1\infty}$ is the number density of molecules of the vapor in equilibrium with its bulk liquid at the system temperature. Clearly, the vapor-to-liquid transition can occur only if $\zeta > 1$; at sufficiently large values of $\zeta$, it will occur as spinodal decomposition, otherwise it will proceed via nucleation.

Denote the distribution function of droplets with respect $\nu$ at time $t$ by $g(\nu, t)$. Assuming that the droplets exchange matter with the vapor via the absorption and emission of single molecules, the temporal evolution of $g(\nu, t)$ is governed by the balance equation

$$\frac{\partial g(\nu, t)}{\partial t} = - \left[ (W^+(\nu)g(\nu, t) - W^-(\nu + 1)g(\nu + 1, t)) - (W^+(\nu - 1)g(\nu - 1, t) - W^-(\nu)g(\nu, t)) \right],$$

(1)

where $W^+(\nu)$ and $W^-(\nu)$ are the numbers of molecules that a droplet $\nu$ absorbs and emits, respectively, per unit time. A differential equation governing the temporal evolution of $g(\nu, t)$ can be obtained from the discrete balance equation (1) through the Taylor series expansions of $W^-(\nu \pm 1)$, $W^+(\nu \pm 1)$, and $g(\nu \pm 1, t)$ (on its RHS) with respect to the deviation of their arguments from $\nu$.

According to classical thermodynamics, the equilibrium distribution function has the form

$$g_e(\nu) = n \exp[-F(\nu)],$$

(2)

where $F(\nu)$ is the free energy of formation of a droplet of size $\nu$ (in units $k_B T$, $k_B$ being the Boltzmann constant). In the framework of CNT, $F(\nu)$ can be written\textsuperscript{4,5} as

$$F(\nu) = -b\nu + a\nu^{2/3},$$

(3)
where \( b = \ln \zeta \) and \( a = 4\pi (3v_l/4\pi)^{2/3}(\sigma/k_B T) \), with \( v_l \) being the volume per molecule in the liquid phase and \( \sigma \) the droplet surface tension (assumed to be equal to the surface tension of the bulk liquid).

When condensation occurs via nucleation, the function \( F(\nu) \) has a maximum at some \( \nu_c = (2a/3b)^{3/2} \), with \( v_l \) being the volume per molecule in the liquid phase and \( \sigma \) the droplet surface tension (assumed to be equal to the surface tension of the bulk liquid).

A droplet with \( \nu = \nu_c \) is called “nucleus”; the subscript “c” will mark quantities related thereto.

Defining the quantity \( \Delta\nu_c \) by the equality

\[
\frac{1}{2} |F''_c| (\Delta\nu_c)^2 = 1, \tag{4}
\]

where \( F'' = \partial^2 F/\partial \nu^2 \), Kuni and Grinin\(^4\) pointed out that the free energy of droplet formation \( F(\nu) \) and equilibrium distribution \( g_e(\nu) \) can be accurately represented as

\[
F(\nu) \simeq F_c + \frac{1}{2} F''_c (\nu - \nu_c)^2, \quad g_e(\nu) \simeq g_e(\nu_c) \exp\left[-\frac{1}{2} F''_c (\nu - \nu_c)^2\right], \tag{5}
\]

respectively, over the entire region \( (|\nu - \nu_c| \lesssim \Delta\nu_c) \) of the substantial change of \( g_e(\nu) \) in the vicinity of \( \nu_c \) if

\[
\Delta\nu_c/\nu_c \ll 1. \tag{6}
\]

The relative inaccuracy of representations (5) within the near-critical region \( |\nu - \nu_c| \lesssim \Delta\nu_c \) is of the order of \( \Delta\nu_c/\nu_c \).

As clear from eq.(5), \( \Delta\nu_c \) represents the characteristic scale of the substantial change of the equilibrium distribution function \( g_e(\nu) \) in the vicinity of \( \nu_c \). Moreover, Kuni and Grinin\(^4\) showed that in that vicinity \( \Delta\nu_c \) also represents the characteristic scale of the substantial change of the steady-state distribution function \( g_s(\nu) \) as well as of the distribution \( g(\nu, t) \), so

\[
\frac{1}{g(\nu, t)} \frac{\partial g(\nu, t)}{\partial \nu} \sim \frac{1}{g_s(\nu)} \frac{dg_s(\nu)}{d\nu} \sim \frac{1}{g_e(\nu)} \frac{dg_e(\nu)}{d\nu} \sim \frac{1}{\Delta\nu_c}. \tag{7}
\]

The absorption rate \( W^+(\nu) \) of a droplet (in eq.(1)) is determined from the gas-kinetic theory,\(^1\)–\(^5\)

\[
W^+(\nu) = \frac{1}{4} n \overline{v}_T A(\nu), \tag{8}
\]

\[ n = \rho/(\pi \overline{v}_T^2) \]
where $\bar{v}_T = \sqrt{8k_BT/\pi m}$ is the mean thermal velocity of vapor molecules (of mass $m$) and $A(\nu) = 4\pi(3\nu/4\pi)^{2/3}\nu^{2/3}$ is the surface area of the droplet. On the other hand, the droplet emission rate $W^-(\nu)$ is determined through $W^+(\nu)$ from the principle of detailed balance, stipulating that for the equilibrium distribution of droplets $W^-(\nu)g_e(\nu) = W^+(\nu - 1)g_e(\nu - 1)$, so that, according to eq.(2),

$$W^-(\nu) = W^+(\nu - 1)\exp\left[F(\nu) - F(\nu - 1)\right].$$

(9)

Carrying out the Taylor series expansions on the RHS of eq.(1) and taking into account eqs.(3)-(9), Kuni and Grinin$^4$ showed that for the resulting differential equation in the near-critical region $|\nu - \nu_c| \lesssim \Delta\nu_c$ to be accurately approximated by the Fokker-Planck equation

$$\frac{\partial g(\nu, t)}{\partial t} = -W_c^+ \frac{\partial}{\partial \nu} \left(-F'(\nu) - \frac{\partial}{\partial \nu}\right) g(\nu, t)$$

(10)

with the drift/force coefficient $F'(\nu) = \partial F/\partial \nu$ a linear function of $\nu$, the strong inequality

$$\frac{1}{\Delta\nu_c} \ll 1$$

(11)

must be fulfilled in addition to condition (6). The parameters $\Delta\nu_c/\nu_c$ and $1/\Delta\nu_c$ can be considered to represent the small parameters of the macroscopic theory of condensation.

Thus, for the Fokker-Planck approximation to be suitable in the kinetic equation of nucleation, there must exist some near-critical region whereof the half-width $\Delta\nu_c$, defined by constraint (3), satisfies the following requirements:

a) $\Delta\nu_c$ is large enough to represent the characteristic scale of substantial change of the equilibrium distribution function in the vicinity of $\nu_c$.

b) $\Delta\nu_c$ is small enough that the quadratic approximation (eq.(5)) for the free energy of formation is acceptable across the entire near-critical vicinity.

c) $\Delta\nu_c$ is much greater than the elementary change of the droplet variable; this requirement ensures that in the Taylor series expansions of the RHS of eq.(1) the terms with the third and higher order
derivatives of the distribution function $g(\nu, t)$ can be neglected compared to the term containing the second order derivative of $g(\nu, t)$.

Note that (in unary condensation theory only!) the requirements b) and c) are expressed through strong inequalities (6) and (11), whereas the requirement a), expressed as the operator estimates in eq.(7), is automatically satisfied due to constraint (4) if the requirement b) is satisfied.

2.2 Multicomponent nucleation

Now, consider a metastable $N$-component vapor mixture at temperature $T$, within which liquid droplets of an $N$-component solution form as a result of isothermal condensation via nucleation. Again, in the framework of the capillarity approximation (whereon the thermodynamics of macroscopic theory of multicomponent condensation is based) the droplets are treated as spheres with sharp boundaries, internal thermodynamic equilibrium, and with the surface tension of the bulk liquid of the same composition.\(^7\)-\(^9\)

Let $\nu_i$ ($i = 1, \ldots, N$) be the number of molecules of component $i$ in a droplet. Because the temperature of the droplet is constant (and equal to $T$), the state of the droplet is completely determined by the set $\{\nu\} \equiv (\nu_1, \ldots, \nu_N)$ which can be thus chosen as the independent variables of state of the droplet; the capillarity approximation implies that $\nu_i \gg 1$ ($i = 1, \ldots, N$). The droplet chemical composition can be characterized by a set $\{\chi\} \equiv (\chi_1, \ldots, \chi_N)$ of mole fractions $\chi_i \equiv \chi_i(\{\nu\}) = \nu_i/\nu$ ($i = 1, \ldots, N$) (with $\nu = \sum_i \nu_i$ the total number of molecules in the droplet), of which only $n - 1$ are independent because $\sum_i \chi_i = 1$. The metastability of the vapor mixture can be characterized by the set of saturation ratios $\zeta_i = n_i/n_i^\infty$ ($i = 1, \ldots, N$) of its component vapors, where $n_i$ is the partial number density of molecules of vapor $i$ and $n_i^\infty$ is the number density of molecules of vapor $i$ in equilibrium with its pure bulk liquid at temperature $T$.

Denote the distribution function of droplets with respect $\{\nu\}$ at time $t$ by $g(\{\nu\}, t)$. Introduce
the “complementary” variable $\tilde{\nu}_i$ to include all but one of the variables of state of a droplet, with the “excluded” variable being $\nu_i$; any function $f$ of variables $\nu_1, ..., \nu_N$ can be thus represented as either $f(\nu_1, ..., \nu_N)$ or $f(\nu_i)$ or $f(\nu_i, \tilde{\nu}_i)$. For instance, $g(\nu_i, t) = g(\nu_i, \tilde{\nu}_i, t) = g(\nu_1, ..., \nu_N, t)$.

If the droplets exchange matter with the vapor via absorption and emission of single molecules (as usually assumed in multicomponent CNT), the temporal evolution of the distribution $g(\nu_i, t)$ is governed by the balance equation

$$\frac{\partial g(\nu_i, t)}{\partial t} = -\sum_{i=1}^{N} \left[ (W_i^+(\nu_i))g(\nu_i, t) - W_i^-(\nu_i + 1, \tilde{\nu}_i)g(\nu_i + 1, \tilde{\nu}_i, t) \right] - \left[ (W_i^- - 1, \tilde{\nu}_i)g(\nu_i - 1, \tilde{\nu}_i, t) - W_i^-(\nu_i)g(\nu_i, t) \right], \quad (12)$$

where $W_i^+(\nu)$ and $W_i^-(\nu)$ $(i = 1, ..., N)$ are the numbers of molecules of component $i$ that a droplet $\nu$ absorbs and emits, respectively, per unit time. A differential equation governing the temporal evolution of $g(\nu_i, t)$ can be obtained from the discrete balance equation (12) through the Taylor series expansions of $W_i^-(\nu_i \pm 1, \tilde{\nu}_i), W_i^+(\nu_i \pm 1, \tilde{\nu}_i)$, and $g(\nu_i \pm 1, \tilde{\nu}_i, t)$ (on its RHS) with respect to the deviation of their arguments from $\nu_i$ $(i = 1, ..., N)$.

According to classical thermodynamics, the equilibrium distribution function has the form

$$g_e(\nu_i) = n_i \exp[-F(\nu_i)], \quad (13)$$

where $n_i$ is the normalization factor and $F(\nu_i)$ is the free energy of formation of a droplet $\nu$ (in units of $k_B T$). It can be written in the form$^{1,8,9}$

$$F(\nu_i) = -\sum b_i \nu_i + a(\nu_i)(\sum \nu_i)^{2/3}, \quad (14)$$

where $b_i \equiv b_i(\nu_i) = \ln[\chi_{i/\chi_i} f_i(\nu_i)]$ $(i = 1, ..., N)$, $f_i(\nu_i)$ is the activity coefficient of component $i$ in the droplet, and $a(\nu_i) = 4\pi(3\nu_i/4\pi)^{2/3}(\sigma(\nu_i)/k_B T)$, with $\nu_i(\nu_i)$ being the composition-dependent average volume per molecule in the liquid phase and $\sigma(\nu_i)$ the droplet surface tension (assumed equal to the surface tension of a bulk liquid solution of droplet composition $\nu_i$).
The function $F = F(\nu_1, ..., \nu_N)$ determines a free-energy surface in an $(N+1)$-dimensional space. Under conditions when condensation occurs via nucleation, it has the form of a hyperbolic paraboloid ("saddle-like" shape in three dimensions). A droplet, whereof the variables $(\nu_1, ..., \nu_N)$ coincide with the coordinates of the saddle point, is called "nucleus"; these coordinates are determined as the solution of $N$ simultaneous equations

$$F'_i(\nu|c) = 0 \quad (i = 1, ..., N).$$

where $F'_i = \partial F(\nu)/\partial \nu_i \quad (i = 1, ..., N)$. Quantities for the nucleus will be again marked with the subscript "c".

Let us define the quadratic approximation (QA) region $\Omega_{2\nu}$ in the space of variables $\{\nu\}$ as the vicinity of the saddle point within which $F - F_c$ can be accurately approximated as a quadratic form

$$F - F_c = \frac{1}{2} \sum_{i,j=1}^{N} F''_{ijc} \Delta \nu_i \Delta \nu_j \quad (\{\nu\} \in \Omega_{2\nu}),$$

where $F''_{ij} = \partial^2 F/\partial \nu_i \partial \nu_j \quad (i, j = 1, ..., N)$ and $\Delta \nu_i = \nu_i - \nu_{ic} \quad (i = 1, ..., N)$. In this approximation, the equilibrium distribution can be represented as

$$g_e(\nu) \simeq g_e(\nu_c) \exp[- \frac{1}{2} \sum_{i,j=1}^{N} F''_{ijc} \Delta \nu_i \Delta \nu_j] \quad (\{\nu\} \in \Omega_{2\nu}).$$

Approximation (16) is equivalent to neglecting the cubic and higher order terms in the Taylor series expansion of $F(\nu)$ with respect to deviations $\Delta \nu_i$ in the vicinity of the saddle point. Therefore, considering that $1/3$ is already much smaller than 1, the QA region $\Omega_{2\nu}$, wherein approximation (16) is acceptable, can be determined by the condition

$$\epsilon_{32}(\nu) \lesssim \frac{1}{3},$$

where

$$\epsilon_{32}(\nu) = \frac{|\sum_{i,j,k=1}^{N} b_{ijk}(\Delta \nu_i)(\Delta \nu_j)(\Delta \nu_k)|}{|\sum_{i,j=1}^{N} a_{ij}(\Delta \nu_i)(\Delta \nu_j)|}.$$
with
\[ a_{ij} \equiv \frac{1}{2!} \frac{\partial^2 F(\{\nu\})}{\partial \nu_i \partial \nu_j} \bigg|_c, \quad b_{ijk} = \frac{1}{3!} \frac{\partial^2 F(\{\nu\})}{\partial \nu_i \partial \nu_j \partial \nu_k} \bigg|_c \quad (i, j, k = 1, \ldots, N) \] (20)

Let us define the saddle-point (SP) region \( \Omega_\nu \) in the space of variables \( \{\nu\} \) as the minimal vicinity of the saddle point within which the equilibrium distribution \( g_e(\{\nu\}) \) changes substantially. According to eq.(17), its boundary should thus satisfy the constraint (analogous to constraint (4) of the unary nucleation theory\(^4\))
\[ | \Delta \nu^T A \Delta \nu | \equiv \left| \frac{1}{2} \sum_{i,j=1}^{N} F''_{ijc}(\nu_i - \nu_ic)(\nu_j - \nu_jc) \right| = 1, \] (21)
where the matrix notation was introduced with a real symmetric \( N \times N \)-matrix \( A = [a_{ij}] \) \((i, j = 1, \ldots, N)\) and a real column-vector \( \Delta \nu = [\Delta \nu_i] \) \((i = 1, \ldots, N)\) of length \( N \), where \( A = [a_{ij}] \) \((i, j = 1, \ldots, N)\) is a real symmetric \( N \times N \)-matrix and \( \Delta \nu = [\Delta \nu_i] \) \((i = 1, \ldots, N)\) is a real column-vector of length \( N \), the superscript “T” marking the transpose of a matrix or vector.

Because the matrix \( A \) is real and symmetric, it is orthogonally diagonalizable, according to the spectral theorem.\(^{10}\) Therefore, there exists a real orthogonal \( N \times N \)-matrix \( P \equiv [p_{\alpha\gamma}] \) \((\alpha, \gamma = 1, \ldots, N)\) (such that \( P^{-1} = P^T \)) diagonalizing the matrix \( A \), so the matrix \( D = P^T A P \) is a real diagonal \( N \times N \) matrix (hereafter the Greek subscripts \( \alpha, \gamma = 1, \ldots, N \) do not indicate the relation to the chemical components 1, \ldots, \( N \) in the system). By virtue of the spectral theorem,\(^{10}\) the columns of the matrix \( P \) are linearly independent orthonormal eigenvectors of \( A \). The corresponding eigenvalues \( \lambda_1, \ldots, \lambda_N \) are the diagonal elements of \( D \). When the free energy surface has the shape of a hyperbolic paraboloid, one of these eigenvalues is negative (say, \( \lambda_1 < 0 \)), while all others are positive, hence \( \det(A) < 0 \).

Let us introduce the new variables \( \{x\} \equiv (x_1, \ldots, x_N) \) as
\[ x_\alpha = \sum_{i=1}^{N} p_{i\alpha} \Delta \nu_i \quad (\alpha = 1, \ldots, N), \] (22)
comprising a column-vector \( x \equiv [x_\alpha] \) \((\alpha = 1, \ldots, N)\) of length \( N \). Because the difference \( F - F_c \) does not depend on the choice of independent variables of state of a droplet, and \( \Delta \nu^T A \Delta \nu = x^T Dx \),
approximation (16) for $F$ in variables $\{x\}$ becomes

$$F - F_c = \sum_{\alpha} \lambda_\alpha x_\alpha^2 \quad (\{x\} \in \Omega_{2x}),$$

(23)

and approximation (17) for the equilibrium distribution transforms into an approximation for the equilibrium distribution $q_e(\{x\})$ in variables $\{x\}$ (with a new normalization factor $n_x$):

$$q_e(\{x\}) \simeq q_e(\{x_c\}) \exp[-\sum_{\alpha} \lambda_\alpha x_\alpha^2] \quad (\{x\} \in \Omega_{2x}).$$

(24)

Thus, the quadratic form in eq.(21), determining the boundary of the SP region $\Omega_\nu$ in variables $\{\nu\}$, becomes a diagonal quadratic form in variables $\{x\}$. That only one eigenvalue of $A$ is negative ($\lambda_1 < 0$), whereas all others are positive ($\lambda_\alpha > 0$ ($\alpha \neq 1$)), allows one to identify $x_1$ as the single thermodynamically unstable variable and $x_2, \ldots, x_N$ as thermodynamically stable ones. This allows one to impose standard boundary condition on the multidimensional kinetic equation,\textsuperscript{11,12}

$$\frac{q(\{x\}, t)}{q_e(\{x\})} = \begin{cases} 1 & (x_1 \to -\infty \text{ and } \sum_\alpha \lambda_\alpha x_\alpha^2 < 0), \\ 0 & (x_1 \to \infty \text{ and } \sum_\alpha \lambda_\alpha x_\alpha^2 < 0), \end{cases}$$

(25)

$$q(\{x\}, t) \to 0 \text{ as } \sum_\alpha \lambda_\alpha x_\alpha^2 \to \infty.$$

requiring that in variables $\{x\}$ the distribution function $q(\{x\}, t)$ of small sub-critical droplets smoothly transition into the equilibrium distribution, whereas for large super-critical droplets $q(\{x\}, t)$ smoothly transition into stationary distribution (by convention, sub-critical and super-critical droplets are assigned negative and positive values, respectively, of the unstable variable $x_1$; in specific applications, these signs depend on the coefficients of transformation (22), i.e., on the orthogonal matrix $P$).

These boundary conditions to eq.(12) are imposed on the boundary of the SP region $\Omega_\nu$ of substantial change of $g(\{\nu\}, t)$. In variables $\{x\}$, the constraint

$$|\sum_{\alpha=1}^N \lambda_\alpha x_\alpha^2| = 1 \quad (\lambda_1 < 0, \lambda_\alpha > 0 \quad (\alpha \neq 1))$$

(26)
will determine the boundary of SP region $\Omega_x$ in variables $\{x\}$; this equation is simpler than eq.(21). Once the boundary of the SP region is determined in variables $\{x\}$, it can be also found in variables $\{\nu\}$ via transformation (22).

One can then evaluate the accuracy of approximation (16) within the SP region $\Omega_\nu$ by calculating the ratio $\varepsilon_{32}(\{\nu\})$ for $\{\nu\} \in \Omega_\nu$. According to eq.(18), the boundaries of the QA region $\Omega_2\nu$, where this approximation is acceptably accurate, are determined by the equality $\varepsilon_{32}(\{\nu\}) = 1/3$.

Strictly speaking, approximation (16) is needed in the entire SP region $\Omega_\nu$ (at boundaries of which conditions (25) are imposed) in order for the kinetic equation of CNT therein to have the Fokker-Planck form with its force coefficients being linear functions of $\{\nu\}$; in other words, it is necessary that $\Omega_\nu \subseteq \Omega_2\nu$. However, even if approximation (16) is not fulfilled in some (relatively small) part(s) of $\Omega_\nu$, one can expect the Fokker-Planck equation with linear force coefficients to be an acceptable approximation for the kinetic equation in the entire $\Omega_\nu$ if the parameter

$$\omega = \frac{\mu[\Omega_\nu \setminus (\Omega_\nu \cap \Omega_2\nu)]}{\mu[\Omega_\nu]} \tag{27}$$

(with $\mu[\Omega]$ denoting the measure of a set (region) $\Omega$) is negligibly small. Clearly, the smaller $\omega$, the more accurate the kinetic equation of CNT. One can roughly assume that this accuracy is sufficient if approximation (16) fails only in 10% of $\Omega_\nu$ or less, and require that

$$\omega \lesssim 0.1. \tag{28}$$

In the case of isothermal binary nucleation ($N = 2$), the space of droplet variables is two-dimensional, and the measure $\mu[\Omega]$ of any region $\Omega$ therein is the surface area of $\Omega$; for isothermal ternary nucleation ($N = 3$), the space of droplet variables is three-dimensional, and the measure $\mu[\Omega]$ of a region $\Omega$ therein is the volume of $\Omega$.

In contrast to the unary nucleation theory, one cannot obtain the operator estimates for the derivatives $\partial g(\{\nu\}, t)/\partial \nu_i$ in the Taylor series expansions of $g(\nu_i \pm 1, \tilde{\nu}_i, t)$ on the RHS of the balance
eq.(12) in a straightforward manner because of the presence of mixed terms $a_{ij} \Delta \nu_i \Delta \nu_j$ ($i, j = 1, \ldots, N$) in the exponential of eq.(17) for $g_e(\{\nu\})$. However, the lower limits of the half-widths of the SP region $\Omega_\nu$ in variables $\{x\}$ can be estimated to be $\Delta \nu_i \equiv 1/\sqrt{|\lambda_1|}$, $\Delta \nu_2 \equiv 1/\sqrt{|\lambda_2|}$, ..., $\Delta \nu_N \equiv 1/\sqrt{|\lambda_N|}$ along the axes $x_1, x_2, \ldots, x_N$, respectively, so

$$1 \frac{\partial g(\{\nu\}, t)}{\partial \nu_i} \sim 1 \frac{\partial q_s(\{\nu\})}{\partial \nu_i} \sim 1 \frac{\partial q_e(\{\nu\})}{\partial \nu_i} \sim \frac{1}{\Delta \nu_i} (\alpha = 1, \ldots, N).$$

Therefore, because

$$\frac{\partial g(\{\nu\}, t)}{\partial \nu_i} = \sum_{\alpha=1}^{N} \frac{\partial J g(\{x\}, t)}{\partial x_\alpha} \frac{\partial x_\alpha}{\partial \nu_i},$$

(where $J$ is the Jacobian of transformation $\Delta \nu = P x$) and $\partial x_\alpha / \partial \nu_i = p_{i\alpha}$, one can obtain estimates

$$1 \frac{\partial g(\{\nu\}, t)}{\partial \nu_i} \sim 1 \frac{\partial q_s(\{\nu\})}{\partial \nu_i} \sim 1 \frac{\partial q_e(\{\nu\})}{\partial \nu_i} \lesssim \sum_{\alpha=1}^{N} p_{i\alpha} \sqrt{\lambda_\alpha}. \ (i = 1, \ldots, N).$$

Expanding the procedure of Kuni and Grinin\textsuperscript{4} to multicomponent nucleation, performing the Taylor series expansions of $W_i^- (\nu_i \pm 1, \tilde{\nu}_i), W_i^+ (\nu_i \pm 1, \tilde{\nu}_i)$, and $g(\nu_i \pm 1, \tilde{\nu}_i, t)$ on the RHS of eq.(12), and taking into account eq.(30), one can show that for the resulting differential equation to be accurately approximated by the conventional Fokker-Planck equation of multicomponent CNT

$$\frac{\partial g(\{\nu\}, t)}{\partial t} = - \sum_{i=1}^{N} W_{i\nu} \frac{\partial}{\partial \nu_i} \left( - F_i'(\{\nu\}) - \frac{\partial}{\partial \nu_i} g(\{\nu\}, t) \right)$$

with $F_i'(\{\nu\})$ ($i = 1, \ldots, N$) being linear superpositions of $\Delta \nu_i$ ($i = 1, \ldots, N$) in the SP region $\Omega_\nu$, the parameters

$$\frac{1}{\Delta \nu_i} \equiv \left| \sum_{\alpha=1}^{N} p_{i\alpha} \sqrt{\lambda_\alpha} \right| \ (i = 1, \ldots, N),$$

must fulfill the strong inequalities

$$\frac{1}{\Delta \nu_i} \ll 1 \ (i = 1, \ldots, N),$$

in addition to the parameter $\omega$ satisfying constraint (28).
Thus, the parameters $\omega$ and $1/\Delta^\nu_i$ ($i = 1, \ldots, N$) represent the small parameters of the macroscopic theory of multicomponent nucleation. The violation of any one of constraints (28) or (33) will necessitate going beyond the framework of the conventional Fokker-Planck equation with linear force coefficients usually adopted for the kinetic equation in the multicomponent CNT.

If constraint (33) on the parameters $1/\Delta^\nu_i$ ($i = 1, \ldots, N$) is not satisfied for some $i$, then the kinetic equation will include contributions of the third and higher order partial derivatives of the distribution function $g(\{\nu\}, t)$ with respect to $\nu_i$. This constraint can be referred to as the SP region constraint, because it characterizes how smoothly the distribution function varies in the SP region. An elegant method (based on the combination the Enskog-Chapman method and method of complete separation of variables) for solving such a non-Fokker-Planck kinetic equation was developed by Kuni and Grinin\textsuperscript{13} (see also references 14,15 for its applications).

On the other hand, if the parameter $\omega$ does not satisfy constraint (28), then the QA region $\Omega_{2\nu}$ of quadratic approximation (16) for $F(\{\nu\})$ does not cover a sufficiently large part of the SP region $\Omega_\nu$ and it is necessary to retain the cubic and perhaps even higher order (in $\Delta^\nu_i$ ($i = 1, \ldots, N$)) terms in the Taylor series expansion for $F(\{\nu\})$. This constraint can be referred to as the QA region constraint, because it characterizes the extent of the QA region. As a result, the first derivatives $F'_i$ in the kinetic equation (31) will not be linear superpositions of deviations $\Delta^\nu_i$ ($i = 1, \ldots, N$) (they will be quadratic at least, or of even higher orders). Hence the force coefficients of equation (31) will no longer be linear functions of $\{\nu\}$, i.e., the kinetic equation will differ from the conventional Fokker-Planck equation of multicomponent CNT. We are not aware of any work addressing the solution of such a kinetic equation in the theory of multicomponent nucleation.
3 Numerical evaluations

As a numerical illustration of the foregoing, we have carried out calculations for isothermal condensation in five binary systems:

(a) 1-butanol (component 1) – 1-hexanol (component 2);
(b) water (component 1) – methanol (component 2);
(c) water (component 1) – ethanol (component 2);
(d) water (component 1) – 1-propanol (component 2);
(e) water (component 1) – 1-butanol (component 2);

These systems were chosen as representative of the nucleation of droplets of ideal (a) and increasingly nonideal (b)-(e) binary solutions whose physical and chemical properties, necessary for the evaluation of parameters $\omega$ and $\Delta \nu_i$ ($i = 1, ..., N$) in eqs.(27) and (32), are relatively well known. For each system, the molecular volumes $v_1$ and $v_2$ of pure liquids were obtained from the density data of \textit{Lide},\textsuperscript{16} and the mean molecular volume of solution in the droplet was approximated as $v = \chi v_1 + (1 - \chi)v_2$, with $\chi = \chi_1$. All calculations were carried out for the same system temperature $T = 293.15$ K.

Although the saturation ratios $\zeta_1$ and $\zeta_2$ were different in different systems, they were always chosen so that the height of the nucleation barrier at the saddle point was in the range from 30 to 50, which would ensure a greater than $1 \text{ cm}^{-3}\text{s}^{-1}$ nucleation rate (according to binary CNT\textsuperscript{1,9,17,18}).

The surface tension of 1-butanol(1)–1-hexanol(2) solution (which can be considered as nearly ideal) was assumed to depend on $\chi (= \chi_1)$ as $\sigma(\chi) = \chi \sigma_1 + (1 - \chi)\sigma_2$, where $\sigma_1$ and $\sigma_2$ are the surface tensions of pure liquid butanol and pure liquid hexanol, respectively; $\sigma_1 = 25.39 \text{ dyn/cm}$ was obtained by linear interpolation of data from \textit{Lide}\textsuperscript{16} and $\sigma_2 = 26.20 \text{ dyn/cm}$ was taken from \textit{Gallant}.\textsuperscript{19} The activity coefficients of both butanol and hexanol in this solution were set equal to unity (ideal solution approximation).
For the composition dependence of the surface tension in systems (b)-(e) we used the expression

\[ \sigma(\chi) = a + b/(d - \chi) + c/(d - \chi)^2 \]  

(34)

(with \( \chi = \chi_1 \) and the dimension of \( \sigma \) dyn/cm), where a set of parameters \( a, b, c, d \) for each system. These parameters were determined with the help of Mathematica 12.1 by fitting expression (34) to appropriate experimental data (of Vazquez et al.\textsuperscript{20} for the systems (b)-(d)) and of Teitelbaum et al.\textsuperscript{21} for the system (e):

(b) \( a = 16.3343, b = 8.85203, c = -1.85715 \times 10^{-7}, d = 1.160977 \) (water(1)–methanol(2));

(c) \( a = 19.6512, b = 3.25232, c = -2.24934 \times 10^{-8}, d = 1.0880297 \) (water(1)–ethanol(2));

(d) \( a = 23.4678, b = 0.43188, c = -2.53012 \times 10^{-10}, d = 1.02205 \) (water(1)–1-propanol(2));

(e) \( a = 24.5474, b = -0.0309657, c = 0.00338759, d = 1.00811323 \) (water(1)–1-butanol(2)).

The composition dependence of the activity coefficients in systems (b)-(e) was described by the van Laar equations

\[ \ln f_1(\chi) = \frac{A_{12}}{(1 + \frac{A_{12}\chi}{A_{21}(1-\chi)})^2}, \quad \ln f_2(\chi) = \frac{A_{21}}{(1 + \frac{A_{21}(1-\chi)}{A_{12}\chi})^2}. \]  

(35)

with pairs \( A_{12} \) and \( A_{21} \) from refs.\textsuperscript{22, 23}:

(b) \( A_{12} = 0.5619 \) and \( A_{21} = 0.8041 \) (water(1)–methanol(2) solution);

(c) \( A_{12} = 0.9227 \) and \( A_{21} = 1.6798 \) (water(1)–ethanol(2) solution);

(d) \( A_{12} = 1.1572 \) and \( A_{21} = 2.9095 \) (water(1)–1-propanol(2) solution);

(e) \( A_{12} = 1.0996 \) and \( A_{21} = 4.1760 \) (water(1)–1-butanol(2) solution).

Some results of numerical calculations are presented in Figures 1-5. Saturation ratios \( \zeta_1 \) and \( \zeta_2 \) of vapor mixture components are indicated in the figure captions.

In each Figure, panel a) shows the SP region \( \Omega_x \) and the QA region \( \Omega_{2x} \) in variables \( \{x\} \), whereas panel b) shows the SP region \( \Omega_\nu \) and the QA region \( \Omega_{2\nu} \) in variables \( \{\nu\} \); both \( \Omega_{2x} \) and \( \Omega_{2\nu} \) are shown as grayish areas in these Figures. The solid curves indicate the borders of SP regions, whereas the
dashed ones indicate the boundaries of QA regions. In panel a) of each Figure, the thin dashed lines delineate the rectangular central part $\Omega_c^x$ of the SP region $\Omega_x$ of half-widths $\Delta_1^x$ and $\Delta_2^x$ which were used in calculating the parameters $1/\Delta_1^\nu$ and $\Delta_2^\nu$ according to eq.(32). In panel b) of each Figure, the corresponding central part $\Omega_c^\nu$ of the SP region $\Omega_\nu$ is also shown, delineated by thin dashed lines forming a parallelogram. The arrows show the direction of the growth of droplets at the saddle point.

As evident from these Figures, in each system the QA region only partially covers the SP region. Moreover, the QA region does not even cover the central parts of the SP region; approximation (16) fails to hold even on some segments of its sub-critical and super-critical borders, at which the stricter boundary conditions to the kinetic equation (31) are imposed.

Thus, for all the systems studied, the quadratic approximation (16) for $F(\nu)$ is accurate not in the entire SP region, and it is necessary to retain the cubic and perhaps even higher order (in $\Delta \nu_i$ ($i = 1, .., N$)) terms in the Taylor series expansion for $F(\nu)$. As a result, the first derivatives $F_i'$ in the kinetic equation (31) will not be linear superpositions of deviations $\Delta \nu_i$ ($i = 1, .., N$) (they will be quadratic or even of higher orders). Hence, the force coefficients of equation (31) will no longer be linear functions of $\nu$, i.e., the kinetic equation will differ from the conventional Fokker-Planck equation of multicomponent CNT. Therefore, the conventional expression for the steady-state binary nucleation rate, obtained on the basis of approximation (16), is not adequate for comparing theoretical predictions with experimental data in these systems.

We have also evaluated the parameters $1/\Delta_1^\nu$, $1/\Delta_2^\nu$, and $\omega$ in all systems (a)-(e). For simplicity, $\omega$ was estimated from below by calculating the ratio

$$\bar{\omega} = \frac{\mu[\Omega_\nu \setminus (\Omega_\nu \cap \Omega_2\nu)]}{\mu[\Omega_\nu]} \sum_{\nu \in \Omega_\nu} \frac{\nu}{\nu} \quad (36)$$

only within the central part $\Omega_c^\nu$ of the SP region $\Omega_\nu$. As clear from panels a) of the Figures, calculating the RHS of eq.(27) in increasingly larger enclosures (rectangles) will result in increasingly larger
results, because beginning from some large enough enclosing enclosure the surface area of the region \((\Omega_\nu \cap \Omega_{2\nu})\) will remain constant while the surface area \(\Omega_\nu\) will continue to increase asymptotically approaching its limiting value, while the RHS of eq.(27) asymptotically approaches \(\omega\) from below. Therefore, one can guarantee that \(\omega > \tilde{\omega}\), and if \(\tilde{\omega} \gtrsim 0.1\), then constraint (28) will certainly \textit{not} hold. (Recall that the measures of any region \(\Omega\) in variables \(\{\nu\}\) and \(\{x\}\) are related as \(\mu[\Omega(\{\nu\})] = \int \mu(\Omega(\{x\}))\).

Constraint (33) on the parameters \(1/\Delta_1^\nu\) and \(1/\Delta_2^\nu\) is necessary for neglecting the terms with the third and higher order derivatives in the Taylor series expansions on the RHS of the balance equation (12) and thus ensuring the Fokker-Planck form of the kinetic equation. As clear from the Table, the smallness of these parameters under metastability conditions that we considered is fulfilled well. However, they are sensitive to the saturation ratios \(\zeta_1\) and \(\zeta_2\), so their smallness at given \(\zeta_1, \zeta_2\) does not guarantee their smallness at different metastability of the vapor mixture.

On the other hand, constraint (28) on the parameter \(\omega\) is necessary in order to ensure that the force coefficients of the Fokker-Planck equation are linear functions of droplet variables in the predominant part of \(\Omega_\nu\). As evident from the Table, under considered metastability conditions this constraint is not satisfied in any of the systems studied. We note again, however, that \(\omega\) is quite sensitive to the saturation ratios \(\zeta_1\) and \(\zeta_2\), so its smallness at a given pair of \(\zeta_1, \zeta_2\) does not guarantee its smallness at different metastability of the vapor mixture.

Thus, both constraints (28) and (33) must be verified at given \(T, \zeta_1, \zeta_2\), and only if they hold, can one confidently use the conventional CNT expression for the binary nucleation rate \(J_s\) for purposes of comparing theoretical predictions with experimental data. Otherwise, another, more adequate theoretical expression for \(J_s\) must be obtained by solving a properly modified kinetic equation (which may be of non-Fokker-Planck form).
Table: Small parameters $1/\Delta'_1$, $1/\Delta'_2$, and $\tilde{\omega}$ ($< \omega$) of the Fokker-Planck approximation with linear force coefficients in the kinetic equation of binary nucleation at $T = 293.15$ K.

| Binary system                  | $\zeta_1$ | $\zeta_2$ | $F_c$  | $1/\Delta'_1$ | $1/\Delta'_2$ | $\tilde{\omega}$ ($\omega > \tilde{\omega}$) |
|--------------------------------|-----------|-----------|--------|---------------|---------------|-----------------------------------------------|
| 1-butanol(1)–1-hexanol(2)      | 2.88      | 3.41      | 40.11  | 0.19          | 0.04          | 0.15                                          |
|                                | 2.07      | 3.41      | 49.96  | 0.16          | 0.02          | 0.12                                          |
|                                | 2.88      | 1.95      | 49.95  | 0.15          | 0.08          | 0.19                                          |
|                                | 4.30      | 3.41      | 30.07  | 0.23          | 0.11          | 0.21                                          |
|                                | 2.88      | 6.39      | 30.21  | 0.25          | 0.01          | 0.15                                          |
| water(1)–methanol(2)           | 1.45      | 0.81      | 40.14  | 0.01          | 0.09          | 0.51                                          |
|                                | 1.29      | 0.81      | 50.14  | 0.07          | 0.04          | 0.14                                          |
|                                | 1.45      | 0.68      | 50.11  | 0.07          | 0.06          | 0.15                                          |
|                                | 1.71      | 0.81      | 30.21  | 0.12          | 0.08          | 0.19                                          |
|                                | 1.45      | 1.01      | 30.17  | 0.11          | 0.05          | 0.18                                          |
| water(1)–ethanol(2)            | 1.52      | 0.9       | 39.81  | 0.07          | 0.08          | 0.21                                          |
|                                | 1.39      | 0.90      | 50.22  | 0.06          | 0.05          | 0.19                                          |
|                                | 1.52      | 0.69      | 49.93  | 0.05          | 0.09          | 0.18                                          |
|                                | 1.71      | 0.90      | 30.14  | 0.09          | 0.12          | 0.24                                          |
|                                | 1.52      | 1.21      | 30.07  | 0.09          | 0.06          | 0.23                                          |
| water(1)–1-propanol(2)         | 1.3       | 1.9       | 39.86  | 0.01          | 0.06          | 0.42                                          |
|                                | 1.1       | 1.9       | 49.93  | 0.07          | 0.01          | 0.14                                          |
|                                | 1.3       | 1.55      | 50.82  | 0.01          | 0.04          | 0.54                                          |
|                                | 1.45      | 1.9       | 30.35  | 0.07          | 0.06          | 0.53                                          |
|                                | 1.3       | 2.4       | 29.89  | 0.09          | 0.03          | 0.30                                          |
| water(1)–1-butanol(2)          | 1.32      | 2.6       | 40.07  | 0.09          | 0.02          | 0.28                                          |
|                                | 1.02      | 2.6       | 50.21  | 0.10          | 0.01          | 0.13                                          |
|                                | 1.32      | 2.16      | 50.03  | 0.02          | 0.06          | 0.32                                          |
|                                | 1.48      | 2.95      | 30.45  | 0.01          | 0.09          | 0.74                                          |
|                                | 1.32      | 3.37      | 30.25  | 0.12          | 0.03          | 0.27                                          |
4 Concluding remarks

We have attempted to shed some light on the conditions necessary for the Fokker-Planck equation with linear force coefficients to be an adequate approximation to the kinetic equation of nucleation in a macroscopic theory of isothermal homogeneous multicomponent condensation. Starting with a discrete equation of balance, governing the temporal evolution of the distribution function of an ensemble of multicomponent droplets, and reducing it (by means of Taylor series expansions) to the differential form in the vicinity of the saddle point of the free energy surface, we have obtained the constraints necessary for the resulting kinetic equation to have the form of the Fokker-Planck equation and for its force coefficients to be linear functions of droplet variables; we have also identified the corresponding “small” parameters.

If those (saddle point (SP) region and quadratic approximation (QA) region) constraints are not satisfied, then either contributions from the third or higher order partial derivatives of the distribution function in the kinetic equation will be significant (when the SP constraint does not hold) or the force coefficients of the Fokker-Planck equation will become non-linear functions of droplet variables (when the QA constraint does not hold), or both. In any of these cases, the conventional kinetic equation of multicomponent nucleation and its predictions would become inaccurate.

As a numerical illustration, we have carried out calculations for isothermal condensation in five binary systems (at $T = 293.15$ K and vapor mixture metastabilities typical of experimental conditions): butanol–hexanol, water–methanol, water–ethanol, water–1-propanol, water–1-butanol. These systems were chosen as representatives for the nucleation of droplets of ideal (a) and increasingly nonideal (b-e) binary solutions. Our results suggest that the SP constraint on the smoothness of the droplet distribution in the SP region is well fulfilled, which substantiates neglecting the third and higher order derivatives of the distribution function in the conventional kinetic equation, i.e.,
its generic Fokker-Planck form. However, the QA constraint on the quadratic approximation in the Taylor series expansion of the free energy of droplet formation in the saddle point region is not satisfied; therefore, the force coefficients in that generic Fokker-Planck equation are not linear functions of droplet variables. Hence, the kinetic equation of binary nucleation does not have the form adopted in the binary CNT, so the conventional expressions$^{1-3,8,9,17,18}$ for the steady-state distribution of binary droplets and steady-state rate of binary nucleation can be of insufficient accuracy for making comparisons with experimental data.

Moreover, numerical calculations show that whether the constraints on the small parameters are satisfied or not is quite sensitive to the saturation ratios $\zeta_1, \zeta_2$ and this sensitivity increases with increasing non-ideality of the liquid solution in droplets. Therefore, for many conditions of likely interest, it is necessary to obtain the steady-state solutions of the modified kinetic equation, going beyond the framework of the Fokker-Planck equation of CNT due to the non-fulfillment of either the SP region constraint (when the third or even higher order derivatives of the distribution function are present in the kinetic equation) or the QA region constraint (when the force coefficients in the generic Fokker-Planck equation are not linear functions of droplet variables) or both. Clearly, such solutions are needed for consistently comparing theoretical predictions and experimental data obtained under conditions when the corresponding constraints are not fulfilled. This will be an object of our further research.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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Captions

to Figures 1 to 5 of the manuscript “On the Fokker-Planck approximation in the kinetic equation of multicomponent classical nucleation theory” by Y. S. Djikaev, E. Ruckenstein, and Mark Swihart

Figure 1. The saddle point (SP) and quadratic approximation (QA) regions of the space of droplet variables for binary nucleation in 1-butanol(1)–1-hexanol(2) vapor mixture at $T = 293.15$ K, $\zeta_1 = 2.88$, and $\zeta_2 = 3.49$. a) The SP region $\Omega_x$ and the QA region $\Omega_{2x}$ in variables $\{x\}$. b) The SP region $\Omega_\nu$ and the QA region $\Omega_{2\nu}$ in variables $\{\nu\}$. The dashed and solid curves indicate the boundaries of the SP and QA regions, respectively. Both $\Omega_{2x}$ and $\Omega_{2\nu}$ are shown as grayish areas. The thin-dashed quadrilateral delineates the central part of the SP region (see the text); vertices of the same color correspond to one same droplet in variables $\{x\}$ (a) and $\{\nu\}$ (b). The arrow points from the saddle point (red dot) toward super-critical droplets.

Figure 2. The saddle point (SP) and quadratic approximation (QA) regions of the space of droplet variables for binary nucleation in water(1)–methanol(2) vapor mixture at $T = 293.15$ K, $\zeta_1 = 1.45$, and $\zeta_2 = 0.81$. a) The SP region $\Omega_x$ and the QA region $\Omega_{2x}$ in variables $\{x\}$. b) The SP region $\Omega_\nu$ and the QA region $\Omega_{2\nu}$ in variables $\{\nu\}$. The dashed and solid curves indicate the boundaries of the SP and QA regions, respectively. Both $\Omega_{2x}$ and $\Omega_{2\nu}$ are shown as grayish areas. The thin-dashed quadrilateral delineates the central part of the SP region (see the text); vertices of the same color correspond to one same droplet in variables $\{x\}$ (a) and $\{\nu\}$ (b). The arrow points from the saddle point (red dot) toward super-critical droplets.

Figure 3. The saddle point (SP) and quadratic approximation (QA) regions of the space of droplet variables for binary nucleation in water(1)–ethanol(2) vapor mixture at $T = 293.15$ K, $\zeta_1 = 1.52$, ...
and $\zeta_2 = 0.90$. a) The SP region $\Omega_x$ and the QA region $\Omega_{2x}$ in variables $\{x\}$. b) The SP region $\Omega_\nu$ and the QA region $\Omega_{2\nu}$ in variables $\{\nu\}$. The dashed and solid curves indicate the boundaries of the SP and QA regions, respectively. Both $\Omega_{2x}$ and $\Omega_{2\nu}$ are shown as grayish areas. The thin-dashed quadrilateral delineates the central part of the SP region (see the text); vertices of the same color correspond to one same droplet in variables $\{x\}$ (a) and $\{\nu\}$ (b). The arrow points from the saddle point (red dot) toward super-critical droplets.

Figure 4. The saddle point (SP) and quadratic approximation (QA) regions of the space of droplet variables for binary nucleation in water(1)–1-propanol(2) vapor mixture at $T = 293.15$ K, $\zeta_1 = 1.30$, and $\zeta_2 = 1.90$. a) The SP region $\Omega_x$ and the QA region $\Omega_{2x}$ in variables $\{x\}$. b) The SP region $\Omega_\nu$ and the QA region $\Omega_{2\nu}$ in variables $\{\nu\}$. The dashed and solid curves indicate the boundaries of the SP and QA regions, respectively. Both $\Omega_{2x}$ and $\Omega_{2\nu}$ are shown as grayish areas. The thin-dashed quadrilateral delineates the central part of the SP region (see the text); vertices of the same color correspond to one same droplet in variables $\{x\}$ (a) and $\{\nu\}$ (b). The arrow points from the saddle point (red dot) toward super-critical droplets.

Figure 5. The saddle point (SP) and quadratic approximation (QA) regions of the space of droplet variables for binary nucleation in water(1)–1-butanol(2) vapor mixture at $T = 293.15$ K, $\zeta_1 = 1.32$, and $\zeta_2 = 2.6$. a) The SP region $\Omega_x$ and the QA region $\Omega_{2x}$ in variables $\{x\}$. b) The SP region $\Omega_\nu$ and the QA region $\Omega_{2\nu}$ in variables $\{\nu\}$. The dashed and solid curves indicate the boundaries of the SP and QA regions, respectively. Both $\Omega_{2x}$ and $\Omega_{2\nu}$ are shown as grayish areas. The thin-dashed quadrilateral delineates the central part of the SP region (see the text); vertices of the same color correspond to one same droplet in variables $\{x\}$ (a) and $\{\nu\}$ (b). The arrow points from the saddle point (red dot) toward super-critical droplets.
Figure 1:
Figure 2:
Figure 3:
Figure 4:
Figure 5: