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Quasi-one-component theory of homogeneous binary nucleation

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An effective quasi-one-component model for homogeneous vapor-liquid nucleation of nonideal binary mixtures in the regime of retrograde condensation is proposed. A transformation from the original binary to an effective unary system is accompanied by renormalization of the surface tension. A generalized Fisher droplet model for the cluster distribution is formulated and applied at the effective saturation point within the framework of a kinetic approach. Unknown parameters of the renormalized surface tension are found from the equations for pressure, vapor density, and isothermal compressibility of the effective system. The theory contains no adjustable parameters. A *n*-nonane–methane mixture is studied at conditions corresponding to the retrograde condensation (pressures >10 bar). Calculated nucleation rates agree fairly well with the recent experimental data whereas predictions of the classical binary nucleation theory are quite poor especially for high pressures (>30 bar).

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I. INTRODUCTION

The theory of homogeneous nucleation in binary mixtures was formulated by Reiss [1] as a generalization of the classical Becker-Döring-Zeldovich phenomenological theory of one-component nucleation [2,3]. According to [1], the Gibbs free formation energy $\Delta G(n_A,n_B)$ of a liquid droplet, containing n_A molecules of component A and n_B molecules of component B, in a supersaturated vapor mixture forms a saddle-shaped surface such that ΔG^* represents the height at the saddle. The steady-state nucleation rate J is given by

$$J=J_0\exp(-\Delta G^*/k_BT) , \tag{1}$$

where T is the temperature and k_B the Boltzmann constant. Kinetics of binary nucleation (contained in the preexponential factor J_0), first discussed by Reiss, was based on the fact that droplet growth across the saddle point goes in the direction of steepest descent on the ΔG surface; in other words, the form of $\Delta G(n_A,n_B)$ alone determines the direction of droplet growth. Stauffer [4] improved the approach of Reiss; his main result states that the growth kinetics is determined from a combination of energetic and kinetic factors and not only by the steepest descent direction on the energy surface. An approximate expression for the kinetic prefactor based on the concept of virtual monomers was proposed recently by Kulmala and Viisanen [5].

A peculiar thing about mixtures (not only binary) is the existence of *surface enrichment* [6], meaning that the composition inside the droplet can be different from that near its surface (due to surface adsorption)—an effect that is not present in a single-component case. Wilemski [6] proposed "a revised classical theory" in which surface enrichment is taken into account under the capillarity approximation by distinguishing between bulk and surface molecules n_i and n_i^{surf}, respectively, of each species ($i=A,B$) and applying the Gibbs-Duhem equation for the bulk and the Gibbs adsorption equation for the surface. The Reiss-Wilemski-Stauffer theory represents what is called now the classical theory of binary nucleation (CBN). A careful analysis of CBN shows that its thermodynamical part remains incomplete: extra relationships determining n_i^{surf} are necessary for calculation of the free energy surface in the vicinity of the saddle point. However, the influence of these quantities, contained in J_0, on the nucleation rate is small because the latter is dominated by the exponent ΔG^*.

The crucial point of the theory is the choice of a model for ΔG. This choice manifests itself in the determination of the size and composition of the critical nucleus. The nucleation rate depends sensitively on these quantities as well as on the curvature of the nucleus. Recent experiments by Strey, Wagner, and Viisanen [7,8] showed, in agreement with earlier studies by Mirabel and Katz [9] and Schmitt *et al.* [10], that the CBN fails because it inaccurately predicts the composition of the critical nucleus and does not take into account the curvature effects. Experimental investigations until now focused on nearly ideal mixtures. For *nonideal* mixtures, exhibiting a retrograde condensation behavior, composition, size, and curvature effects should be even more pronounced.

In the present paper we study binary nucleation at conditions of retrograde condensation. We propose an effective (quasi-)one-component model of binary nucleation and treat it within the framework of a semiphenomenological kinetic approach. This approach proved to be successful for one-component nucleation [11,12], which gives hope that it can be also useful for the binary case. An effective one-component model is introduced in Sec. II; its thermodynamics is discussed in Sec. III. Section IV contains the results on steady-state nucleation rate and critical cluster size. The proposed theory is applied to the *n*-nonane–methane mixture at conditions corresponding to retrograde condensation (Sec. V). Conclusions are formulated in Sec. VI.

II. FORMULATION OF AN EFFECTIVE ONE-COMPONENT MODEL

We consider a nonideal binary mixture of components A and B at initially gaseous state characterized by the total pressure p_0, temperature T_0, and molar fractions y_A and y_B; $y_A+y_B=1$ (no inert carrier gas is present). After fast expansion the system is brought to a nonequilibrium state–characterized by the total pressure p, temperature T, and (the same) molar fraction y_A—where nucleation starts.

We focus on the regime of retrograde condensation: the nucleation point $(p,T;y_A)$ is situated *inside the coexistence region* of the phase diagram (see Fig. 1); the boundary of this region (a "coexistence envelope") represents a set of equilibrium pressure-temperature points corresponding to the fixed value y_A of the vapor molar fraction of component A. At given p and T inside the coexistence region the binary liquid-vapor equilibrium can exist. The latter is characterized by the *equilibrium* vapor molar fractions $y_{i,0}(p,T)$, the equilibrium liquid molar fractions $x_{i,0}(p,T)$ $(\sum_i y_{i,0}=\sum_i x_{i,0}=1)$, and the molecular volumes $v_0^v(p,T), v_0^l(p,T)$ of the vapor and the liquid phase, respectively; a degree of metastability of component i can be characterized by a partial supersaturation

$$S_{i,0}=y_i/y_{i,0}(p,T) \quad (i=A,B) \ . \tag{2}$$

A peculiarity of the binary system is a dependence of ΔG^* on the *a priori* unknown bulk composition of the critical nucleus $x_i^*=n_i^*/(n_A^*+n_B^*)$ (the asterisk refers to the critical nucleus), which should be determined from a certain thermodynamic model. Our aim is to formulate an effective one-component system with the same nucleation behavior as for the original binary system. It implies that an effective system should have the same energy barrier.

Though the CBN model for x_i^* is not quite satisfactory one can use it as a first guess for defining the parameters of the effective system. The CBN equations read [6]

$$\Delta\mu_A^*+\frac{2\gamma^* v_A^{l*}}{r^*}=0 \ , \tag{3}$$

$$\Delta\mu_B^*+\frac{2\gamma^* v_B^{l*}}{r^*}=0 \ , \tag{4}$$

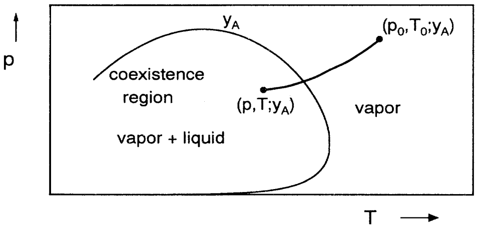

FIG. 1. Schematic representation of nucleation in a binary mixture in the regime of retrograde condensation: $(p_0,T_0;y_A)$, initial gaseous state; $(p,T;y_A)$, nucleation point situated inside the coexistence region.

where $\Delta\mu_i^*(p,T)=\mu_i^{l*}(p,T)-\mu_i^v(p,T)$ is the difference between chemical potentials in the liquid and the vapor phase taken at the same pressure p, r^* is the radius of the critical nucleus, γ^* is the surface tension, and v_i^{l*} is a molecular volume of the component i in the liquid phase. The value of the free energy barrier is then given by $\Delta G^*=(4\pi/3)\gamma^* r^{*2}$ (clusters are assumed to be spherical). Multiplying Eq. (3) by x_A^* and Eq. (4) by x_B^* and summing them up we obtain

$$r^*=-\frac{2\gamma^* v^*}{x_A^*\Delta\mu_A^*+x_B^*\Delta\mu_B^*} \ ,$$

where $v^*=x_A^* v_A^{l*}+x_B^* v_B^{l*}$ is a mean bulk molecular volume in the liquid phase. Thus the energy barrier reads

$$\Delta G^*=\frac{16\pi}{3}\frac{\gamma^{*3} v^{*2}}{(x_A^*\Delta\mu_A^*+x_B^*\Delta\mu_B^*)^2} \ . \tag{5}$$

The classical *one-component* nucleation theory gives for the energy barrier the result [13]

$$\Delta G^*\equiv\Delta G_{n_c}=\frac{16\pi}{3}\frac{\gamma^3 v^{l2}}{(\Delta\mu)^2} \ , \tag{6}$$

where n_c is the number of particles in the critical (one-component) cluster, γ is surface tension, v^l is the molecular volume in the liquid phase, and $\Delta\mu$ is the chemical potential difference. An obvious similarity between Eqs. (5) and (6) suggests that an effective system should have parameters satisfying in the first approximation the conditions $\gamma=\gamma^*$, $v^l=v^*$, and $\Delta\mu=\Delta\mu^*\equiv x_A^*\Delta\mu_A^*+x_B^*\Delta\mu_B^*$.

For a binary liquid droplet with radius r^* and composition x_A^* in equilibrium with surrounding binary vapor at temperature T we can write, using the incompressibility of the liquid phase [14],

$$\frac{2\gamma^*}{r^*}=\frac{k_B T}{v_i^{l*}}\ln\frac{z_i}{z_i^{\text{coex}}}-(p-p^{\text{coex}}), \quad i=A,B \ , \tag{7}$$

where $p^{\text{coex}}(x_A^*,T)$ is the pressure corresponding to coexistence between the bulk vapor and the binary liquid (plane interface) with the same composition x_A^*, z_i is the fugacity of component i, and z_i^{coex} is the same quantity referring to a plane interface. A comparison of this expression with Eqs. (3) and (4) shows that $\Delta\mu_i^*$ can be related to a partial critical supersaturation of component i, S_i^*, via

$$\Delta\mu_i^*=-k_B T\ln S_i^* \quad (i=A,B) \ ,$$

where

$$S_i^*=\frac{z_i}{z_i^{\text{coex}}}\exp\left[-\frac{(p-p^{\text{coex}})v_i^{l*}}{k_B T}\right] \ . \tag{8}$$

If we assume the vapor to be a perfect gas mixture and furthermore neglect $(p-p^{\text{coex}})$ in Eq. (7), then the general expression (8) is converted to a simple one (see, e.g., [15]): $S_i^*=p_i^v/p_i^{\text{coex}}$, where $p_i^v=y_i p$ is an actual partial vapor pressure of component i and $p_i^{\text{coex}}(x_A^*,T)$ is the same quantity at coexistence. Thus

$$\Delta\mu^* = -k_B T \ln[S_A^{*x_A^*} S_B^{*x_B^*}] \ . \tag{9}$$

A comparison of Eq. (9) with its one-component analog $\Delta\mu = -k_B T \ln S$, where S is a supersaturation of a one-component vapor, shows that in the same approximation the quantity in the square brackets on the right-hand side of Eq. (9)

$$S^* = S_A^{*x_A^*} S_B^{*x_B^*}$$

represents a supersaturation in the effective unary system. From the input conditions (p, T, y_A) the critical composition is unknown. Therefore to proceed we will use the *equilibrium* composition of the binary system at (p, T) as a reference. We rewrite S^* as

$$S^* = \bar{S}(1+\Psi^*) \ , \tag{10}$$

where

$$\bar{S} = S_{A,0}^{x_{A,0}} S_{B,0}^{x_{B,0}} \ , \tag{11}$$

$S_{i,0}$ are given by Eq. (2) and Ψ^* is an unknown function depending on the pressure, the temperature, and the composition of the critical cluster. Note that the quantity $\bar{S}$ has the same structure as S^* and is completely determined by the input conditions (and by the equilibrium model). The unknown function Ψ^* accounts for composition, surface enrichment, and curvature effects incorporated in S^*; it should vanish when the radius of the critical nucleus becomes large: then its composition should not differ from the equilibrium composition of the bulk binary liquid $x_{A,0}(p, T)$. It is reasonable therefore to assume a power law form for Ψ^*,

$$\Psi^* = \alpha_s^{(0)} \left[\frac{1}{r^*} \right]^{h+1} \ , \tag{12}$$

where $\alpha_s^{(0)}(p, T)$ and $h(p, T)$ are some unknown functions of pressure and temperature. One can also expect that in the "single-component limit," i.e., if only one of the components is condensing, say, $x_{A,0} = 1$, the function Ψ^* should vanish for all r^* and $S^* \to S_{A,0}$. In what follows we will assume that $\Psi^* \ll 1$.

Substituting Eq. (10) into the energy barrier given by Eq. (5) and linearizing in Ψ^* we obtain

$$\Delta G^* = \frac{16\pi}{3} \frac{[\gamma^*(1+\Psi_1^*)]^3 v^{*2}}{(-k_B T \ln\bar{S})^2} \ , \tag{13}$$

where Ψ_1^* is proportional to Ψ^*

$$\Psi_1^* = -\frac{2}{3} \frac{1}{\ln\bar{S}} \Psi^* \ .$$

Analyzing Eq. (13) we can conclude that nucleation in the original binary system is similar to nucleation in the effective one-component system having supersaturation equal to $\bar{S}$ and characterized by the renormalized surface tension

$$\gamma_1^* = \gamma^*(1+\Psi_1^*) \ .$$

Thus the supersaturation of the effective system can be considered to be fixed by the input conditions (p, T, y_A) whereas composition, surface enrichment, and curvature effects incorporated in S^* are "hidden" in the renormalized surface tension. From the definition of $\bar{S}$ and Eq. (2) it follows that the effective pressure $\bar{p}$ of the one-component system is equal to

$$\bar{p} = y_A^{x_{A,0}} y_B^{x_{B,0}} p \tag{14}$$

and the effective saturation pressure $\overline{p_{\text{sat}}}$ is given by

$$\overline{p_{\text{sat}}} = y_{A,0}^{x_{A,0}} y_{B,0}^{x_{B,0}} p \ . \tag{15}$$

The ratio of these two quantities yields $\bar{p}/\overline{p_{\text{sat}}} = \bar{S}$, which is a common definition of the supersaturation of a one-component vapor. The effective molecular volume can be approximated by the molecular volume of the binary system in the liquid phase in equilibrium at (p, T): $v^* \approx v_0^l(p, T)$. The (bare) surface tension of the critical cluster γ^* can be written in a curvature-dependent form similar to Tolman's result for a spherical interface [16]

$$\gamma^* = \gamma_0(p, T) \left[1 + \alpha_\gamma^{(1)} \frac{1}{r^*} \right] \ ,$$

where the leading term $\gamma_0(p, T)$ is the surface tension of the infinite plane interface for the original binary system in equilibrium at (p, T). An unknown function $\alpha_\gamma^{(1)}(p, T)$ represents a "Tolman length." The classical one-component nucleation theory [13] establishes the following relationship between the supersaturation $\bar{S}$ and the radius of the critical cluster r^*:

$$\frac{1}{\ln\bar{S}} = \frac{k_B T}{2\gamma_0 v_0^l} r^* \ .$$

Then the renormalized quantity γ_1^*, playing the role of the surface tension in the effective system, reads

$$\gamma_1^* = \gamma_0(p, T) \left[1 + \alpha_\gamma^{(1)} \frac{1}{r^*} + \alpha_s^{(1)} \left[\frac{1}{r^*} \right]^h \right] \ , \tag{16}$$

where

$$\alpha_s^{(1)}(p, T) = -\frac{1}{3} \frac{k_B T}{\gamma_0 v_0^l} \alpha_s^{(0)}$$

denotes a new unknown function.

On the right-hand side of Eq. (16) we have skipped the term proportional to $(1/r^*)^{h+1}$, keeping the first two terms in powers of $(1/r^*)$. For large values of r^* both correction terms should vanish, therefore $h(p, T) > 0$. It is important to note that Eq. (16) is not a Taylor series of surface tension in powers of inverse radius: the last term on the right-hand side appears due to renormalization procedure described above.

The radius of the critical cluster should be found from the solution of the one-component nucleation problem (Sec. IV). On the basis of these considerations we can write the surface tension of an n-cluster (cluster containing n "particles") in the effective one-component system in a curvature-dependent form

$$\overline{\gamma_1}(n) = \gamma_0[1 + \alpha_\gamma n^{-1/3} + \alpha_s n^{-h/3}] \ , \tag{17}$$

where $\alpha_\gamma(p,T)$, $\alpha_s(p,T)$, and $h(p,T)$ are unknown parameters to be found from a thermodynamic model (see Sec. III); we took into account that the radius of an n-cluster is proportional to $n^{1/3}$. Thus $\gamma_1^* = \overline{\gamma_1}(n_c)$, where n_c is the critical cluster size.

III. THERMODYNAMICS OF THE EFFECTIVE SYSTEM

The aim of the present section is to determine the values of parameters α_γ, α_s, and h. They can be found from analysis of thermodynamics of the one-component system, formulated in the preceding section, at the (effective) saturation point. About the effective system we assume (as is commonly done in nucleation models) that it can be viewed as a collection of noninteracting clusters (intracluster interactions are, of course, important). Let q_n be the configuration integral for the n-cluster in a domain of volume V and z the fugacity. The grand partition function of the system can be written in an exponential form [17]

$$\Xi = \exp\left[\sum_{n=1}^{\infty} q_n z^n\right] .$$

As a result, the pressure equation of state, which we apply at the saturation point $\overline{p_{\rm sat}} V = k_B T (\ln \Xi)_{\rm sat}$, reads

$$\frac{\overline{p_{\rm sat}}}{k_B T} = \sum_{n=1}^{\infty} \left[\frac{q_n}{V} z^n\right]_{\rm sat} \tag{18}$$

and the number density of n-clusters at the same point is

$$\rho_{n,\rm sat} = \left[\frac{q_n}{V} z^n\right]_{\rm sat} .$$

With the help of the standard thermodynamic transformations the right-hand side of this expression can be rewritten in terms of the grand potential of the n-cluster $\Omega_{n,\rm sat}$,

$$\rho_{n,\rm sat} = \frac{1}{V} e^{-\beta \Omega_{n,\rm sat}}, \quad \beta = 1/k_B T . \tag{19}$$

Thus $\Omega_{n,\rm sat}$ represents an energy barrier to form an n-cluster at the saturation point. The pressure equation is therefore a sum of ideal gas contributions of various clusters

$$\frac{\overline{p_{\rm sat}}}{k_B T} = \sum_{n=1}^{\infty} \rho_{n,\rm sat} . \tag{20}$$

The right-hand side of Eq. (18) represents a generating function: various thermodynamic properties can be expressed in terms of its derivatives with respect to z. In particular, for the vapor density $\rho^v_{\rm sat}$ and the isothermal compressibility of the vapor at the saturation point $\chi_{\rm sat} \equiv [(1/\rho^v)(\partial \rho^v/\partial p)]_{\rm sat}$ we obtain [17]

$$\rho^v_{\rm sat} = \sum_{n=1}^{\infty} n \rho_{n,\rm sat} , \tag{21}$$

$$k_B T (\rho^v_{\rm sat})^2 \chi_{\rm sat} = \sum_{n=1}^{\infty} n^2 \rho_{n,\rm sat} . \tag{22}$$

It must be noted that Eqs. (20)–(22) are quite general and do not depend on a specific form of the configuration integral or, equivalently, a form of $\Omega_{n,\rm sat}$.

We will specify $\Omega_{n,\rm sat}$ by formulating a *generalized Fisher droplet model,* which is an extension of the classical Fisher model [17] to a binary mixture described in terms of an effective unary system

$$\beta \Omega_{n,\rm sat} = \beta \overline{\gamma_1}(n) s_1 n^{2/3} + \overline{\tau} \ln n - \ln(\overline{q_0} V) . \tag{23}$$

The first term on the right-hand side represents a dimensionless surface energy of a cluster; $s_1(p,T) = (36\pi)^{1/3} (v_0^l)^{2/3}$. Terms with the effective Fisher parameters $\overline{q_0}$ and $\overline{\tau}$ arise from various degrees of freedom of a cluster and from configurational effects. We define $\overline{q_0}$ and $\overline{\tau}$ by the following simplest mixing rules satisfying the single-component limit:

$$\overline{\tau} = x_{A,0} \tau_A + x_{B,0} \tau_B ,$$

$$\overline{q_0} = x_{A,0} q_{0,A} + x_{B,0} q_{0,B} ,$$

where τ_i and $q_{0,i}$ are the individual Fisher parameters of the component i. Those are related to its critical state parameters—pressure $p_{c,i}$, temperature $T_{c,i}$, and numbers density $\rho_{c,i}$—via [18]:

$$\rho_{c,i} = q_{0,i} \zeta(\tau_i - 1), \quad p_{c,i} = q_{0,i} k_B T_{c,i} \zeta(\tau_i) ,$$

where $\zeta(x) = \sum_{n=1}^{\infty} n^{-x}$ is the Riemann zeta function. From Eqs. (23), (19), and (17) we obtain for the cluster distribution

$$\rho_{n,\rm sat} = \overline{q_0} \exp[-\theta_0 (1 + \alpha_\gamma n^{-1/3} + \alpha_s n^{-h/3}) \times n^{2/3} - \overline{\tau} \ln n] , \tag{24}$$

where

$$\theta_0 = \frac{\gamma_0(p,T) s_1(p,T)}{k_B T}$$

is a dimensionless macroscopic surface tension. For the three unknown parameters α_γ, α_s, and h we have three equations (20), (21), and (22). The left-hand sides are known for given (p,T): the saturation pressure is determined by Eq. (15) and the vapor density and the compressibility can be expressed, e.g., with the help of the virial expansion of the third order at the saturation point [19]:

$$\rho^v_{\rm sat} = \frac{\overline{p_{\rm sat}}}{k_B T} - \overline{B} \left[\frac{\overline{p_{\rm sat}}}{k_B T}\right]^2 + (2\overline{B}^2 - \overline{C}) \left[\frac{\overline{p_{\rm sat}}}{k_B T}\right]^3 ,$$

$$k_B T (\rho^v_{\rm sat})^2 \chi_{\rm sat} = \frac{\overline{p_{\rm sat}}}{k_B T} - 3\overline{B} \left[\frac{\overline{p_{\rm sat}}}{k_B T}\right]^2 + (10\overline{B}^2 - 4\overline{C}) \left[\frac{\overline{p_{\rm sat}}}{k_B T}\right]^3 ,$$

where $\overline{B}$ and $\overline{C}$ are the second and the third virial coefficients of the effective system, respectively; they can be calculated using the individual virial coefficients of the components at temperature T and corresponding mixing rules.

One special case of the system parameters should be discussed separately. If $h=1$ then renormalization of surface tension results only in renormalization of the dimensionless Tolman length; Eq. (17) in this case reads

$$\overline{\gamma_1}(n)=\gamma_0(p,T)[1+\alpha'_\gamma n^{-1/3}] \tag{25}$$

with $\alpha'_\gamma=\alpha_\gamma+\alpha_s$ being a new unknown Tolman length. It can be found from the pressure equation (20); density and compressibility equations are not needed (see also [20]).

Therefore, in what follows we will search for α_γ, α_s, and h excluding the case $h=1$. Not too close to the critical conditions (when $\theta_0 \geq 1$) the series on the right-hand side of Eqs. (20)–(22) rapidly converge due to exponent in $\rho_{n,\text{sat}}$. Truncating each series at $n=3$ we obtain a system of three linear equations with respect to number densities of monomers, dimers, and trimers. This system has a unique solution:

$$\frac{\rho_{1,\text{sat}}}{\overline{q_0}}=Z_0+q_B+\frac{q_C}{2}\,,$$

$$\frac{\rho_{2,\text{sat}}}{\overline{q_0}}=-q_B-\frac{2q_B^2}{Z_0}\,,$$

$$\frac{\rho_{3,\text{sat}}}{\overline{q_0}}=\frac{2q_B^2}{Z_0}-\frac{q_C}{2}\,,$$

where the dimensionless quantities on the right-hand side are $Z_0=\overline{p_{\text{sat}}}/(\overline{q_0}k_BT)$, $q_B=\overline{q_0}BZ_0^2$, and $q_C=\overline{q_0}^{\,2}CZ_0^3$.

Having defined the densities we can obtain from Eq. (24) the set of three equations for α_γ, α_s, and h. Introducing for simplicity the notations

$$a\equiv 2^{1/3},\quad b\equiv 3^{1/3},\quad y\equiv\frac{\ln 3}{\ln 2}$$

and a new variable

$$c_h=2^{-h/3},\quad 0\leq c_h\leq 1,\quad c_h\neq\frac{1}{a}\,,$$

these equations can be written as

$$1+\alpha_\gamma+\alpha_s=-\frac{1}{\theta_0}\ln\left[\frac{\rho_{1,\text{sat}}}{\overline{q_0}}\right], \tag{26}$$

$$a^2+a\alpha_\gamma+a^2\alpha_s c_h=-\frac{1}{\theta_0}\ln\left[2^{\bar{\tau}}\frac{\rho_{2,\text{sat}}}{\overline{q_0}}\right], \tag{27}$$

$$b^2+b\alpha_\gamma+b^2\alpha_s c_h^y=-\frac{1}{\theta_0}\ln\left[3^{\bar{\tau}}\frac{\rho_{3,\text{sat}}}{\overline{q_0}}\right]. \tag{28}$$

Excluding α_γ and α_s from Eqs. (26) and (27) we obtain a nonlinear equation for c_h:

$$c_h^y=\frac{a}{b}(1+Q)c_h-\frac{Q}{b}\,. \tag{29}$$

Here $Q(p,T)$ is a parameter characterizing a given state of the system

$$Q=\frac{1}{b}\,\frac{-\dfrac{1}{\theta_0}\ln\left[3^{\bar{\tau}}\dfrac{\rho_{3,\text{sat}}}{\overline{q_0}}\right]a+\dfrac{1}{\theta_0}\ln\left[2^{\bar{\tau}}\dfrac{\rho_{2,\text{sat}}}{\overline{q_0}}\right]b-ab^2+a^2b}{-\dfrac{1}{\theta_0}\ln\left[2^{\bar{\tau}}\dfrac{\rho_{2,\text{sat}}}{\overline{q_0}}\right]+\dfrac{1}{\theta_0}\ln\left[\dfrac{\rho_{1,\text{sat}}}{\overline{q_0}}\right]a-a^2+a}\,. \tag{30}$$

An analysis of Eq. (29) can be made on the basis of its graphic representation shown in Fig. 2. For all values of Q there is at least one solution (point A in Fig. 2) $c_h=1/a\equiv 2^{-1/3}$ [it follows from the obvious identity $(1/a)^y=1/b$]. This root corresponds to $h=1$ and therefore has to be excluded. For $Q<0$ there are no other solutions; physically it means that for the states with negative Q the renormalized surface tension has the Tolman form (25) and $\alpha_s\equiv 0$.

For $0<Q<Q_*$, where

$$Q_*=y-1\approx 0.585$$

[the straight line given by the right-hand side of Eq. (29) with $Q=Q_*$ tangential to the curve c_h^y at the point A], there is a root in the interval $0<c_h<1/a$, corresponding to $1<h<\infty$. For $Q_*<Q<Q_{**}$, where

$$Q_{**}=\frac{b-a}{a-1}\approx 0.701$$

(the straight line with $Q=Q_{**}$ intersects the curve c_h^y at $c_h=1$), there is a root in the interval $1/a<c_h<1$, corre-

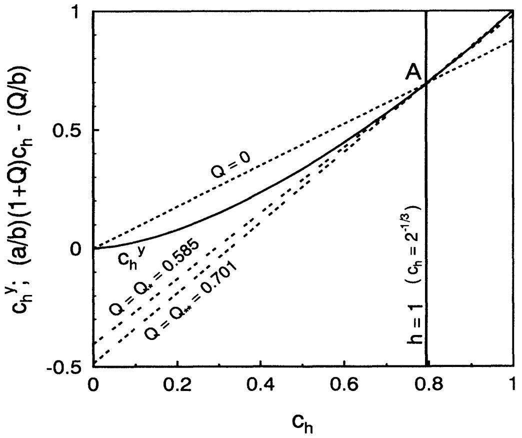

FIG. 2. Graphic representation of Eq. (29): $Q(p,T)$ characterizes the state of the system. The curved line is c_h^y; the straight lines correspond to the right-hand side of (29) with three different values of Q: $Q=0$, $Q_*\approx 0.585$, and $Q_{**}\approx 0.701$. All lines intersect at point A.

sponding to $0<h<1$. When c_h is found the other two parameters are calculated from Eqs. (26) and (27):

$$\alpha_s=\frac{1}{a^2}\,\frac{-\frac{1}{\theta_0}\ln\left[2^{\bar{\tau}}\frac{\rho_{2,\mathrm{sat}}}{\bar{q}_0}\right]+\frac{1}{\theta_0}\ln\left[\frac{\rho_{1,\mathrm{sat}}}{\bar{q}_0}\right]a-a^2+a}{c_h-\frac{1}{a}}\ ,$$

$$\alpha_\gamma=-\frac{1}{\theta_0}\ln\left[\frac{\rho_{1,\mathrm{sat}}}{\bar{q}_0}\right]-\alpha_s-1\ .$$

For $Q>Q_{**}$ we find ourselves again in the Tolman regime. The state with $Q(p,T)=Q_*$ yields a singularity in the behavior of thermodynamic parameters α_γ and α_s. For this particular state we have to return to the Tolman regime, though predictions of the nucleation theory can become poor. We accomplished the discussion of thermodynamics of the effective system so that all thermodynamic parameters are defined.

IV. STEADY-STATE NUCLEATION RATE

Kinetics of nucleation in the effective unary system is supposed to satisfy the following usual assumptions: (a) cluster growth and decay are dominated by monomer addition (condensation) and monomer extraction (evaporation) and (b) mass accommodation coefficients are equal to unity. The kinetic process rapidly reaches a steady nonequilibrium state. In the framework of the kinetic approach to one-component nucleation formulated by Katz and Wiedersich [21] (see also [12]), the steady-state nucleation rate in the effective system reads

$$J=\left[\frac{H''(n_c)}{2\pi}\right]^{1/2}\nu s_{n_c}\bar{S}^{\,n_c}\rho_{n_c,\mathrm{sat}}\ . \tag{31}$$

Here $s_n=s_1 n^{2/3}$ is the surface area of an n-cluster,

$$\nu=\frac{\bar{p}}{\sqrt{2\pi\bar{m}_1 k_B T}}$$

is monomer flux to the unit surface $\bar{m}_1=\bar{M}/N_A$, N_A is the Avogadro number, and

$$\bar{M}=x_{A,0}M_A+x_{B,0}M_B$$

is an (effective) molar weight, M_i being the individual molar weight of the component i of the original binary system. The function $H(n)$ is defined as

$$H(n)=\ln(\nu s_n\bar{S}^{\,n}\rho_{n,\mathrm{sat}})\ .$$

The critical cluster size n_c is given by minimization of function H:

$$H'(n_c)=0\ ,$$

where the prime denotes the differentiation with respect to the argument. Using the results obtained in the previous sections, this equation takes the form

$$-n_c\ln\bar{S}+\tfrac{2}{3}\theta_0 n_c^{2/3}+\tfrac{1}{3}\theta_0\alpha_\gamma n_c^{1/3}-\frac{h-2}{3}\theta_0\alpha_s n^{-(h-2)/3}+\bar{\tau}-\tfrac{2}{3}=0 \tag{32}$$

while the final expression for the nucleation rate reads

$$J=\frac{1}{3}\left\{\frac{\theta_0}{\pi}\left[1+\alpha_\gamma n_c^{-1/3}-\frac{(h-2)(h+1)}{2}\alpha_s n_c^{-h/3}\right]+\frac{9}{2\pi}\left[\bar{\tau}-\frac{2}{3}\right]n_c^{-2/3}\right\}^{1/2}\frac{\bar{p}s_1}{\sqrt{2\pi\bar{m}_1 k_B T}}\bar{q}_0\bar{S}^{\,n_c}\times\exp[-\theta_0(1+\alpha_\gamma n_c^{-1/3}+\alpha_s n_c^{-h/3})n_c^{2/3}-\bar{\tau}\ln n_c]\ . \tag{33}$$

V. NUCLEATION OF A BINARY *N*-NONANE–METHANE MIXTURE

We apply the proposed theory to the binary mixture of hydrocarbons n-nonane (A)–methane (B). At high pressures ($p>10$ bar) the real gas effects are highly pronounced and both of the components are present in the condensed phase in considerable amounts.

A. Thermophysical data

Individual thermophysical properties of the components are listed in Table I, where in addition to the properties mentioned earlier we present the values of Pitzer's acentric factor ω and parachor $[P]$ [used for calculation of $\gamma_0(p,T)$ and virial coefficients].

The second virial coefficient for n-nonane is given by [11]

$$B_A=\frac{1}{N_A}[369.2-705.3/t_A+17.9/t_A^2-427.0/t_A^3-8.9/t_A^8]$$

and for methane by [22]

$$B_B=\frac{k_B T_{c,B}}{p_{c,B}}[0.083-0.422/t_B^{1.6}+\omega_B(0.139-0.172/t_B^{4.2})]\ ,$$

where $t_i=T/T_{c,i}$ is reduced temperature of the component i. The effective second virial coefficient is built on the basis of the standard mixing rule

$$\bar{B}=x_{A,0}^2 B_A+x_{B,0}^2 B_B+2x_{A,0}x_{B,0}B_{AB}\ ,$$

TABLE I. Thermophysical properties of n-nonane and methane [22].

Component	M (g/mol)	T_c (K)	p_c (bar)	ρ_c (cm^{-3})	ω	$[P]$
n-nonane	128.259	594.6	23.13	1.09×10^{21}	0.445	387.6
methane	16.043	190.4	46.0	6.07×10^{21}	0.001	53.9

where B_{AB} is given in [22], Chap. 4.

For the third virial coefficient the generalized empirical correlation developed by Orbey and Vera [23] is used:

$$C_i = \left[\frac{k_B T_{c,i}}{p_{c,i}} \right]^2 (f_i^{(0)} + \omega_i f_i^{(1)}), \quad i = A,B$$

with

$$f_i^{(0)} = 0.014\,07 + 0.024\,32/t_i^{2.8} - 0.003\,13/t_i^{10.5}$$

and

$$f_i^{(1)} = -0.026\,76 + 0.017\,70/t_i^{2.8} + 0.040/t_i^{3.0} - 0.003/t_i^{6.0} - 0.002\,28/t_i^{10.5} \, .$$

We have to note that this correlation gives fair estimates for nonpolar gases for the reduced temperatures $t > 1$, which is the case for methane at the nucleation point (p,T) in Fig. 1. For $t < 1$, which is the case for n-nonane, the third virial coefficient rapidly decreases and becomes negative. The negative branch of $C(T)$ is very hard to observe experimentally [19], therefore predictions of $C(T)$ in this temperature domain become less reliable. The effective third virial coefficient reads

$$\bar{C} = x_{A,0} C_A + x_{B,0} C_B \, .$$

Equilibrium properties of the binary mixture at (p,T) are found from the Redlich-Kwong-Soave equation of state

$$p = \frac{\rho k_B T}{1 - b_m \rho} - \frac{a_m \rho^2}{1 + b_m \rho} \, .$$

Expressions for the parameters a_m and b_m are given in [22], Chap. 4. Figure 3 shows the equilibrium p-T lines for the mixture; each line corresponds to a fixed value of the equilibrium vapor molar fraction of n-nonane, $y_{A,0}$.

There is a lack of experimental data on surface tension of mixtures at high pressures. For estimating $\gamma_0(p,T)$ we use an empirical "parachor method" (MacLeod-Sugden correlation) [22], Chap. 12:

$$[\gamma_0(p,T)]^{1/4} = \sum_{i=A}^{B} [P_i] \left[\frac{x_{i,0}}{v_0^l} - \frac{y_{i,0}}{v_0^v} \right] .$$

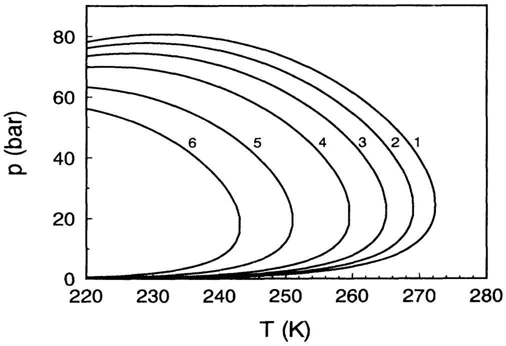

FIG. 3. Equilibrium p-T diagram for the n-nonane–methane mixture. Each line corresponds to a fixed value of the equilibrium vapor molar fraction of n-nonane: 1, $y_{A,0} = 1 \times 10^{-4}$; 2, $y_{A,0} = 8 \times 10^{-5}$; 3, $y_{A,0} = 6 \times 10^{-5}$; 4, $y_{A,0} = 4 \times 10^{-5}$; 5, $y_{A,0} = 2 \times 10^{-5}$; 6, $y_{A,0} = 1 \times 10^{-5}$.

B. Results

We analyze nucleation in the n-nonane–methane mixture at temperature $T = 240$ K and pressures $1 \le p \le 60$ bar and compare it with experimental data of Looijmans, Luijten, and van Dongen [24] and predictions of CBN.

The behavior of thermodynamic parameters $Q, \alpha_\gamma, \alpha_s, h$ defined in Sec. III is shown in Fig. 4. Negative Q corresponds to the low pressure domain $p < 18$ bar; the surface tension in this domain has the Tolman form. A physical explanation of this result follows from the fact that at low pressures the light component (methane) is present in the liquid phase at relatively small amounts $x_{B,0} \ll x_{A,0}$ and nucleation of the binary mixture does not differ much from the nucleation of the pure heavy component (nonane); therefore in this domain only the Tolman correction term for the surface tension survives. However, the *numerical value* of the Tolman length α_γ effectively takes into account the presence of a certain amount of methane in the condensed phase. A Tolman regime is found again for large pressures $p > 54$ bar, but in this domain due to possible mutual cancellation of various effects.

In the intermediate domain of pressures $18 < p < 54$ bar both the Tolman and the α_s terms in (17) are important. The exponent h decreases with pressure. The singularity point $Q = Q_*$ corresponds to $p \approx 44$ bar.

The results for the nucleation rate for $T = 240$ K are presented in Fig. 5 along with the experimental data of [24]. In this figure labels are the corresponding pressures in bars: horizontal labels refer to the theoretical lines, inclined labels to the sets of experimental points. Theoretical predictions appear to agree well with experiment for $10 \le p \le 30$ bar: the difference between experiment and theory is approximately one order of magnitude. The comparison becomes worse for $p = 40$ bar—about a two to three orders of magnitude differences; however, for this pressure experimental data possess rather large scattering. Figure 6 displays the predictions of CBN [25] along with the same set of experimental data as in Fig. 5. CBN essentially underestimates the nucleation rate: the

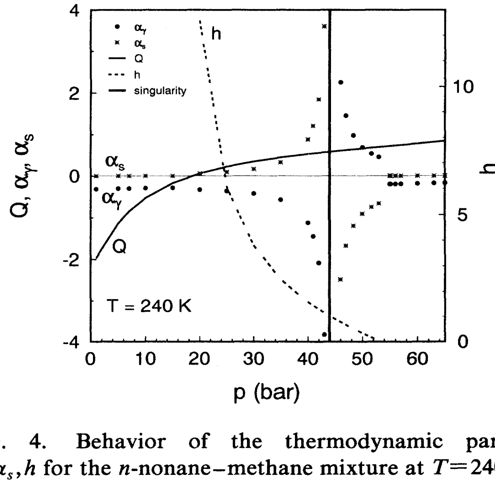

FIG. 4. Behavior of the thermodynamic parameters $Q, \alpha_\gamma, \alpha_s, h$ for the n-nonane–methane mixture at $T = 240$ K as a function of pressure. The singularity point $Q = Q_*$ (thick vertical line) corresponds to $p \approx 44$ bar.

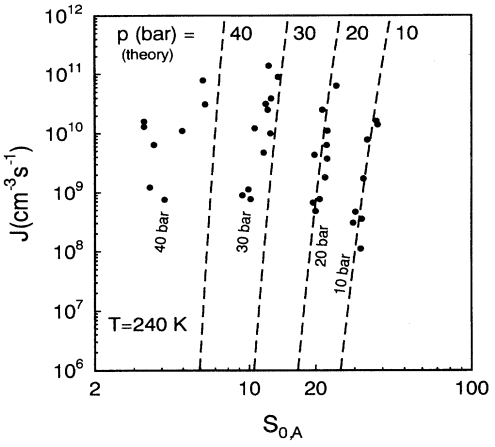

FIG. 5. Nucleation in the *n*-nonane–methane mixture at $T=240$ K as a function of partial supersaturation of *n*-nonane $S_{A,0}$. Dashed lines, present theory; closed circles, experimental data of [24]. Labels are the corresponding pressures in bars (horizontal labels refer to the lines, inclined labels to experimental data).

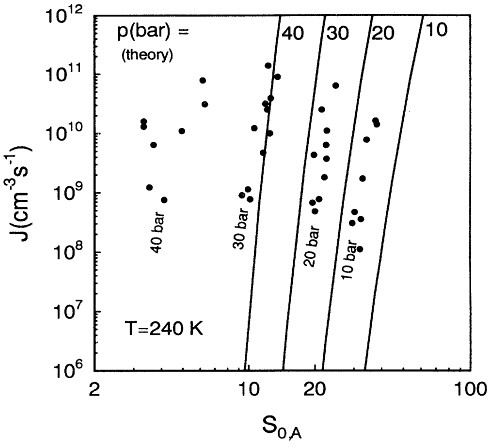

FIG. 6. Nucleation in the *n*-nonane–methane mixture at $T=240$ K as a function of partial supersaturation of *n*-nonane $S_{A,0}$. Solid lines, CBN; closed circles, experimental data of [24]. Labels are the corresponding pressures in bars (horizontal labels refer to the lines, inclined labels to experimental data).

discrepancy with experiments varies from three orders of magnitude at $p=10$ and 20 bar up to nearly 15 orders of magnitude at 40 bar.

It must be noted that accuracy of our theoretical predictions is related to the accuracy of surface tension for the plane interface $\gamma_0(p,T)$ and accuracy of the third virial coefficient.

VI. CONCLUSIONS

We have proposed an effective one-component model for homogeneous vapor-liquid nucleation of nonideal binary mixtures in the region of retrograde condensation. A transformation from the original binary to an effective unary system is accompanied by renormalization of surface tension. The latter quantity effectively takes into account composition, surface enrichment, and curvature effects. The thermodynamics of the effective system is based on the generalized Fisher droplet model with the renormalized surface tension; this model is applied at the effective saturation point. This is different from the phenomenological model for the energy barrier inherent to CBN. The theory results in a closed form expression for the nucleation rate Eq. (33). It contains no adjustable parameters. As is common for an effective medium approach, "individual" information about species in the critical cluster is lost: particles of the effective system are indistinguishable.

The theory was applied to the *n*-nonane–methane mixture at conditions corresponding to the retrograde condensation. Calculated nucleation rates agree fairly well with the recent experimental data whereas predictions of CBN are poor: for high pressures the discrepancy between CBN and experiment is up to 15 orders of magnitude. One of the merits of the present approach is that it can be extended to nucleation in multicomponent mixtures.

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