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Semiphenomenological effective-medium theory of multicomponent nucleation

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We propose an effective-medium approach for homogeneous vapor-liquid nucleation of multicomponent mixtures in the regime of retrograde condensation. Transformation to an effective unary system is accompanied by renormalization of the surface tension. We formulate a generalized Fisher droplet model [M. E. Fisher, Physics **3**, 255 (1967)] for the cluster distribution in the effective system. A closed-form expression for the nucleation rate is obtained within the framework of the kinetic approach to nucleation. The theory contains no adjustable parameters. Two- and four-component mixtures of hydrocarbons are studied and theoretical predictions are compared with available experimental data. [S1063-651X(97)14602-5]

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I. INTRODUCTION

Theory of multicomponent homogeneous nucleation was proposed by Hirschfelder in 1974 [1] as an extension of the classical binary nucleation theory of Reiss [2]. The latter is in its turn a generalization of the Becker-Döring-Zeldovich phenomenological theory of one-component nucleation [3,4]. According to [1] the Gibbs free formation energy $\Delta G(n_1, \ldots, n_N)$ of a liquid droplet, containing $n_1, \ldots, n_N$ molecules of components $1, \ldots, N$, respectively, in a supersaturated vapor mixture forms a saddle-shaped surface in the N-dimensional space such that ΔG^* represents the height at the saddle. The steady-state nucleation rate is given by

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

where T is the temperature and k_B the Boltzmann constant. In Hirschfelder's approach the kinetics of nucleation (contained in the preexponential factor J_0) is based on the assumption, inherited from Reiss' theory, that droplet growth across the saddle point goes in the direction of steepest descent on the ΔG surface; in other words the form of $\Delta G(n_1, \ldots, n_N)$ alone determines the direction of growth. In 1976 Stauffer [5] proposed a different expression for the prefactor J_0 in the binary nucleation model. 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. More recently, Trinkaus [6] generalized Stauffer's result for multicomponent systems.

A peculiar thing about mixtures is the existence of surface enrichment [7], meaning that the composition inside the droplet can be different from that near its surface (due to adsorption)—an effect not present in a single-component case. Wilemski [7] proposed ''a revised classical binary nucleation theory,'' in which surface enrichment is taken into account under the capillarity approximation by distinguishing between bulk and surface molecules of each species and applying the Gibbs-Duhem equation for the bulk and the Gibbs adsorption equation for the surface. Obviously, Willemski's considerations hold for general multicomponent systems. It is worth noting that the thermodynamical part of the theory remains incomplete: extra relationships specifying surface composition *in the vicinity* of the saddle point are necessary for calculation of the free energy surface. However, this incompleteness affects only the prefactor J_0 which has a minor influence on the nucleation rate as the latter is dominated by the exponent ΔG^*. Thus, the crucial point of any nucleation theory is the choice of a model for the energy barrier of cluster formation. This choice manifests itself in determination of the size and composition of the critical nucleus.

Recent experiments by Looijmans *et al.* [8,9] on nucleation of binary mixtures of hydrocarbons exhibiting a retrograde condensation behavior showed, in agreement with earlier studies [10–13], that the classical binary model fails because it inaccurately predicts the composition of the critical nucleus and does not take into account curvature effects. Similar remarks can be referred to the multicomponent model of [1]. Unfortunately, there is a lack of experimental data on multicomponent nucleation in spite of its significance from the fundamental and application point of view. One of the important application aspects of the problem is the formation of a mist of droplets during expansion of natural gas (which is a mixture of more than 40 components, predominantly hydrocarbons). Condensation of natural gas in a Wilson expansion cloud chamber has been studied recently by Muitjens *et al.* [14], who determined the onset of condensation by means of a light scattering technique.

As far as the theoretical description of the multicomponent problem is concerned, it seems to be practically hopeless to solve it straightforwardly in view of its large dimensionality (e.g., natural gas). Therefore, an effective-medium approach is a plausible and appropriate approximation. Besides dimensionality, one has to bear in mind that a purely phenomenological model by its nature has obvious drawbacks which show up already in a single-component case. A *semiphenomenological approach* representing a combination of statistical mechanical treatment of clusters and empirical data seems to be most promising, especially as far as a quantitative description of nucleation in complex substances is concerned. For a single-component nucleation this has been demonstrated by various authors [15–17].

Recently we have formulated an effective-medium approach to binary nucleation at conditions of retrograde condensation [18,19]. In the present paper we extend it to multicomponent nucleation at conditions of retrograde condensation. The main objective of this approach is to propose a theory resulting in quantitative predictions of nucleation rate which could be directly compared with experiment. To achieve this goal we replace the problem of nucleation in the original multicomponent system by nucleation in an effective unary system. In view of the exponential dependence of the nucleation rate on ΔG^*, an effective one-component system to be defined should possess the same energy barrier as the original one. Once an effective system is formulated it can be treated within the framework of the semiphenomenological kinetic approach [17].

An effective one-component model is introduced in Sec. II; its thermodynamics is discussed in Sec. III. Section IV contains the resulting expressions for the steady-state nucleation rate and critical cluster size. The proposed theory is applied to binary mixtures methane–nonane and methane–octane and a 4-component mixture methane–nonane–decane–undecane 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 mixture of totally miscible components $1,\ldots,N$ at an initially gaseous state characterized by the total initial pressure p_0, initial temperature T_0, and mole composition $\mathbf{y}=(y_1,\ldots,y_N)$; $\Sigma_{i=1}^N y_i=1$. After fast expansion the system is brought to a nonequilibrium state—characterized by the total pressure p, temperature T, and (the same) composition $\mathbf{y}$, where nucleation starts.

We focus on the regime of retrograde condensation: the nucleation point $(p,T,\mathbf{y})$ is situated *inside the vapor-liquid coexistence region* of the phase diagram. Two-phase equilibrium of the N-component mixture is characterized by equality of pressure, temperature, and each of the chemical potentials μ_i [20]:

$$\begin{gathered} p^l(T,v_0^l,\mathbf{x}^0)=p,\\ p^v(T,v_0^v,\mathbf{y}^0)=p, \qquad (2)\\ \mu_i^l(T,v_0^l,\mathbf{x}^0)=\mu_i^v(T,v_0^v,\mathbf{y}^0), \quad i=1,\ldots,N. \end{gathered}$$

Subscripts "l" and "v" refer to the liquid and vapor phase, respectively; $\mathbf{x}^0=(x_1^0,\ldots,x_N^0)$ and $\mathbf{y}^0=(y_1^0,\ldots,y_N^0)$ are the equilibrium liquid and vapor composition, respectively; v_0 is the molecular volume. In view of the normalization $\Sigma_{i=1}^N x_i^0=\Sigma_{i=1}^N y_i^0=1$, the conditions (2) represent a system of $N+2$ equations containing $2+2(N-1)=2N$ unknowns: $v_0^l,v_0^v;x_1^0,\ldots,x_{N-1}^0$; $y_1^0,\ldots,y_{N-1}^0$. The system of equations can be completed by conservation laws for particles of each species resulting in

$$\mathbf{x}^0L_f+\mathbf{y}^0(1-L_f)=\mathbf{y}, \qquad (3)$$

where L_f (an extra unknown variable) denotes the liquid molar fraction (i.e., ratio of the number of moles in the liquid phase to the total number of moles in the system). Condition (3) results in $N-1$ independent equations. Thus, we have $2N+1$ unknowns and the same number of independent equations. They can be solved with the help of an appropriate equation of state for a mixture (see, e.g., [21]). Our assumption that the nucleation point $(p,T,\mathbf{y})$ describes the retrograde condensation means that there exists a unique nontrivial solution of Eqs. (2) and (3). At the p-T plane (see Fig. 1) the boundary of the coexistence region (a "coexistence envelope") can be thought of as a set of equilibrium pressure-temperature points corresponding to $L_f=0$. Inside the coexistence region equilibrium p-T lines correspond to (can be parametrized by) $L_f>0$. Outside the coexistence envelope there is no two-phase equilibrium.

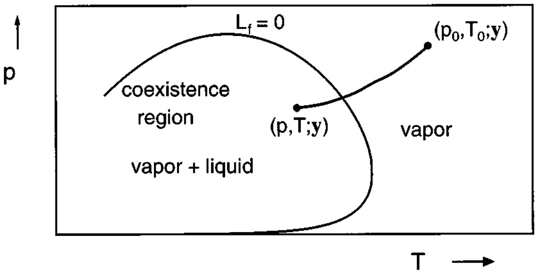

FIG. 1. Schematic representation of nucleation in a multicomponent mixture in the regime of retrograde condensation: $(p_0,T_0,\mathbf{y})$, initial gaseous state; $(p,T,\mathbf{y})$, nucleation point situated inside the coexistence region. Coexistence envelope corresponds to $L_f=0$.

A degree of metastability of component i can be characterized by a "metastability parameter"

$$S_i=\frac{y_ip}{y_i^0p}=\frac{y_i}{y_i^0}, \quad i=1,\ldots,N \qquad (4)$$

which is an experimentally controllable quantity. It has a direct analogy in a single-component nucleation where it reduces to a familiar definition of a supersaturation. Note that the language of the vapor-phase activities $a_i^v\equiv y_ip/p_{\mathrm{sat},i}(T)$, where $p_{\mathrm{sat},i}(T)$ is a saturation vapor pressure of a pure component i at the temperature T, cannot always be appropriate: for some of the components the critical temperature can be lower than T and therefore $p_{\mathrm{sat},i}(T)$ does not exist (see Sec. V).

A peculiarity of the multicomponent nucleation problem is a dependence of the energy barrier ΔG^* on the *a priori* unknown bulk composition of the critical nucleus $x_i^*=n_i^*/\Sigma_{i=1}^N n_i^*$ (the upper star 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 N-component system. It implies that an effective system should have the same energy barrier. Though the classical 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 equations for the critical cluster read [1]

$$\Delta\mu_i^*+\frac{2\gamma^*v_i^{l*}}{r^*}=0, \quad i=1,\ldots,N, \qquad (5)$$

where $\Delta\mu_i^* = \mu_i^{l*} - \mu_i^{v*}$ is the difference between chemical potentials of component i in the liquid and vapor phases at the same total vapor pressure p, temperature T, and composition $\mathbf{x}^*$; r^* is the radius of the critical nucleus, γ^* the surface tension, and v_i^{l*} a molecular volume of the component i in the liquid phase. The value of the free energy barrier is then given by

$$\Delta G^* = \frac{4\pi}{3}\gamma^* {r^*}^2$$

(clusters are assumed to be spherical). Multiplying Eq. (5) by x_i^* and summing up over all i, we obtain

$$r^* = -\frac{2\gamma^* v^*}{\sum_{i=1}^{N} x_i^* \Delta\mu_i^*}$$

where $v^* = \Sigma_{i=1}^{N} x_i^* v_i^{l*}$ is a mean bulk molecular volume in the liquid phase. Thus, the energy barrier reads

$$\Delta G^* = \frac{16\pi}{3}\,\frac{{\gamma^*}^3 {v^*}^2}{\left(\sum_{i=1}^{N} x_i^* \Delta\mu_i^*\right)^2}. \tag{6}$$

The classical *single-component* nucleation theory gives for the energy barrier the following result [22]:

$$\Delta G^* \equiv \Delta G_{n_c} = \frac{16\pi}{3}\,\frac{\gamma^3 {v^l}^2}{(\Delta\mu)^2}, \tag{7}$$

where n_c is the number of particles in the critical cluster, γ the surface tension, v^l the molecular volume in the liquid phase, and $\Delta\mu$ the chemical potential difference. An obvious similarity between Eqs. (6) and (7) suggests that an effective system should have parameters satisfying in the first approximation the following conditions: $\gamma = \gamma^*, v^l = v^*$,

$$\Delta\mu = \Delta\mu^* \equiv \sum_{i=1}^{N} x_i^* \Delta\mu_i^*. \tag{8}$$

For an N-component liquid droplet with radius r^* and composition $\mathbf{x}^*$ in equilibrium with a surrounding N-component vapor we can write, using incompressibility of the liquid phase [23],

$$\frac{2\gamma^*}{r^*} = \frac{k_B T}{v_i^{l*}} \ln\left(\frac{p_i}{p_i^{\mathrm{coex}}}\right) - (p - p^{\mathrm{coex}}), \quad i = 1, \dots, N, \tag{9}$$

where $p^{\mathrm{coex}}(\mathbf{x}^*, T)$ is the pressure corresponding to coexistence between bulk vapor and bulk liquid (plane interface) with composition $\mathbf{x}^*$; p_i is the partial pressure of component i, p_i^{coex} the same quantity referring to a plane interface. Comparison of this expression with Eq. (5) shows that $\Delta\mu_i^*$ can be written in the form

$$\Delta\mu_i^* = -k_B T \ln S_i^* \quad (i = 1, \dots, N),$$

where the quantity S_i^* is defined as

$$S_i^* = \frac{p_i}{p_i^{\mathrm{coex}}} \exp\left[-\frac{(p - p^{\mathrm{coex}}) v_i^{l*}}{k_B T}\right]. \tag{10}$$

In view of Eq. (5) all $\Delta\mu_i^*$ are negative and therefore all S_i^* are larger than unity; thus, one can say that S_i^* describes a supersaturation of component i in the critical cluster. From Eqs. (8) and (10) we obtain

$$\Delta\mu^* = -k_B T \ln\left[\prod_{i=1}^{N} (S_i^*)^{x_i^*}\right]. \tag{11}$$

Comparison of Eq. (11) with its single-component analog $\Delta\mu = -k_B T \ln S$, where S is a supersaturation of a single-component vapor, shows that in the same approximation the quantity

$$S^* = \prod_{i=1}^{N} (S_i^*)^{x_i^*} \tag{12}$$

plays the role of a supersaturation in the effective unary system. An important feature of our effective-medium approach is the self-consistency with respect to S^*: the definition of S^* contains the critical cluster composition in the original multicomponent system, which itself is a function of the supersaturation. This is an essential difference with the pure single-component case in which supersaturation is an independent parameter.

We suppose that the difference between the actual total pressure p and $p^{\mathrm{coex}}(\mathbf{x}^*, T)$ is small, which means that $\mathbf{x}^*$ does not differ much from the equilibrium composition $\mathbf{x}^0(p, T, \mathbf{y})$. Then one can develop a perturbation model *in the liquid composition difference* $\Delta\mathbf{x}^* = (\mathbf{x}^* - \mathbf{x}^0)$. In its framework S_i^* can be related to a metastability parameter as

$$S_i^* = S_i[1 + \epsilon_i(\Delta\mathbf{x}^*)],$$

where the unknown function $\epsilon_i \rightarrow 0$ as $\Delta\mathbf{x}^* \rightarrow 0$. These considerations applied to Eq. (12) yield

$$S^* = \overline{S}(1 + \Psi^*), \tag{13}$$

where the reference contribution

$$\overline{S} = \prod_{i=1}^{N} S_i^{x_i^0} \tag{14}$$

has the same structure as S^* but the unknown critical composition is replaced by the known equilibrium composition. The function Ψ^* is treated as an unknown small perturbation accounting for composition, surface enrichment, and curvature effects incorporated in S^*. It should vanish as $\Delta x^* \rightarrow 0$ which corresponds to the large values of the critical radius. It is reasonable, therefore, to assume a power law form:

$$\Psi^* = \alpha_s^{(0)} \left(\frac{1}{r^*}\right)^{h+1}, \tag{15}$$

where $\alpha_s^{(0)}$ and $h\,(h > -1)$ are unknown parameters to be determined. Substituting Eq. (13) into the energy barrier given by Eq. (6) and linearizing in Ψ^* we obtain

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

where

$$\Psi_1^* = -\,\frac{2}{3}\,\frac{1}{\ln \overline{S}}\,\Psi^*. \tag{17}$$

Analyzing Eq. (16) one can conclude that nucleation in the original multicomponent system is similar to nucleation in the effective one-component system having a supersaturation $\overline{S}$ and characterized by the *renormalized surface tension*

$$\gamma_1^* = \gamma^*(1+\Psi_1^*). \tag{18}$$

This consideration gives us a possibility of operating with the effective system since its supersaturation is now fixed by the input conditions $(p,T,\mathbf{y})$; composition, surface enrichment, and curvature effects incorporated in S^* are ''transformed'' to the renormalized surface tension. From Eqs. (4) and (14) it follows that the effective pressure, $\overline{p}$, of the one-component system can be written as

$$\overline{p} = \left[\prod_{i=1}^{N} y_i^{x_i^0}\right] p, \tag{19}$$

while the effective saturation pressure reads

$$\overline{p_{\mathrm{sat}}} = \left[\prod_{i=1}^{N} (y_i^0)^{x_i^0}\right] p. \tag{20}$$

The ratio of these two quantities yields a common definition of the supersaturation of a one-component vapor: $\overline{p}/\overline{p_{\mathrm{sat}}} = \overline{S}$. The effective molecular volume can be approximated by the equilibrium liquid-phase molecular volume of the original system: $v^* \approx v_0^l$.

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 [25]:

$$\gamma^* = \gamma_0\left[1 + \alpha_\gamma^{(1)}\frac{1}{r^*}\right], \tag{21}$$

where the leading term, γ_0, is the surface tension of the infinite plane interface for the vapor-liquid equilibrium of the original multicomponent system. An unknown function $\alpha_\gamma^{(1)}$ represents a ''Tolman length.'' The classical single-component nucleation theory [22] establishes the following relationship between the supersaturation and the radius of the critical cluster:

$$\frac{1}{\ln \overline{S}} = \frac{k_B T}{2\gamma_0 v_0^l}\, r^*. \tag{22}$$

From Eqs. (15), (17), (18), and (22) γ_1^* reads

$$\gamma_1^* = \gamma_0\left[1 + \alpha_\gamma^{(1)}\frac{1}{r^*} + \alpha_s^{(1)}\left(\frac{1}{r^*}\right)^h\right], \tag{23}$$

where

$$\alpha_s^{(1)}(p,T) = -\,\frac{1}{3}\,\frac{k_B T}{\gamma_0 v_0^l}\,\alpha_s^{(0)}. \tag{24}$$

On the right-hand side of Eq. (23) 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 should be positive. Among the three unknown parameters $\alpha_\gamma^{(1)}$, $\alpha_s^{(1)}$, and h, which have to be determined from a thermodynamic model, the exponent h plays an exceptional role. If h is not a constant but a variable, ranging from zero to infinity, then the value $h=1$ leads to a singularity. Indeed, in this case, as it follows from Eq. (23), the unknown quantities $\alpha_\gamma^{(1)}$ and $\alpha_s^{(1)}$ lose their individual meaning—what matters is only their sum $\alpha_\gamma^{(1)} + \alpha_s^{(1)}$. This situation results in a singularity in thermodynamic properties in the vicinity of the solution with $h=1$ (for binary system it was discussed in [19]). This singularity, however, does not reflect a physical reality and since one cannot *a priori* exclude $h=1$ from the accessible domain it is reasonable to assign h a fixed value. In a pure single-component system it is inappropriate to continue the expansion of surface tension in powers of curvature: the $(1/r^{*2})$ correction results in a constant contribution to surface energy (since the surface area is proportional to r^{*2}) and thus this correction can play no role in the restoring force acting against distortions of the surface [26]. That is why in the *bare* surface tension γ^* we have kept only the term linear in curvature. However, for the *renormalized* quantity γ_1^* it is plausible to continue the expansion up to the second order, thus setting $h=2$. In view of the previous discussion this assumption results in a renormalization of the energy barrier and therefore eventually influences the nucleation rate. We will suppose that the form of Eq. (23) holds for all nucleus sizes (not only for the critical one). Then the surface tension of an n cluster of the effective system (i.e., a cluster containing n ''virtual monomers'') with radius

$$r_n = r_1 n^{1/3} \tag{25}$$

can be written as

$$\overline{\gamma_1}(n) = \gamma_0[1 + \alpha_\gamma n^{-1/3} + \alpha_s n^{-2/3}], \tag{26}$$

where $\alpha_\gamma = \alpha_\gamma^{(1)}/r_1$, $r_1 = [(3/4\pi)v_0^l]^{1/3}$, and

$$\alpha_s = \alpha_s^{(1)}/r_1^2. \tag{27}$$

Unknown parameters α_γ and α_s can be found from thermodynamic considerations presented in Sec. II; $\gamma_1^* = \overline{\gamma_1}(n_c)$, the critical cluster size n_c is given by the solution of the one-component nucleation problem (Sec. IV). We can estimate now the value of the perturbation parameter Ψ^* in Eq. (13). From Eqs. (24) and (27)

$$\alpha_s^{(0)} = -3\,\frac{\gamma_0 v_0^l}{k_B T}\, r_1^2 \alpha_s = -\theta_0 r_1^3 \alpha_s,$$

where

$$\theta_0 = \frac{\gamma_0 s_1}{k_B T} \tag{28}$$

is a dimensionless macroscopic surface tension, $s_1 = 4\pi r_1^2$. Then Eq. (15) with $h=2$ results in

$$\Psi^* = -\frac{\theta_0 \alpha_s}{n_c}. \tag{29}$$

III. THERMODYNAMICS OF THE EFFECTIVE SYSTEM

In this section we formulate a thermodynamic model for the effective system. The latter represents a real gas of indistinguishable particles, namely, virtual monomers. As is commonly done in nucleation models, we assume that the real gas can be viewed as a collection of noninteracting spherical clusters which are associating and dissociating; intracluster interactions are, of course, important. In particular, we will be interested in the cluster distribution at the effective saturation point, $\rho_{n,\mathrm{sat}}$, since the latter quantity enters into the ''kinetic expression'' for the nucleation rate studied in Sec. IV.

Let q_n be the configuration integral for the n cluster in a domain of volume V [27]. The grand partition function of the system can be written in an exponential form [28]:

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

where z is the fugacity. As a result the pressure equation of state, which we apply at the saturation point, $\overline{p}_{\mathrm{sat}} V = k_B T (\ln \Xi)_{\mathrm{sat}}$, reads

$$\frac{\overline{p}_{\mathrm{sat}}}{k_B T} = \sum_{n=1}^{\infty} \left(\frac{q_n}{V} z^n\right)_{\mathrm{sat}} \tag{30}$$

(subscript ''sat'' refers to the effective saturation point). The number density of n clusters is

$$\rho_{n,\mathrm{sat}} = \left(\frac{q_n}{V} z^n\right)_{\mathrm{sat}}.$$

With the help of the standard thermodynamic transformations it can be rewritten in a Boltzmann form:

$$\rho_{n,\mathrm{sat}} = \frac{1}{V} e^{-\beta \Omega_{n,\mathrm{sat}}}, \quad \beta = 1/k_B T, \tag{31}$$

where the grand potential

$$\Omega_{n,\mathrm{sat}} \equiv -k_B T \ln(q_n / \Lambda^{3n}) - n\mu_{\mathrm{sat}} \tag{32}$$

represents the energy barrier for an n-cluster formation at the saturation point, μ_{sat} a chemical potential of a monomer, and Λ its de Broglie wavelength. The equation of state is therefore a sum of ideal gas contributions of various clusters:

$$\frac{\overline{p}_{\mathrm{sat}}}{k_B T} = \sum_{n=1}^{\infty} \rho_{n,\mathrm{sat}}. \tag{33}$$

The overall vapor number density at saturation is then by definition

$$\rho^{v}_{\mathrm{sat}} = \sum_{n=1}^{\infty} n \rho_{n,\mathrm{sat}}. \tag{34}$$

Equations (33) and (34) are quite general and do not depend on a specific form of the configuration integral, or, equivalently, a form of $\Omega_{n,\mathrm{sat}}$. We will specify $\Omega_{n,\mathrm{sat}}$ by formulating a *generalized Fisher droplet model*, which is an extension of the classical Fisher model [28] to a multicomponent mixture:

$$\beta \Omega_{n,\mathrm{sat}} = \beta \overline{\gamma_1}(n) s_1 n^{2/3} + \overline{\tau} \ln n - \ln(\overline{q_0} V). \tag{35}$$

The first term on the right-hand side represents a dimensionless surface energy of a cluster. 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. As it is known, the individual Fisher parameters of the component i, τ_i, and $q_{0,i}$ are related to its critical pressure $p_{c,i}$, temperature $T_{c,i}$, and number density $\rho_{c,i}$ via [29]

$$\rho_{c,i} = q_{0,i} \zeta(\tau_i - 1), \quad p_{c,i} = q_{0,i} k_B T_{c,i} \zeta(\tau_i), \tag{36}$$

where $\zeta(x) = \Sigma_{n=1}^{\infty} n^{-x}$ is the Riemann zeta function; τ_i satisfies $2 < \tau_i < 3$ [17]. It is reasonable to suggest that the effective parameters $\overline{q_0}$ and $\overline{\tau}$ should be related in a similar way to the critical properties of the effective system. The latter can be approximated by the *pseudocritical properties* of the mixture [21]. For the pseudocritical temperature $\overline{T_c}$ and the compressibility factor $\overline{Z_c}$ a simple mole fraction average method is satisfactory:

$$\overline{T_c} = \sum_{i=1}^{N} x_i^0 T_{c,i}, \tag{37}$$

$$\overline{Z_c} = \sum_{i=1}^{N} x_i^0 Z_{c,i}, \tag{38}$$

where $Z_{c,i}$ is the critical compressibility factor of the pure component i. The pseudocritical pressure is given by the modified Prausnitz-Gunn combination:

$$\overline{p_c} = \frac{\overline{Z_c} k_B \overline{T_c}}{\sum_{i=1}^{N} x_i^0 / \rho_{c,i}}. \tag{39}$$

Finally, the pseudocritical number density reads

$$\overline{\rho_c} = \left(\sum_{i=1}^{N} x_i^0 \frac{1}{\rho_{c,i}}\right)^{-1}. \tag{40}$$

The weights according to the liquid composition are chosen in order to ensure that components dominating in the liquid phase give the major contribution to the nucleation behavior, in particular to the energy barrier. From Eq. (36) we find that $\overline{\tau}$ should satisfy the equation

$$\frac{\zeta(\overline{\tau})}{\zeta(\overline{\tau} - 1)} = \overline{Z_c} \tag{41}$$

and $\overline{q_0}$ is given by

$$\overline{q_0}=\frac{\overline{\rho_c}}{\zeta(\overline{\tau}-1)}. \tag{42}$$

From Eqs. (31), (35), (26), and (28) we obtain for the cluster distribution

$$\rho_{n,\mathrm{sat}}=\overline{q_0}\exp[-\theta_0(1+\alpha_\gamma n^{-1/3}+\alpha_s n^{-2/3})n^{2/3}-\overline{\tau}\ln n]. \tag{43}$$

For the two unknown parameters α_γ and α_s we have two equations (33) and (34). The saturation pressure is defined by Eq. (20) and the saturation vapor density [left-hand side of Eq. (34)] can be expressed by means of the virial expansion [30],

$$\rho^v_{\mathrm{sat}}\approx\frac{\overline{p_{\mathrm{sat}}}}{k_BT}-\overline{B}\left(\frac{\overline{p_{\mathrm{sat}}}}{k_BT}\right)^2, \tag{44}$$

where $\overline{B}$ is the second virial coefficient of the effective system. It is calculated using the standard (theoretically rigorous) bilinear mixing rule [31]:

$$\overline{B}=\sum_i\sum_j x_i^0x_j^0B_{ij}, \tag{45}$$

where $B_{ii}\equiv B_i$ are pure component second virial coefficients at temperature T and the structure of unlike terms B_{ij} is described in [21]. Not too close to the critical conditions (i.e., when $\theta_0>1$) the series on the right-hand side of Eqs. (33) and (34) rapidly converge due to the exponent in $\rho_{n,\mathrm{sat}}$. Truncating both of them at $n=2$ we obtain

$$\frac{\rho_{1,\mathrm{sat}}}{\overline{q_0}}=Z_0+q_B,$$

$$\frac{\rho_{2,\mathrm{sat}}}{\overline{q_0}}=\quad -q_B,$$

where the dimensionless quantities on the right-hand side are $Z_0=\overline{p_{\mathrm{sat}}}/(\overline{q_0}k_BT)$, $q_B=\overline{q_0}\overline{B}Z_0^2$. The validity of the truncated virial expansion requires that $|q_B/Z_0|\ll 1$, which means that the number density of dimers should be much less than the number density of monomers. Given $\rho_{1,\mathrm{sat}}$ and $\rho_{2,\mathrm{sat}}$ we find α_γ and α_s from Eq. (43) written for $n=1$ and 2:

$$\alpha_\gamma=\frac{-\frac{1}{\theta_0}\ln\left(2^{\overline{\tau}}\frac{\rho_{2,\mathrm{sat}}}{\overline{q_0}}\right)+\frac{1}{\theta_0}\ln\left(\frac{\rho_{1,\mathrm{sat}}}{\overline{q_0}}\right)}{a-1}-a-1, \tag{46}$$

$$\alpha_s=\frac{-a\frac{1}{\theta_0}\ln\left(\frac{\rho_{1,\mathrm{sat}}}{\overline{q_0}}\right)+\frac{1}{\theta_0}\ln\left(2^{\overline{\tau}}\frac{\rho_{2,\mathrm{sat}}}{\overline{q_0}}\right)}{a-1}+a, \quad a\equiv 2^{1/3}. \tag{47}$$

Thus, all thermodynamic parameters of the effective system are defined.

IV. STEADY-STATE NUCLEATION RATE

Kinetics of nucleation in the effective 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 characterized by the steady-state nucleation rate J. In the framework of the kinetic approach to one-component nucleation formulated by Katz *et al.* [32] (see also [17]),

$$J=\sqrt{\frac{H''(n_c)}{2\pi}}\ \overline{\nu}s_{n_c}(\overline{S})^{n_c}\rho_{n_c,\mathrm{sat}}. \tag{48}$$

Here $s_n=s_1n^{2/3}$ is the surface area of an n cluster,

$$\overline{\nu}=\frac{\overline{p}}{\sqrt{2\pi\overline{m}k_BT}}$$

is monomer flux to the unit surface (effective impingement rate), and $\overline{m}$ the effective molecular mass. In order to determine $\overline{m}$ we note that the molecular masses of the components, $m_i=M_i/N_A$ (M_i is the molar weight of the component i and N_A the Avogadro number), enter the kinetics of the original multicomponent system only via the impingement rates:

$$\nu_i=\frac{p_i}{\sqrt{2\pi m_ik_BT}}, \quad i=1,\dots,N.$$

The effective pressure (19) can be written as

$$\overline{p}=\prod_{i=1}^N p_i^{x_i^0}=\left(\prod_{i=1}^N \nu_i^{x_i^0}\right)\sqrt{2\pi k_BT\left(\prod_{i=1}^N m_i^{x_i^0}\right)}$$

thus yielding

$$\overline{m}=\prod_{i=1}^N m_i^{x_i^0}, \quad \overline{\nu}=\prod_{i=1}^N \nu_i^{x_i^0}. \tag{49}$$

Function $H(n)$ in Eq. (48) is defined as

$$H(n)=\ln[\overline{\nu}s_n(\overline{S})^n\ \ \rho_{n,\mathrm{sat}}]. \tag{50}$$

The critical cluster size is given by minimization of H:

$$H'(n_c)=0, \quad '=d/dn.$$

Substitution of the cluster distribution (43) into this equation yields

$$-n_c\ln\overline{S}+\frac{2}{3}\theta_0n_c^{2/3}+\frac{1}{3}\theta_0\alpha_\gamma n_c^{1/3}+\overline{\tau}-\frac{2}{3}=0. \tag{51}$$

The final expression for the nucleation rate reads

TABLE I. Thermophysical properties of hydrocarbons [21]: M (g/mol), molecular weight; T_c (K), critical temperature; p_c (bar), critical pressure; ρ_c(cm^{-3}), critical number density; ω, Pitzer's acentric factor; $[P]$, parachor.

Component	M (g/mol)	T_c (K)	p_c (bar)	ρ_c (cm^{-3})	ω	$[P]$
methane	16.043	190.4	46.0	6.07×10^{21}	0.001	53.9
octane	114.232	568.8	24.9	1.22×10^{21}	0.398	350.6
nonane	128.259	594.6	23.13	1.09×10^{21}	0.445	387.6
decane	142.286	617.7	21.2	1.00×10^{21}	0.489	429.7
undecane	156.313	638.8	19.7	0.91×10^{21}	0.535	471.0

$$J=\frac{1}{3}\sqrt{\frac{\theta_0}{\pi}(1+\alpha_\gamma n_c^{-1/3})+\frac{9}{2\pi}\left(\overline{\tau}-\frac{2}{3}\right)n_c^{-2/3}}\times\frac{\overline{p}s_1}{\sqrt{2\pi\overline{m}k_BT}}\overline{q_0}\;(\overline{S})^{n_c}\times\exp[-\theta_0(1+\alpha_\gamma n_c^{-1/3}+\alpha_s n_c^{-2/3})n_c^{2/3}-\overline{\tau}\ln n_c]. \tag{52}$$

Concluding formulation of the theory, we note that it is valid provided that $\rho_{2,\mathrm{sat}}/\rho_{1,\mathrm{sat}}\ll 1$ and $|\Psi^*|\ll 1$. These validity conditions can be written as

$$|\epsilon_{\mathrm{vir}}|=\left|\frac{\overline{B}\;\overline{p}_{\mathrm{sat}}}{k_BT}\right|\ll 1 \quad\text{and}\quad |\Psi^*|=\left|\frac{\theta_0\alpha_s}{n_c}\right|\ll 1. \tag{53}$$

V. RESULTS: NUCLEATION IN MIXTURES OF HYDROCARBONS

We apply the proposed theory to hydrocarbons: binary mixtures, nonane–methane and octane–methane, and a 4-component mixture, methane–nonane–decane–undecane. Individual thermophysical properties of the components are listed in Table I. Equilibrium state of a mixture [Eqs. (2) and (3)] is calculated on the basis of the Redlich-Kwong-Soave equation of state [21]:

$$p=\frac{\rho k_BT}{1-b_m\rho}-\frac{a_m\rho^2}{1+b_m\rho}, \tag{54}$$

where ρ is the number density; expressions for coefficients a_m and b_m are given in [21], Chap. 4. Second virial coefficients of the pure components $B_i(T)$ are found from the corresponding state correlation for nonpolar substances [21], Chap. 3:

$$B_i=\frac{k_BT_{c,i}}{p_{c,i}}\left[0.083-\frac{0.422}{t_i^{1.6}}+\omega_i\left(0.139-\frac{0.172}{t_i^{4.2}}\right)\right], \tag{55}$$

where $t_i=T/T_{c,i}$, ω_i is Pitzer's accentric factor. There is a lack of experimental data on surface tension of mixtures at high pressures. For estimating γ_0 we use an empirical ''parachor method'' (MacLeod-Sugden correlation) [21], Chap. 12:

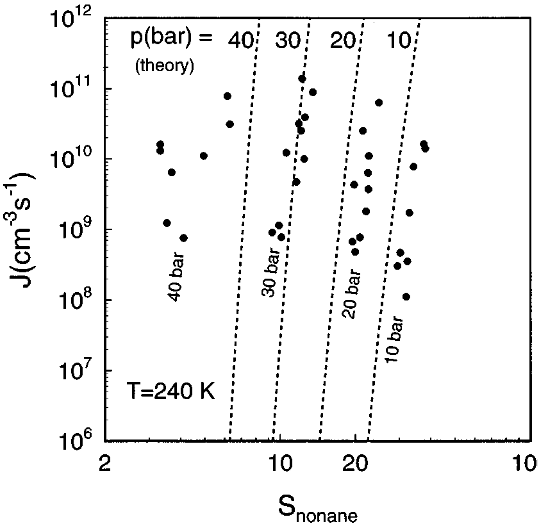

FIG. 2. Nucleation in the mixture nonane–methane at $T=240$ K as a function of a metastability parameter of nonane S_{nonane}. Dashed lines, new theory; closed circles, experiment [8]. Labels are the total nucleation pressures in bars (horizontal labels refer to the lines, inclined labels refer to experimental data).

$$\gamma_0^{1/4}=\sum_{i=1}^{N}[P_i]\left(\frac{x_i^0}{v_0^l}-\frac{y_i^0}{v_0^v}\right), \tag{56}$$

where $[P_i]$ is a parachor of component i.

Calculation steps are summarized as follows: (a) from the input conditions $(p,T,\mathbf{y})$ and the equation of state (54) equilibrium calculations (2) and (3) are performed yielding $\mathbf{x}^0$, $\mathbf{y}^0$, v_0^l, and v_0^v; (b) with the help of the parachor method (56) the equilibrium value of the macroscopic surface tension γ_0 is found; (c) effective parameters—pressure $\overline{p}$, saturation pressure $\overline{p}_{\mathrm{sat}}$, supersaturation $\overline{S}$, second virial coefficient $\overline{B}$, molecular mass $\overline{m}$, Fisher parameters $\overline{\tau}$, and $\overline{q_0}$—are determined from Eqs. (19), (20), (14), (45), (49), (41), and (42), respectively; (d) parameters α_γ and α_s of the renormalized microscopic surface tension are found from Eqs. (46) and (47); (e) the critical cluster size n_c is a (unique) real solution of the cubic equation (51); (f) from Eq. (52) the steady-state nucleation rate J is calculated; the validity conditions (53) are checked.

A. Binary mixtures

The equilibrium state of a binary mixture is determined by fixing two degrees of freedom, p and T. Equations (2) and (3) are thus separated: $x_1^0(p,T)$, $y_1^0(p,T)$, $v_0^l(p,T)$, and $v_0^v(p,T)$ are found from Eq. (2) whereas the liquid fraction is

$$L_f(p,T,y_1)=\frac{y_1-y_1^0(p,T)}{x_1^0(p,T)-y_1^0(p,T)}.$$

1. Nonane–methane

We analyze nucleation in the mixture n-nonane–methane at a temperature $T=240$ K and total nucleation pressures $10\leqslant p\leqslant 40$ bars. At high pressures the real gas effects are highly pronounced and both of the com-

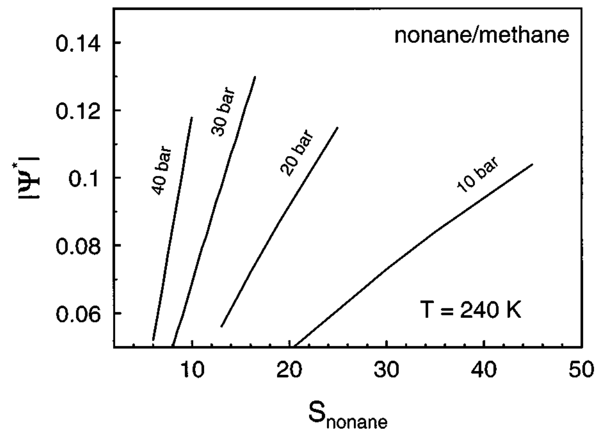

FIG. 3. Behavior of Ψ^* for the mixture nonane–methane at $T = 240$ K as a function of a metastability parameter of nonane $S_{\rm nonane}$. Labels are total pressures in bars.

ponents are present in the condensed phase in considerable amounts. Nucleation rate vs the metastability parameter of nonane $S_{\rm nonane}$ is presented in Fig. 2 along with the experimental data of [8]. A peculiar feature of these experiments is that a very small amount of nonane ($y_{\rm nonane} \sim 10^{-4}$–$10^{-5}$) causes considerable nucleation involving methane into the critical cluster. Should it be pure, methane would never condense at $T = 240$ K since its critical temperature is lower than T (see Table I). In Fig. 2 labels are the corresponding total nucleation pressures in bars; horizontal labels refer to the theoretical lines, inclined labels refer to the sets of experimental points. Theoretical predictions appear to agree well with experiment for $10 \leqslant p \leqslant 30$ bars: the difference between experiment and theory is approximately 1–2 orders of magnitude. Comparison becomes worse for $p = 40$ bars; however, for this pressure experimental data possess rather large scattering. Figure 3 shows the behavior of the perturbation parameter Ψ^*. For all the results presented it remains small ($|\Psi^*| < 0.14$) thus satisfying the validity condition (53). Calculated values of the parameters θ_0, α_γ, and α_s of the renormalized surface tension are given in Table II along with the values of the virial expansion parameter $\epsilon_{\rm vir}$. The latter remains small in agreement with condition (53). As the total pressure increases the macroscopic surface tension θ_0 drops as an increasing amount of methane is dissolved in the liquid phase. An interesting feature of these results is that α_γ and α_s have different signs, which means that they lead to mutually competing contributions to the microscopic surface tension and therefore to the nucleation barrier.

Figure 4 displays the predictions of classical binary nucleation theory [33] along with the same set of experimental data as in Fig. 2. Classical theory essentially underestimates the nucleation rate: the discrepancy with experiments varies from 3 orders of magnitude at $p = 10$ bars up to 15 orders of magnitude at 40 bars.

TABLE II. Thermodynamic parameters of the binary mixture nonane–methane at the temperature $T = 240$ K.

p (bar)	θ_0	α_γ	α_s	$\lvert\epsilon_{\rm vir}\rvert$
10.000	15.108	-0.443	0.132	0.18×10^{-3}
20.000	13.121	-0.530	0.224	0.61×10^{-3}
30.000	11.287	-0.641	0.339	0.19×10^{-2}
40.000	9.600	-0.780	0.483	0.55×10^{-2}

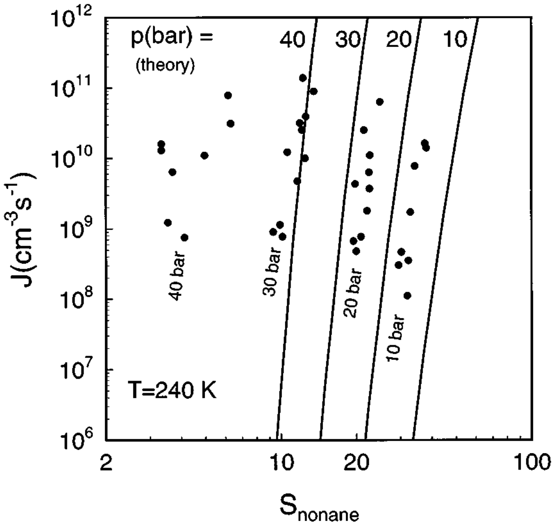

FIG. 4. Nucleation in the mixture nonane–methane at $T = 240$ K as a function of a metastability parameter of nonane $S_{\rm nonane}$. Solid lines, classical theory [33]; closed circles, experiment [8]. Other notations are the same as in Fig. 2.

2. Octane–methane

Calculation of the nucleation behavior of the mixture octane–methane at the same temperature $T = 240$ K and total nucleation pressures $10 \leqslant p \leqslant 40$ bars is presented in Figs. 5 (new theory) and 6 (classical theory). Results possess the same features as those of nonane–methane.

B. Four-component mixture

On the basis of the proposed theory we have studied nucleation in a 4-component mixture of hydrocarbons—methane–nonane–decane–undecane—with a composition

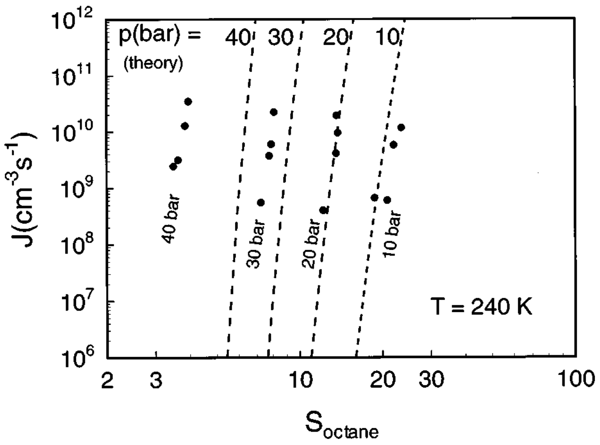

FIG. 5. Nucleation in the mixture octane–methane at $T = 240$ K as a function of a metastability parameter of octane $S_{\rm octane}$. Dashed lines, new theory; closed circles, experiment [9]. Other notations are the same as in Fig. 2.

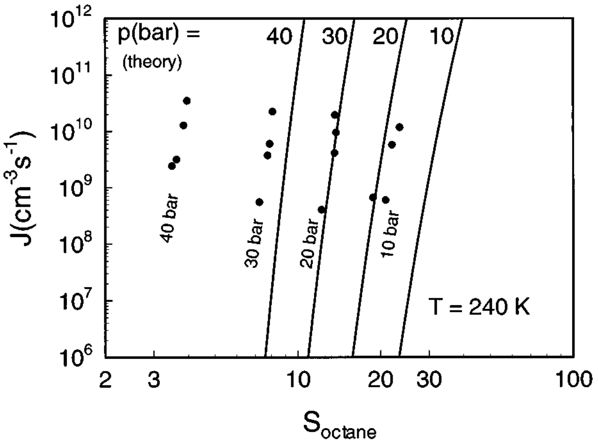

FIG. 6. Nucleation in the mixture octane–methane at $T=240$ K as a function of a metastability parameter of octane S_{octane}. Solid lines, classical theory; closed circles, experiment [9]. Other notations are the same as in Fig. 2.

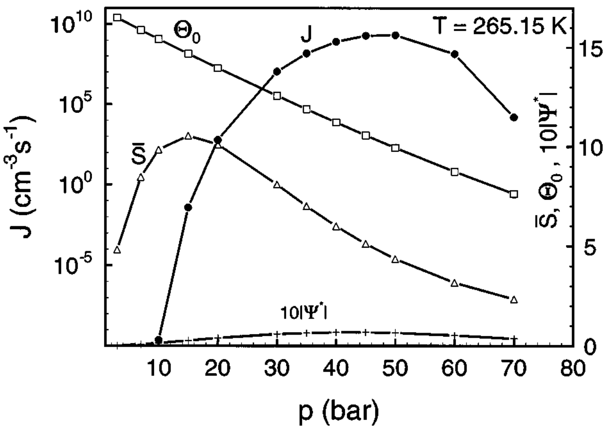

FIG. 7. Nucleation in the mixture methane–nonane–decane–undecane. Pressure dependence of nucleation rate J, effective supersaturation $\bar{S}$, and macroscopic surface tension θ_0 at $T=265.15$ K. Also shown is the behavior of Ψ^*.

approximately corresponding to that of natural gas [14] (see Table III). A peculiar feature of the natural gas is similar to the one we discussed earlier, namely, a very small total molar fraction of heavy hydrocarbons (nonane, decane, undecane)—$\approx 4\times 10^{-4}$ in Table III—causes considerable nucleation involving the light component (methane) into the critical cluster. Figure 7 shows the dependence of the nucleation rate on the total nucleation pressure p at $T=265.15$ K. As one can see, J has a maximum $\sim 10^9$ $\text{cm}^{-3}\,\text{s}^{-1}$ at $p\approx 50$ bars. Its presence can be understood from the p-T diagram of Fig. 1: by increasing pressure we ‘‘move’’ the system along the line $T=$ const from the lower to the upper branch of the coexistence envelope. On both branches of it $J=0$ and $\bar{S}=1$. $\bar{S}(p)$ has also a maximum which corresponds, however, to a different pressure $p_{\bar{S}}\approx 15$ bars. Separation of these two maxima can be explained by a monotonous decrease of surface tension with pressure (the same tendency as in Table II). It is interesting to note that $\bar{S}(p)$ and $\theta_0(p)$ are competing factors for J if pressure is beyond $p_{\bar{S}}$.

If the number of components is large it is important to ascertain which of them gives the major contribution to the nucleation behavior. Figure 8 shows the values of a metastability parameter S_i, the equilibrium liquid composition x_i^0, and the factor $S_i^{x_i^0}$ for one particular pressure $p=40$ bars; components are ordered by their molecular weight. Heavy components are characterized by large values of S_i (S_i monotonically increases with i). At the same time the equilibrium liquid fraction x_i^0 demonstrates a nonmonotonical character: for the heaviest components (undecane) it rapidly decreases. This statement remains valid for the natural gas studied in [14]. The quantity $S_i^{x_i^0}$ has a maximum falling (in our case) on decane. Effective supersaturation $\bar{S}=\Pi_{i=1}^4 S_i^{x_i^0}\approx 6.01$.

On the basis of these considerations one can make a qualitative conclusion that the heaviest components, though characterized by increasingly high values of metastability parameter, play a minor role in the nucleation behavior. This role actually reduces to redistribution of the vapor composition $y_1,\ldots,y_N$ among the components. We hope that the qualitative and quantitative results obtained in this section will encourage experimental interest in the problem of multicomponent nucleation.

TABLE III. Composition **y** of the 4-component mixture methane–nonane–decane–undecane.

Number	Component	$y_i\times 10^6$
1	methane	999661
2	*n*-nonane	42.2600
3	*n*-decane	288.720
4	*n*-undecane	8.02

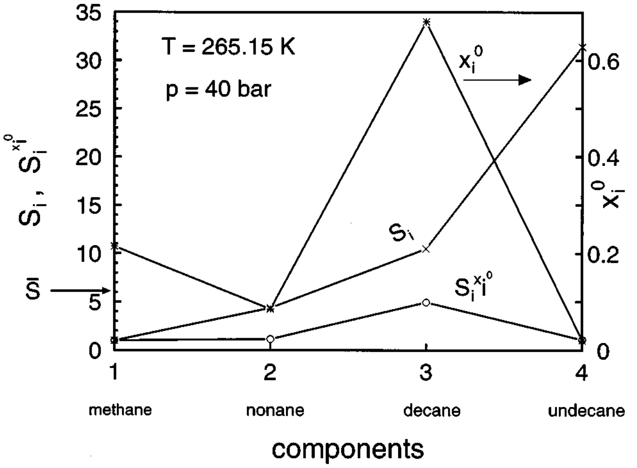

FIG. 8. Model parameters for the mixture methane–nonane–decane–undecane at $T=265.15$ K and $p=40$ bars. S_i (left y axis) and x_i^0 (right y axis) are the metastability parameter and the equilibrium liquid molar fraction of the component i. Components are ordered by their molecular weight. Also shown is $S_i^{x_i^0}$ (left y axis). Lines are drawn for visual convenience. Effective supersaturation of the mixture is $\bar{S}=\Pi_{i=1}^4 S_i^{x_i^0}\approx 6.01$.

VI. CONCLUSIONS

We have proposed an effective one-component model for homogeneous vapor-liquid nucleation of multicomponent mixtures in the regime of retrograde condensation. A transformation from the original multicomponent 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. 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. The theory results in a closed-form expression (52) for the nucleation rate. It contains no adjustable parameters.

The theory was applied to binary mixtures nonane–methane and octane–methane - and to the 4-component mixture methane–nonane–decane–undecane at conditions corresponding to the retrograde condensation. Calculated nucleation rates for binary mixtures agree fairly well with the recent experimental data, whereas predictions of the classical binary nucleation theory are rather poor. Theoretical predictions for the 4-component mixture need to be verified in future experiments.

ACKNOWLEDGMENTS

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