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Gradient theory computation of the radius-dependent surface tension and nucleation rate for *n*-nonane clusters

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The Van der Waals-Cahn-Hilliard gradient theory (GT) is applied to determine the structure and the work of formation of clusters in supersaturated *n*-nonane vapor. The results are analyzed as functions of the difference of pressures of the liquid phase and vapor phase in chemical equilibrium, which is a measure for the supersaturation. The surface tension as a function of pressure difference shows first a weak maximum and then decreases monotonically. The computed Tolman length is in agreement with earlier results [L. Gránásy, *J. Chem. Phys.* **109**, 9660 (1998)] obtained with a different equation of state. A method based on the Gibbs adsorption equation is developed to check the consistency of GT results (or other simulation techniques providing the work of formation and excess number of molecules), and to enable an efficient interpolation. A cluster model is devised based on the density profile of the planar phase interface. Using this model we analyze the dependency of the surface tension on the pressure difference. We find three major contributions: (i) the effect of asymmetry of the density profile resulting into a linear increase of the surface tension, (ii) the effect of finite thickness of the phase interface resulting into a negative quadratic term, and (iii) the effect of buildup of a low-density tail of the density profile, also contributing as a negative quadratic term. Contributions (i)–(iii) fully explain the dependency of the surface tension on the pressure difference, including the range relevant to nucleation experiments. Contributions (i) and (ii) can be predicted from the planar density profile. The work of formation of noncritical clusters is derived and the nucleation rate is computed. The computed nucleation rates are closer to the experimental nucleation rate results than the classical Becker-Döring theory, and also the dependence on supersaturation is better predicted. © 2007 American Institute of Physics.
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I. INTRODUCTION

The classical theory of nucleation of droplets from supersaturated vapors has been elaborated by Becker and Döring¹ and others. One of the fundamentals of this theory is modeling the cluster as a droplet with a sharp phase interface. In reality, the thickness of the phase interface is often comparable to the radius of the droplet. Possibly, the cluster may not even possess a core identifiable with the bulk liquid phase. It is, therefore, more realistic to consider a diffuse interface model, in which the density varies continuously across the phase interface. Such a model has been devised already by Van der Waals.² In this model, the local Helmholtz energy density not only depends on the local molar density and temperature, but also on the molar density gradient. Several interesting applications of the density gradient theory have been elaborated by Cahn and Hilliard.³ The last authors also first applied the gradient theory to nucleation.⁴ Theoretical foundations of the gradient theory and the related statistical physics background are given in the books by Rowlinson and Widom,⁵ Davis,⁶ and Kalikmanov.⁷ A recent

study of the gradient theory with comparison to molecular simulations was given by Baidakov *et al.*⁸ The gradient theory is closely related to the density functional theory, first applied to gas-liquid nucleation by Oxtoby and Evans.⁹ Both theories are based on the mean-field approximation. The gradient theory can be easily related to the classical capillarity approach. This relation is facilitated by the fact that both approaches are based on an equation of state—in the capillarity theory the equation of state is only used for the homogeneous liquid and gas regions, while in the gradient theory one single equation of state is used for the whole system, including the phase interface. The value of the capillarity theory is that it provides a simple mathematical framework and it is evidently correct for macroscopic droplets, and its weakness being that it does not give any advice concerning the dependency of the surface tension on the curvature of the phase interface. The dependency of the surface tension on curvature was first studied by Tolman,¹⁰ and semiphenomenological models were developed among others by Dillmann and Meier,¹¹ Delale and Meier,¹² and Laaksonen *et al.*¹³ A novel nucleation theory introducing a concept of microscopic surface tension was recently proposed by Kalikmanov.¹⁴

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This work represents a continuation of a long-term research of nucleation in natural gas.^{15–17} *n*-nonane represents heavy hydrocarbons dissolved in the raw natural gas. In this study, pure *n*-nonane is considered as an initial point for the analysis of nucleation in mixtures of *n*-nonane and methane at high pressures where a peculiar behavior was observed.^{18,19} The properties of *n*-nonane are well suited for nucleation experiments. Nucleation rate data are available and are obtained using expansion cloud chambers,^{20–22} static diffusion cloud chambers,^{23–27} and an expansion wave tube.^{17,28} Numerous theoretical studies concerning *n*-nonane nucleation exist. Nyquist *et al.*²⁹ computed the work of formation of critical *n*-nonane clusters using density functional theory with either the Yukawa potential and the Lennard-Jones potential. They found that the two computations almost overlapped. Gránásy^{30,31} computed the Tolman length for *n*-nonane represented with the van der Waals equation of state using the gradient theory. Barrett³² compared density functional computations with gradient theory computations based on the Peng-Robinson³³ equation of state and on the van der Waals equation of state with the Carnahan-Starling³⁴ repulsive term. Barrett³⁵ also developed a correction of the nucleation rates computed with density functional theories for inclusion of the cluster translation. Natarajan *et al.*³⁶ studied evaporation of *n*-nonane clusters by molecular dynamics. They also provided instructive snapshots of simulated clusters of sizes similar to those treated in the present work.

The paper is organized as follows. In Sec. II we give an outline of the Gibbsian droplet model and we introduce the gradient theory. Both concepts are needed because a focus of the paper is to interpret the gradient theory results within the Gibbsian framework. In Sec. III we provide the results of the gradient theory computations and develop a thermodynamics-based tool to check the internal consistency of the computations and to accurately interpolate the results. In Sec. IV we develop a model of a cluster based on the density profile of the planar phase interface. We identify several contributions to the dependency of the surface tension on the pressure difference (or supersaturation). In Sec. V we derive the work of formation of noncritical clusters and provide an expression for the nucleation rate. We compare the nucleation rates with available nucleation rate data and with the classical nucleation theory. In Sec. VI we draw conclusions. Some lengthier derivations are given in Appendix A, and a summary of thermophysical properties is given in Appendix B.

II. THEORY

A. Gibbsian droplet model

One assumes that the interior of the cluster—modeled as a microscopic droplet—is formed by a liquid at pressure p_L , which is higher than the pressure p_G of the surrounding gas phase due to the Laplace pressure,

$$p_L - p_G \equiv \Delta p = \frac{2\sigma}{r_s}, \quad (1)$$

where σ is the surface tension and r_s is the radius of the droplet. More accurately, r_s is the radius of the sphere of tension.⁵ Only for this radius definition the Laplace equation can be written in the simple form of Eq. (1). Of special importance in the classical nucleation theory is the critical cluster. The radius of the critical cluster is such that the probabilities of growing and shrinking are equal. In thermodynamic language this translates to the equality of chemical potentials of the liquid and gas phases,

$$\mu_L(p_L, T) = \mu_G(p_G, T). \quad (2)$$

In a supersaturated vapor the gas pressure p_G is greater than p_∞ , the pressure of the saturated vapor above a flat phase interface ($r_s \rightarrow \infty$). Then, Eq. (2) gives a liquid pressure p_L greater than p_∞ , and a positive pressure difference Δp . The computation is done using an equation of state valid for bulk liquid and vapor (here, the Peng-Robinson equation of state³³). The liquid density ρ_L corresponds to a compressed bulk liquid at pressure p_L . This provides a realistic picture for large clusters: Allowing for the liquid compressibility in the classical nucleation theory brings a significant improvement.³⁷ However, if the cluster is so small that the thickness of the phase interface is similar to the cluster radius, the density at the center of the cluster does not reach the bulk liquid value ρ_L . Despite that, we keep on using p_L obtained from Eq. (2) and the corresponding ρ_L in deriving the surface tension and related quantities from the results of the gradient theory, literally maintaining the Gibbsian framework. The pressure difference Δp will serve as a suitable measure of supersaturation.

If the surface tension is known, the work of formation $\Delta\Omega$ of the critical cluster can be computed as

$$\Delta\Omega = \frac{1}{3}\sigma A_s, \quad (3)$$

where $A_s = 4\pi r_s^2$ now is the surface area of the (critical) droplet. An inherent part of the classical nucleation theory is the so-called capillarity approximation: We approximate the actual surface tension of the cluster with the surface tension of the flat phase interface at thermodynamic equilibrium, a quantity which can be found in tables. Accepting the capillarity approximation, the set of equations, Eqs. (1)–(3), is complete and we can compute the work of formation.

In the present work we go beyond the capillarity approximation. Using the gradient theory we will directly compute the work of formation $\Delta\Omega$ for given conditions of the gas phase. Then, using Eqs. (1) and (3), we compute the corresponding radius and surface tension,

$$r_s = \left(\frac{3\Delta\Omega}{2\pi\Delta p} \right)^{1/3}, \quad (4)$$

$$\sigma = \left(\frac{3\Delta\Omega\Delta p^2}{16\pi} \right)^{1/3}. \quad (5)$$

The gradient theory also allows computation of the excess number of molecules ΔN . In the Gibbsian picture the excess number of molecules is given as

$$\Delta N = V_s \Delta \rho + A_s \Gamma, \quad (6)$$

where $V_s = \frac{4}{3}\pi r_s^3$ is the volume of the sphere of tension, $\Delta \rho \equiv \rho_L - \rho_G$, and Γ is the surface excess of molecules or adsorption. Equation (6) will be used to extract the adsorption Γ from gradient theory computations. From the differential analysis of the equations defining the droplet model it follows that the surface tension and adsorption are related by the Gibbs adsorption equation,⁵

$$d\sigma = -\Gamma d\mu. \quad (7)$$

This equation is valid for isothermal changes of the critical cluster and it is used such that Eq. (2) is satisfied along the path of differentiation.

Alternatively, the droplet can be modeled as a discontinuous profile without surface excess, thus defining the so-called equimolar surface and equimolar radius r_e ,

$$\Delta N = \frac{4}{3}\pi r_e^3 \Delta \rho. \quad (8)$$

The difference of the two radii is the Tolman¹⁰ length,

$$\delta \equiv r_e - r_s. \quad (9)$$

The importance of the Tolman length is in its relation to the dependence of the surface tension on the radius. In the present work we discuss rather the dependence on the pressure difference Δp . [Both are related by Eq. (1).] Using the isothermal Gibbs-Duhem equations for both phases we derive

$$d\mu = \frac{d\Delta p}{\Delta \rho}. \quad (10)$$

Substituting this expression into the Gibbs adsorption equation [Eq. (7)] we find

$$d\sigma = -t d\Delta p, \quad (11)$$

where

$$t \equiv \Gamma / \Delta \rho \quad (12)$$

has a dimension of length. For a future reference we relate t directly to the excess number of molecules ΔN . Combining Eqs. (6) and (12), we have

$$t = \frac{1}{A_s} \left(\frac{\Delta N}{\Delta \rho} - V_s \right). \quad (13)$$

The lengths δ and t can be related by comparing Eqs. (6) and (8),

$$t = \delta + \frac{\delta^2}{r_s} + \frac{\delta^3}{3r_s^2}. \quad (14)$$

For the planar interface ($r_s \rightarrow \infty$) these lengths are equal: $t_\infty = \delta_\infty$.

B. Gradient theory

The gradient theory²⁻⁴ operates with continuous density profiles $\rho(r)$. The local Helmholtz energy density of an inhomogeneous fluid comprises two terms,

$$\Phi = \Phi_{\text{hom}}(\rho) + \frac{1}{2}c \left(\frac{d\rho}{dr} \right)^2. \quad (15)$$

The first term is the Helmholtz energy density of a homogeneous fluid at the actual local density. The second term is a correction for inhomogeneity. This is represented by the gradient square term and a positive coefficient c , called the influence parameter. In this work the influence parameter is taken as independent of density. The influence parameter can be related to the direct correlation function of the homogeneous fluid. This approach is not practical for nonspherical molecules. Rather, the influence parameter is obtained by matching the experimental value of the surface tension of the flat phase interface as discussed later. The chemical potential is homogeneous throughout the system. Therefore, the grand potential density is given as

$$\omega = \Phi - \rho \mu_G. \quad (16)$$

In the homogeneous gas phase, the grand potential density reduces to $-p_G$. The work of formation of a cluster can be expressed as a difference between the grand potential of a system containing the cluster and the gas phase and the grand potential of the system containing the gas phase only,

$$\Delta \Omega = \int_0^\infty \left[\Delta \omega_{\text{hom}}(\rho) + \frac{1}{2}c \left(\frac{d\rho}{dr} \right)^2 \right] 4\pi r^2 dr, \quad (17)$$

where the excess grand potential density $\Delta \omega_{\text{hom}}$ is given as

$$\Delta \omega_{\text{hom}}(\rho) \equiv \Phi_{\text{hom}}(\rho) - \rho \mu_G + p_G. \quad (18)$$

The function $\Delta \omega_{\text{hom}}(\rho)$ is obtained from a suitable equation of state of the fluid. The surface tension of the flat interface can be obtained in a very similar fashion,

$$\sigma_\infty = \int_{-\infty}^\infty \left[\Delta \omega_{\text{hom}}(\rho) + \frac{1}{2}c \left(\frac{d\rho}{dz} \right)^2 \right] dz, \quad (19)$$

where z is a coordinate perpendicular to the phase interface. To be able to compute the work of formation of a cluster using Eq. (18), the density profile $\rho(r)$ is required.

For the flat surface, the density profile is found by utilizing the general principle that a thermodynamic system of given volume, temperature, and chemical potential will equilibrate in a state of lowest grand potential. The task is to find a density profile minimizing integral [Eq. (19)]. The necessary condition is that the profile is stationary, i.e., for small perturbations around this profile the value of the integral will not change. This functional problem can be reduced to Euler-Lagrange equation,

$$\frac{d^2 \rho}{dz^2} = \frac{1}{c} \Delta \mu(\rho), \quad (20)$$

where

$$\Delta\mu \equiv \frac{\partial\Delta\omega_{\text{hom}}}{\partial\rho} = \mu(\rho) - \mu_G. \quad (21)$$

Equation (20) is to be solved for boundary conditions $\rho(-\infty)=\rho_L$ and $\rho(\infty)=\rho_G$, where ρ_L and ρ_G are densities of the homogeneous liquid (*L*) and gaseous (*G*) phases in thermodynamic equilibrium, determined by equating the pressures and chemical potentials. A first integral of Eq. (20) can easily be found yielding expressions for the density profile and surface tension,

$$z = \int_{\rho(0)}^{\rho(z)} \left[\frac{c}{2\Delta\omega_{\text{hom}}(\rho)} \right]^{1/2} d\rho, \quad (22)$$

$$\sigma_\infty = (2c)^{1/2} \int_{\rho_G}^{\rho_L} [\Delta\omega_{\text{hom}}(\rho)]^{1/2} d\rho. \quad (23)$$

The density profile $\rho(r)$ of the critical cluster will not minimize the grand potential, because the critical cluster is in labile (not stable) equilibrium with the gas phase. The critical density profile corresponds with a saddle point of the grand potential. Roughly speaking, it is a minimum of the grand potential with respect to variations of the shape of the cluster, and a maximum with respect to variations of its radius. This problem has been discussed by Oxtoby and Evans⁹ and by Barrett.³⁵ In the gradient theory it is possible to solve both the planar and the spherical cases by differential Euler-Lagrange equations. For the critical cluster, the Euler-Lagrange equation corresponding to the functional (17) is

$$\frac{d^2\rho}{dr^2} + \frac{2}{r} \frac{d\rho}{dr} = \frac{1}{c} \Delta\mu(\rho). \quad (24)$$

Equation (24) must be solved numerically for boundary conditions $\rho(r \rightarrow \infty) = \rho_G$ and $(d\rho/dr)(r=0) = 0$.

The above given equations are sufficient for the computation of the density profiles, the planar surface tension, and the work of formation of clusters. In addition, we mention formulas which proved useful in assessing the numerical accuracy of the computed density profiles. Let us assume that a profile $\rho(z)$ satisfies the Euler-Lagrange equation [Eq. (20)]. We use the chain rule $(d\Delta\omega_{\text{hom}}/dz) = \Delta\mu \cdot (d\rho/dz)$. Then, with Eq. (20) we obtain $d\Delta\omega_{\text{hom}}/dz = \frac{1}{2}c[d(d\rho/dz)^2/dz]$. By integration and substitution in Eq. (19), we find

$$\sigma_\infty = \int_{-\infty}^{\infty} c \left(\frac{d\rho}{dz} \right)^2 dz. \quad (25)$$

Using this result, the density gradient can be eliminated from Eq. (19). In this way we obtain

$$\sigma_\infty = 2 \int_{-\infty}^{\infty} \Delta\omega_{\text{hom}} dz. \quad (26)$$

In Eq. (25) the surface tension only depends on the density gradient. On the other hand, in Eq. (26) the surface tension is given as an integral of a function of density. Comparison of the planar surface tensions computed using these two formulas is an efficient test of the numerical accuracy of the computed profile $\rho(z)$.

Formulas analogous to Eqs. (25) and (26) for σ_∞ can be derived for the work of formation of the critical cluster,

$$\Delta\Omega = \frac{1}{3} \int_0^\infty c \left(\frac{d\rho}{dr} \right)^2 4\pi r^2 dr, \quad (27)$$

$$\Delta\Omega = -2 \int_0^\infty \Delta\omega_{\text{hom}} 4\pi r^2 dr. \quad (28)$$

These equations have a practical importance for checking the accuracy of gradient theory computations. The derivation of Eqs. (27) and (28) follows about the same line as for the planar case but requires some additional labor. We give the derivation in Appendix A. Another important output of the gradient theory computations is the excess number of molecules. For the continuous profile it is computed straightforwardly as [cf. Eq. (6)]

$$\Delta N = \int_0^\infty [\rho(r) - \rho_G] 4\pi r^2 dr. \quad (29)$$

The limit $r_s \rightarrow \infty$ (planar phase interface) deserves special attention. The Tolman length for the planar phase interface can be expressed as

$$\delta_\infty = z_e - z_s, \quad (30)$$

where z_e is the position (height) of the equimolar surface (a horizontal plane), and z_s is the position of the surface of tension. Provided that the liquid phase exists at $z \rightarrow -\infty$ and the gas phase exists at $z \rightarrow \infty$, the equimolar surface is at a position

$$z_e = \frac{1}{\rho_L - \rho_G} \left\{ \int_{-\infty}^0 [\rho(z) - \rho_L] dz + \int_0^\infty [\rho(z) - \rho_G] dz \right\}. \quad (31)$$

The position of the equimolar surface obtained in this way represents a limiting case of the equimolar surface of a spherical cluster introduced in Eq. (8). The position of the surface of tension with respect to the same coordinate system is computed based on the first moment of the gradient square term,

$$z_s = \frac{1}{\sigma_\infty} \int_{-\infty}^{\infty} c \left(\frac{d\rho}{dz} \right)^2 z dz. \quad (32)$$

Derivation of this formula is more difficult. The proof is given in Appendix A along with some other derivations.

III. RESULTS OF THE GRADIENT THEORY COMPUTATIONS

The gradient theory computations were based on the Peng-Robinson equation of state.³³ The influence parameter was obtained by fitting the orthobaric surface tension data for *n*-nonane by Jasper *et al.*³⁸ The influence parameter was computed using Eq. (23) valid for the planar phase interface. The experimental surface tension data were represented within their accuracy using a constant (temperature-independent) influence parameter $c = 3.031 \times 10^{-66} \text{ J m}^5$.

FIG. 1. Density profiles of *n*-nonane clusters at 230 K computed with the gradient theory. Profiles are computed for vapor pressure multiples $p_C/p_{\text{sat,PR}}=8, 11, 15, 22, 30, 40, 50, 70, 100, 140, 200, 300, 400, 500, 600, 800, 1000, 1200, 1500, 2000, \dots, 19000, 19500, 20000, 21000, 32000, 33000$.

The gradient theory computations of critical clusters were performed at 230 K. This isotherm was chosen because of the availability of experimental nucleation rate data. The corresponding vapor pressure computed from the Peng-Robinson equation of state was $p_{\text{sat,PR}}=3.204$ Pa. We computed 69 density profiles for vapor pressures ranging from $8p_{\text{sat,PR}}$ to $33\,000p_{\text{PR}}$. The profiles are shown in Fig. 1. For pressures smaller than $8p_{\text{sat,PR}}$ the iteration did not reach our convergence criterion (discussed below). From above, the pressure range was limited by the vapor-liquid spinodal at 1.080 bar. The computation has been carried out using the BVP4 solver in MATLAB.

Figure 2 shows the works of formation computed as an arithmetic average of formulas (27) and (28). Figure 3 shows the excess numbers of molecules, computed using Eq. (29).

FIG. 2. The work of formation $\Delta\Omega$ of *n*-nonane clusters at 230 K as a function of the pressure difference Δp . The solid line is based on Eq. (33).

FIG. 3. Excess number of molecules ΔN of *n*-nonane clusters at 230 K as a function of the pressure difference Δp . The solid line is based on Eq. (33).

ΔN is a monotonically decreasing function of Δp except very close to the spinodal where it reaches a minimum and increases again, finally diverging at $\Delta p=1081$ bars, where the spinodal is located. Close to the spinodal, a similarity solution of the Euler-Lagrange equation [Eq. (24)] can be developed as shown by Cahn and Hilliard⁴ and in more detail by Wilemski and Li.³⁹ This is a region of diffuse density fluctuations. The resulting profiles (see Fig. 1) are rather an artifact of the mean-field approximation. The clusters relevant to nucleation (at least in this study) are on the decreasing branch of the ΔN curve.

Figure 4 shows the surface tension computed using Eq. (5) from the previously determined works of formation [Eqs. (27) and (28)]. The difference of the surface tensions computed with these formulas was used as an indicator for terminating the iterative computation of the density profiles, by

FIG. 4. Surface tension of *n*-nonane clusters at 230 K as a function of the pressure difference Δp . The solid line is given by Eq. (33).

FIG. 5. Tolman length δ of n -nonane clusters at 230 K as a function of the pressure difference Δp . The solid line is based on Eq. (33).

requiring the relative difference to be smaller than 1 ppm (1×10^{-6}). Also shown in Fig. 4 is the surface tension for the planar phase interface (diamond at $\Delta p = 0$) computed with Eq. (23). With increasing Δp the surface tension initially slightly increases, reaches a maximum, and then decreases along a line approximately according to a quarter of a circle, finally vanishing at the spinodal.

Figure 5 shows the Tolman lengths (circles) computed with Eqs. (9) and (30). The x symbols are the lengths t computed using Eq. (14). Also shown is the Tolman length for the planar phase interface (diamond), computed using Eqs. (30)–(32).

The solid line in Fig. 4 is obtained by a piecewise cubic interpolation between these points. This line is a piecewise cubic,

$$f_i(\Delta p) = h_{0i} + h_{1i}\Delta p + h_{2i}(\Delta p)^2 + h_{3i}(\Delta p)^3, \quad (33)$$

with coefficients $h_{0i}, \dots, h_{3i}$ obtained from the surface tensions and lengths t in the boundary points, using Eq. (11),

$$f_i(\Delta p_i) = \sigma_i, \quad f'_i(\Delta p_i) = -t_i, \quad (34)$$

$$f_i(\Delta p_{i+1}) = \sigma_{i+1}, \quad f'_i(\Delta p_{i+1}) = -t_{i+1}.$$

For the left conditions of the first interval we use the surface tension σ_∞ and Tolman length δ_∞ for the plane phase interface computed using Eqs. (23) and (30), respectively. A great advantage of Eq. (34) is that it enables an accurate interpolation between the planar interface and the first computed cluster. Another advantage is in checking the numerical consistency of the computations. The values (surface tensions) are computed from the works of formation $\Delta\Omega$ solely, whereas the slopes are computed based on the excess numbers of molecules ΔN . If the computed density profiles were inaccurate, the resulting line would be wavy. The solid line $t(\Delta p)$ interconnecting the t values (crosses) shown in Fig. 5 is a piecewise quadratic curve obtained by derivation of the cubic Eq. (33), $t(\Delta p) = -(df/d\Delta p)$. Here again we observe that the line is fluent. Numerical inconsistency would result

FIG. 6. Scaled density profiles of six largest clusters (solid lines) and the profile of the planar interface (dashed line). The profiles are translated such that the surfaces of tension of all profiles coincide. The scaled and translated density profiles are given as $[\rho(r - r_s) - \rho_G] \times (\Delta\rho_\infty/\Delta p) + \rho_{G\infty}$.

into changes of slope at computed points (the crosses). Using the computed dependency $t(\Delta p)$, the solid line interconnecting the Tolman lengths (circles) is obtained by solving Eq. (14). The solid line $\Delta\Omega(\Delta p)$ showing the dependence of the work of formation on the pressure difference in Fig. 2 is obtained by substituting the interpolated surface tension Eq. (33) into Eq. (5) and solving it for $\Delta\Omega$. The solid line $\Delta N(\Delta p)$ in Fig. 3 is obtained by solving Eq. (13) for ΔN and using the previously computed $t(\Delta p)$ and the radius of tension r_s obtained by substituting the interpolated surface tension Eq. (33) into the Laplace equation [Eq. (1)].

As shown in Fig. 5, the lengths δ and t are initially practically identical and are represented by an almost linear function of Δp . Unlike the original result by Tolman,¹⁰ the Tolman length is initially negative, corresponding to an increase in surface tension. Both lengths turn positive at $\Delta p \approx 200$ bars, where the surface tension has its maximum. For smaller clusters (large Δp) the length t diverges faster from the straight line. On the other hand, the behavior of the Tolman length δ is more complex, showing two inversion points. The observed behavior of the Tolman length is in very good agreement with results by Gránásky³¹ obtained with the Van der Waals equation of state.

IV. DEPENDENCE OF THE SURFACE TENSION OF CRITICAL CLUSTERS ON THE PRESSURE DIFFERENCE Δp

A. A cluster model based on the density profile of the planar phase interface

In Fig. 1, one observes that the density profiles of large clusters appear as copies of a horizontally translated curve. Figure 6 shows profiles of six largest clusters and the profile of the planar interface translated such that the surfaces of tension of all profiles coincide. It can be seen that the profiles almost collapse into one single curve. The only noticeable

difference is the low-density tail which builds up on the gaseous side of the profile as the gas pressure is increased. This feature will be discussed later in greater detail. Besides the fact that the profiles almost coincide, we emphasize the circumstance that this happens when the *surfaces of tension* are taken as the origin of coordinates. A substantially worse result would be obtained when the equimolar surfaces were translated to the origin. This indicates that the position of the surface of tension with respect to the profile is fixed, whereas the position of the equimolar surface changes when the curvature is varied.

Inspired by these observations, we develop an approximate cluster model. Quantities related to the model will be denoted with a subscript m . We construct the density profile of a cluster of given radius of tension r_{sm} in the following manner. Let $\rho_\infty(z)$, $-\infty < z < \infty$, be a density profile of the planar phase interface with the origin positioned in the surface of tension ($z_s=0$). The function $\rho_\infty(r-r_{sm})$ is the profile translated in a manner that the original surface of tension is located at a radius r_{sm} . Further we create a mirror image $\rho_\infty(-r-r_{sm})$, sum up both functions, and scale them linearly to a function

$$y(r) \equiv \frac{\rho_\infty(r-r_{sm}) + \rho_\infty(-r-r_{sm}) - \rho_{L\infty} - \rho_{G\infty}}{\Delta\rho_\infty}. \quad (35)$$

Here we denoted $\Delta\rho_\infty \equiv \rho_{L\infty} - \rho_{G\infty}$. Function $y(r)$ varies between zero (gas) and unity (liquid). The approximate density profile of a cluster is then obtained as

$$\rho_m(r) = \rho_G + \Delta\rho y(r), \quad (36)$$

where $\Delta\rho$ is the difference of densities of the bulk liquid and gas phases. The density difference $\Delta\rho$ depends on r_{sm} , but for now we leave it undetermined. By design, Eq. (36) provides an excellent approximation for relatively large clusters (droplets); for small clusters it is at least qualitatively correct—the derivative of the density with respect to r vanishes at the center.

As a next step we express the excess number of molecules scaled by the density difference,

$$\Delta N_m / \Delta\rho = \frac{1}{\Delta\rho} \int_0^\infty [\rho_m(r) - \rho_G] 4\pi r^2 dr = \int_0^\infty y(r) 4\pi r^2 dr. \quad (37)$$

Equation (37) can already be evaluated numerically. We show the dependence of $\Delta N_m / \Delta\rho$ on the radius of the surface of tension, r_{sm} . We substitute $r=r_{sm}+z$ and by a tedious derivation we obtain a simple result,

$$\begin{aligned} \Delta N_m / \Delta\rho &= \int_{-r_{sm}}^\infty y(r_{sm}+z) 4\pi (r_{sm}+z)^2 dz \\ &= 4\pi \left(\frac{1}{3} r_{sm}^3 + K_0 r_{sm}^2 + 2K_1 r_{sm} + K_2 \right), \end{aligned} \quad (38)$$

where we introduced moments

$$K_k \equiv \frac{1}{\Delta\rho_\infty} \left\{ \int_{-\infty}^0 [\rho_\infty(z) - \rho_{L\infty}] z^k dz + \int_0^\infty [\rho_\infty(z) - \rho_{G\infty}] z^k dz \right\}. \quad (39)$$

We note that $K_0 = \delta_\infty$. For a “symmetric” profile—profile whose derivative $d\rho/dz$ is an even function of z —all even moments ($K_0, K_2, \dots$) vanish. In this sense, δ_∞ is the most significant measure of the asymmetry. Further, we note that all odd moments ($K_1, K_3, \dots$) are necessarily positive. Let us consider a simplistic symmetric profile, linearly decreasing from $\rho_{L\infty}$ at $z=-L/2$ to $\rho_{G\infty}$ at $z=L/2$. The moments of this profile are $K_0=0$, $K_1=L^2/24$, $K_2=0$, $K_3=L^4/320, \dots$. We see that $(K_1)^{1/2}$ characterizes the thickness of the profile, therefore, we introduce a thickness L_1 , defined as

$$L_1 \equiv (24K_1)^{1/2}. \quad (40)$$

Having determined the moments K_0, K_1 , and K_2 , we continue the analysis of the surface tension of clusters. Substituting Eq. (38) for ΔN in Eq. (13) we obtain the length t_m ,

$$t_m = \frac{1}{A_{sm}} \left(\frac{\Delta N_m}{\Delta\rho} - V_{sm} \right) = K_0 + 2K_1 q_{sm} + K_2 q_{sm}^2, \quad (41)$$

where $A_{sm} \equiv 4\pi r_{sm}^2$, $V_{sm} \equiv \frac{4}{3}\pi r_{sm}^3$, and $q_{sm} \equiv 1/r_{sm}$ is the curvature of the surface of tension. According to Eq. (11), the length t determines the dependence of the surface tension on the pressure difference Δp . However, t as given by Eq. (41) is a function of the curvature q , not of Δp . To obtain an integrable equation, we combine Eq. (11) with the Laplace equation Eq. (1) to

$$\frac{d \ln \sigma}{dq} = - \frac{2t(q)}{1 + 2t(q)q}. \quad (42)$$

We substitute Eq. (41) for t and integrate,

$$\frac{\sigma_m}{\sigma_\infty} = \exp \left[-2 \int_0^{q_{sm}} \frac{K_0 + 2K_1 q + K_2 q^2}{1 + 2K_0 q + 4K_1 q^2 + 2K_2 q^3} dq \right]. \quad (43)$$

The integral can be easily evaluated by numerical quadrature. Once the surface tension is given as a function of q_{sm} , we compute the corresponding pressure difference from the Laplace equation $\Delta p = 2\sigma_m q_{sm}$. The corresponding pressure of the gas phase is obtained by solving the equation $\mu_L(p_G + \Delta p) = \mu_G(p_G)$. Liquid and gas densities are obtained from the equation of state for the respective pressures.

For moderate Δp it is possible to develop a Taylor expansion of surface tension with respect to Δp by combining Eq. (43) and the Laplace equation. In this way we find a series

$$\sigma_m = \sigma_\infty - K_0 \Delta p - \frac{K_1}{2\sigma_\infty} \Delta p^2 - \frac{4K_0 K_1 + K_2}{12\sigma_\infty^2} \Delta p^3 + \dots \quad (44)$$

The cubic and higher terms become significant at high Δp , where the center of the cluster is influenced by the phase interface and, consequently, the original function Eq. (43) is

FIG. 7. (Circles) Surface tension computed with the gradient theory. (Solid line) Interpolating function Eq. (34). (Dashed line) Surface tension given by Eq. (43). (Dotted line) Approximation by Eq. (45). (Dash-dotted line) quadratic expansion Eq. (47). The rectangle shows the range of critical clusters relevant for nucleation experiments (Refs. 17, 22, and 24).

inaccurate. Therefore, we reduce our analysis to the quadratic representation of the surface tension,

$$\sigma_m \approx \sigma_\infty - \delta_\infty \Delta p - \frac{L_1^2}{48\sigma_\infty} \Delta p^2, \quad (45)$$

and the corresponding linear expression for the length t ,

$$t_m \approx \delta_\infty + \frac{L_1^2}{24\sigma_\infty} \Delta p. \quad (46)$$

We determined that $\delta_\infty < 0$. Therefore, the function $\sigma_m(\Delta p)$ is initially increasing in exact agreement with the density gradient results. The quadratic term is positive, so that the function $\sigma_m(\Delta p)$ bends down, forming a maximum. However, the magnitude of the coefficient of the quadratic term is insufficient to fully explain the shape of the $\sigma_m(\Delta p)$ curve as computed by the gradient theory.

Figure 7 shows that the quadratic expansion, Eq. (45), is a good approximation to the values obtained from the original approximation given by Eq. (43). Both equations overestimate the surface tension as given by the gradient theory. Also shown is a quadratic expansion of the gradient theory results,

$$\sigma \approx \sigma_\infty + (d\sigma/d\Delta p)_\infty \Delta p + \frac{1}{2} (d^2\sigma/d\Delta p^2)_\infty (\Delta p)^2. \quad (47)$$

The last equation provides a good approximation to the gradient theory results in a broad range of Δp , including the range relevant for nucleation experiments. The linear terms of Eqs. (45) and (47) are equal. The only difference is in the quadratic term. The approximative quadratic coefficient $-L_1^2/(48\sigma_\infty)$ represents a major part (77%, in the case computed) of the accurate coefficient $\frac{1}{2}(d^2\sigma/d\Delta p^2)_\infty$.

B. Effect of the low-density tail of the density profile

A subtle feature can be recognized in Fig. 6: Abuildup of the low-density tail of the density profile. We will show that

FIG. 8. Radial distribution of the residual t_{res} approximated by Eq. (50) for eight largest clusters. The curves are obtained for individual clusters as $dt_{\text{res}}/dr \approx [\rho(r) - \rho_m(r_s; r)]r^2/(\Delta p r_s^2)$, where $\rho(r)$ is the profile given by the gradient theory, and $\rho_m(r_s; r)$ is the cluster model based on the density profile of the planar phase interface. The circles indicate the position of the surface of tension (r_s). The smaller the cluster, the higher the maximum.

this feature is responsible for the difference between the gradient theory results and the predictions based on the cluster model Eq. (36). We analyze the difference in terms of the length t . We define a residual

$$t_{\text{res}} \equiv t - t_m, \quad (48)$$

where t is given by the full gradient theory and t_m is given by Eq. (41). Both t and t_m are evaluated for the same thermodynamic condition of the gas phase, that means for the same Δp . By iterating Eq. (43) and the Laplace equation for the given Δp we find a radius of tension, r_{sm} . Because t_m in Eq. (48) corresponds to the approximate radius r_{sm} , we denote it as $t_m(r_{sm})$. The value of r_{sm} slightly differs from the accurate radius r_s , obtained directly from the gradient theory via Eq. (4). To be able to elucidate the origin of t_{res} , we also construct the model cluster, Eq. (36), for the exact r_s and compute the corresponding $t_m(r_s)$. We modify Eq. (48) to

$$t_{\text{res}} = [t - t_m(r_s)] + [t_m(r_s) - t_m(r_{sm})]. \quad (49)$$

We will show later that the expression in the second square brackets is negligible. The residual t_{res} is essentially given by the first bracketed expression. Using Eqs. (13) and (29) we find

$$t_{\text{res}} \approx t - t_m(r_s) = \int_0^\infty \frac{[\rho(r) - \rho_m(r_s; r)]r^2}{\Delta p r_s^2} dr, \quad (50)$$

where $\rho(r)$ is the density profile of the cluster as given by the gradient theory and $\rho(r_s; r)$ is the density profile of the model cluster Eq. (36) constructed for given accurate r_s . Figure 8 shows the integrands of Eq. (50) for eight largest clusters as functions of the radial coordinate r . The circle on each curve indicates the position of the surface of tension (r_s). Most significant feature is the hump right of the surface of tension, corresponding to the low-density tail of the density profile. The residual t_{res} is essentially given by the area below these

humps. With increasing Δp (and correspondingly decreasing r_s), the width of the humps remains about the same, but the height increases proportionally to Δp . This gives rise to the proportionality of t_{res} to Δp .

We assumed that the expression in the second square brackets in Eq. (49) can be neglected. We prove this assumption. For $t_m(r_{sm})$ we use expression Eq. (41). The same expression, but with q_{sm} exchanged for $q_s \equiv 1/r_s$, can be used for $t_m(r_s)$. In this way we obtain

$$t_m(r_s) - t_m(r_{sm}) = 2K_1(q_s - q_{sm}) + K_2(q_s^2 - q_{sm}^2). \quad (51)$$

Substituting further from the corresponding forms of the Laplace equation $q_s = \Delta p / (2\sigma)$, and $q_{sm} = \Delta p / (2\sigma_m)$, using expansions Eq. (44) for $\sigma_m(\Delta p)$, and Eq. (47) for $\sigma(\Delta p)$, and performing Taylor expansion, we obtain

$$t_m(r_s) - t_m(r_{sm}) = -\frac{K_1}{2\sigma_\infty^2} \left[\frac{K_1}{\sigma_\infty} + \left(\frac{d^2\sigma}{d\Delta p^2} \right)_\infty \right] (\Delta p)^3 + o[(\Delta p)^4]. \quad (52)$$

We conclude that approximation Eq. (50) is accurate except for terms of the order of $(\Delta p)^3$ and higher, which become significant at rather high Δp . This justifies the use of Eq. (50) to explain the origin of the residual t_{res} .

V. VAPOR-LIQUID NUCLEATION OF *n*-NONANE

A. Noncritical clusters and nucleation kinetics

The gradient theory (the density functional theory in general) in the present form only enables computation of critical clusters. However, the works of formation for noncritical clusters can be estimated. The relatively easy case that the vapor is an ideal gas was studied by Talanquer and Oxtoby.⁴⁰ Interaction with the gas phase can be incorporated applying the “noncritical nucleation theorem,” derived by Hruby⁴¹ and Bowles *et al.*⁴² We assume that the cluster is defined by some microscopic constraint. For the case of clusters in the gas phase, a suitable constraint is the number of molecules N forming a cluster. To fix ideas, the Band⁴³-Stillinger⁴⁴ cluster of overlapping spheres can be assumed. When the condition of the vapor changes at constant temperature and constant N , the theorem says that the work of formation is changed as

$$d(\Delta\Omega_N) = -\Delta N_N d\mu_G. \quad (53)$$

From this relation, the classical nucleation theorem⁴⁵ can be derived. Here another aspect is important. By integrating at constant N , changing the condition of the vapor isothermally from the chemical potential μ_N^* , at which the cluster of N molecules is critical, up to the actual chemical potential of the gas phase μ_G , we obtain

$$\Delta\Omega_N(\mu_G) = \Delta\Omega_N(\mu_N^*) - \int_{\mu_N^*}^{\mu_G} \Delta N_N d\mu. \quad (54)$$

Here, $\Delta\Omega_N(\mu_N^*)$ is the work of formation of the cluster of N molecules computed with the gradient theory, and $\Delta\Omega_N(\mu_G)$ is the work of formation of the noncritical cluster. It is always possible to express the excess number of molecules as

$$\Delta N_N = N - V_N \rho_G, \quad (55)$$

where V_N represents the volume of the cluster of N molecules. Unfortunately, N is not defined in the gradient theory. A rational option is to take the volume of the sphere of tension for the volume of the cluster, $V_N = V_s = \frac{4}{3}\pi r_s^3$, and to obtain N from Eq. (55). We proceed with integrating Eq. (54):

$$\Delta\Omega_N(\mu_G) = \Delta\Omega_N(\mu_N^*) - N \cdot (\mu_G - \mu_N^*) + \int_{\mu_N^*}^{\mu_G} V_N \rho_G d\mu. \quad (56)$$

Making an approximation that V_N is independent of the condition of the gas, we find

$$\Delta\Omega_N(\mu_G) = \Delta\Omega_N(\mu_N^*) - N \cdot (\mu_G - \mu_N^*) + V_N \cdot (p_G - p_N^*), \quad (57)$$

where p_N^* is the pressure of the gas phase at the condition when the cluster of N molecules is critical. In comparison with treatment of Talanquer and Oxtoby,⁴⁰ Eq. (57) does not neglect the interactions of the cluster with surrounding gas phase.

The number density of noncritical clusters of N molecules is then obtained as

$$n_N = \frac{1}{\vartheta} \exp \left[-\frac{\Delta\Omega_N(\mu_G)}{k_B T} \right]. \quad (58)$$

In this equation, the prefactor $1/\vartheta$ accounts for the translational degrees of freedom of the cluster. The prefactor is subject to ongoing discussions.^{35,46–48} For the present computations we used the classical¹ choice of $1/\vartheta = n_1 \approx \rho_G$. The next standard step is determining the impingement rate C_N of vapor molecules on the surface of cluster of N molecules,

$$C_N = A_N n_1 \sqrt{\frac{k_B T}{2\pi M}}. \quad (59)$$

Here A_N is the surface area of the cluster, approximated as $4\pi r_s^2$, n_1 is number density of free vapor molecules (monomers), and M is molecular mass of the vapor. By solving the nucleation kinetics in the steady state we obtain the nucleation rate

$$J = \left(\sum_{N=N_{\min}}^{N_{\max}} \frac{1}{C_N n_N} \right)^{-1}. \quad (60)$$

Theoretically, the summation should run from 1 to ∞ . The actual minimum and maximum cluster sizes were taken as $N_{\min} = 2$ and $N_{\max} = 800$. The computed nucleation rates were insensitive to variation of these bounds, because the terms of Eq. (60), corresponding to clusters much smaller or bigger than the critical cluster, are small.

B. Comparison with experimental nucleation rates

The nucleation rate of *n*-nonane in helium has been measured by Hung *et al.*^{24,25} (233–313 K, 5×10^{-5} – $1 \text{ cm}^{-3} \text{ s}^{-1}$) and by Rudek *et al.*²⁷ (257–313 K, 5×10^{-4} – $5 \text{ cm}^{-3} \text{ s}^{-1}$) using an upward diffusion cloud chamber. The two data sets are consistent. Measurements by Rudek *et al.* are not considered

here because they are at higher temperatures. Expansion chamber measurements have been reported by Adams *et al.*,²⁰ Wagner and Strey,²¹ and Viisanen *et al.*²² (in argon at 230 K, ≈ 0.5 bar, $4 \times 10^5 - 2 \times 10^8 \text{ cm}^{-3} \text{ s}^{-1}$). Of the expansion chamber measurements, only the data by Viisanen *et al.* have been considered, because of their superior quality. Expansion wave tube experiments have been reported by Luijten *et al.*^{17,28} The data by Luijten *et al.* are at higher pressures: Nominally 10, 25, and 40 bars. Only the 10 bars measurements were used for the present comparisons.

For the expansion chamber and expansion wave tube experiments we reevaluated the experimental supersaturations starting from the experimental temperatures, pressures, and molar fractions. We used the saturated vapor pressure equation as given by King and Al-Najjar,⁴⁹ which was utilized by Hung *et al.*²⁴ to evaluate their diffusion cloud chamber data. We also considered the real-gas effects on supersaturation. The supersaturations were determined using definition

$$S = \exp\left(\frac{\mu_v - \mu_{v,\text{sat}}}{k_B T}\right), \quad (61)$$

where μ_v is the chemical potential of the vapor (*n*-nonane) in the nucleation condition and $\mu_{v,\text{sat}}$ is the chemical potential of the vapor at phase equilibrium with liquid, in the presence of the background gas (He or Ar) at the same chemical potential μ_g as in the nucleation condition. For the gas phase we used the virial equation of state truncated after the second virial coefficient. For the argon-argon virial coefficient we used the correlation by Bokis and Donohue.⁵⁰ The argon-nonane virial coefficient was computed according to Kaul and Prausnitz.⁵¹ The second virial coefficients for helium-helium and helium-nonane were neglected. The supersaturation [Eq. (61)] also contains the pointing effect due to the pressure of the background gas. As discussed by Fisk and Katz,⁵² the pointing effect influences both the experimental supersaturations and the nucleation theory in a very similar fashion. To enable a direct comparison of nucleation data obtained at different background pressures, we defined a supersaturation reduced to pure vapor condition as

$$S_0 = S \exp\left(\frac{p - p_{v,\text{sat}}}{k_B T \rho_L}\right). \quad (62)$$

The experimental data are at temperatures slightly deviating (up to 4 K) from the $T_{\text{nom}} = 230$ K isotherm. We adjusted the supersaturations further to compensate for this,

$$S_{\text{corr}} = S_0 \frac{S_{\text{ICCT}}(J_{\text{exper}}, T_{\text{nom}})}{S_{\text{ICCT}}(J_{\text{exper}}, T_{\text{exper}})}, \quad (63)$$

where $S_{\text{ICCT}}(J, T)$ is the inverse function to the so-called internally consistent classical nucleation theory as given by Girshick and Chiu.⁴⁶ The experimental nucleation rate data shown in Fig. 9 are corrected according to Eq. (63).

Figure 9 also shows the theoretical line computed with the gradient theory. This line was computed for given supersaturations using Eq. (60). Also shown is the classical nucleation theory by Becker and Döring

FIG. 9. Nucleation rate J of *n*-nonane clusters at 230 K as function of supersaturation S . (Circles, squares, and diamonds) Nucleation rate data by Viisanen *et al.* (Ref. 22), Luijten *et al.* (Refs. 17 and 28), and Hung *et al.* (Refs. 24 and 25), respectively. Following theoretical predictions are computed with the Peng-Robinson equation of state. (Dashed line) Classical nucleation theory (CNT) by Becker and Döring (Ref. 1), (dash-dotted line) internally consistent classical theory (ICCT) by Girshick and Chiu (Ref. 46), and (solid line) gradient theory (GT) (this work).

$$J_{\text{CNT}} = \frac{\rho_G^2}{\rho_{L\infty}} \left(\frac{2\sigma_\infty}{\pi M} \right)^{1/2} \exp\left[-\frac{4\theta^3}{27(\ln S)^2} \right], \quad (64)$$

and the internally consistent theory by Girshick and Chiu

$$J_{\text{ICCT}} = \frac{\rho_G \rho_{G\infty}}{\rho_{L\infty}} \left(\frac{2\sigma_\infty}{\pi M} \right)^{1/2} \exp\left[\theta - \frac{4\theta^3}{27(\ln S)^2} \right], \quad (65)$$

where M is the molecular mass and θ is the dimensionless surface tension,

$$\theta \equiv \sigma_\infty (36\pi)^{1/3} \rho_{L\infty}^{-2/3} / k_B T. \quad (66)$$

We also computed nucleation rates using the classical formula Eq. (64) in which the exponential $\exp[-4\theta^3/27(\ln S)^2]$ was replaced with $\exp(-\Delta\Omega_{\text{crit}}/k_B T)$, where $\Delta\Omega_{\text{crit}}$ was the work of formation of the critical cluster computed with the gradient theory. The resulting nucleation rates were about 10% higher than the nucleation rates computed with the detailed kinetics approach given in Sec. V A.

The gradient theory computations are done with the Peng-Robinson equation of state, which yields rather inaccurate vapor pressure and liquid density for *n*-nonane at 230 K. To enable a comparison of the theories, we computed the classical and internally consistent theories with the liquid density and vapor pressure given by the Peng-Robinson equation of state. The comparison with the classical theory is then quite clear: At low supersaturations the gradient theory gives lower nucleation rates than the classical theory. This is due to the fact that, for the large critical clusters, the surface tension obtained with the gradient theory (Fig. 4) is slightly higher than the planar surface tension used in the classical theory. For higher supersaturations, the critical and near-critical clusters playing the decisive role in the nucleation kinetics get smaller. According to Fig. 4, the corresponding surface tension gets smaller than at the planar phase interface

FIG. 10. Same as Fig. 9, except that the theoretical predictions CNT and ICCT are computed using accurate saturated liquid density and vapor pressure. The the gradient theory results are scaled based on the CNT (see the text).

and the nucleation rate predicted by the gradient theory gets higher than for the classical nucleation theory. As a result, the gradient theory computations predict a steeper $\log J$ versus $\log S$ line. The internally consistent theory predicts nucleation rates much closer to the experimental ones. This is mainly due to a different prefactor $1/\vartheta$ in formula (58), which is subject of ongoing discussions. In this paper we do not want to enter this discussion and we use the prefactor corresponding to the original Becker-Döring theory. In general this prefactor, whatever its value might be, is rather insensitive to supersaturation. It means that the ratio of experimental and theoretical nucleation rates should be almost constant in a broad range of supersaturations. In this respect the gradient theory performs better than the classical nucleation theory.

As already mentioned, the performance of the Peng-Robinson equation of state at 230 K is poor. Because we wanted to maintain the compatibility of the present results with a parallel work on gradient theory in hydrocarbon mixtures, we did not proceed, at this stage, by adjusting the parameters of the Peng-Robinson equation of state. In Fig. 10 we show the nucleation rates predicted with the classical nucleation theory and the internally consistent classical nucleation theory, evaluated for accurate values of saturated liquid density⁵³ and vapor pressure.⁴⁹ Now the ICCT slightly overestimates and the CNT is substantially closer than for the Peng-Robinson values. Because the gradient theory was developed here as a modification of the classical nucleation theory with a specific dependency of the surface tension on Δp , it is possible to estimate the focus of the gradient theory line corrected for the accurate saturated liquid density and saturated vapor pressure: We denote the ratio of densities of saturated liquid as given by Peng-Robinson equation state to the accurate saturated liquid density as $\ell \equiv (\rho_{L\infty})_{P-R}/(\rho_{L\infty})_{\text{accur}}$ and the ratio of densities of saturated vapor as given by Peng-Robinson equation state to the accurate saturated vapor density as $g \equiv (\rho_{G\infty})_{P-R}/(\rho_{G\infty})_{\text{accur}}$. The

scaled supersaturation is given as $S_{\text{scaled}} = S^\ell$ and the scaled nucleation rate as $J_{\text{GT,scaled}} = J_{\text{GT}} \cdot (S_{\text{scaled}}/S)^2 \cdot \ell/g^2$.

The ratio of the experimental data by Hung *et al.*²⁴ and Luijten *et al.*¹⁷ to the scaled results of the gradient theory is practically constant in the whole range of supersaturation. The slope of the data by Viisanen *et al.*²² agrees more with the classical nucleation theory.

VI. CONCLUSIONS

We performed gradient theory computations of the density profiles, works of formation, and excess numbers of molecules of *n*-nonane clusters. These results were interpreted in the framework of the Gibbsian droplet model with variable surface tension. The difference of pressures Δp of the liquid phase and vapor phase in chemical equilibrium was used as a variable characterizing the supersaturation. This interpretation allowed construction of an efficient interpolating scheme [Eq. (33)] and a check of numerical accuracy of the computations.

We devised a cluster model [Eqs. (35) and (36)] allowing us to predict the dependency of the surface tension on the pressure difference based on the density profile of the planar phase interface. The application of the model is quite simple: Using Eq. (22) we compute the density profile of the planar phase interface. Mathematically this is done by quadrature of an integral—a task much easier than solving the boundary value problem for the Euler-Lagrange equation [Eq. (24)]. The position of the surface of tension for the planar density profile is found using Eq. (32), and the origin of coordinates is shifted to the surface tension. Moments K_0 and K_1 of the density profile are obtained using Eq. (39). From these moments we obtain characteristic lengths of the profile: $\delta_\infty = K_0$ characterizes the asymmetry of the density profile; $L_1 = (24K_1)^{1/2}$ characterizes the thickness of the profile. Using these lengths it is possible to compute a quadratic approximation of the surface of tension, Eq. (45).

We demonstrated that the difference of the cluster surface tension as predicted by the cluster model from the gradient theory computations is due to the buildup of low-density tail of the density profile. The tail of the density profile on the gas-phase side grows with increasing supersaturation. This feature breaks the similarity of the density profiles assumed in the cluster model. The buildup of the low-density tail contributes a minor part (23%, in the case computed) to the quadratic term of the function $\sigma(\Delta p)$, but this contribution is important in the supersaturation range corresponding to nucleation experiments. As a consequence, the model significantly overestimates the surface tension in the range relevant to nucleation experiments (cf. Fig. 7). The model is not directly related to the gradient theory—it relies on general Eq. (11). This opens the possibility of using it to estimating the size dependency of the surface tension if the planar density profile and the corresponding surface of tension are determined with different simulation methods.

We also developed a way of estimating the works of formation of noncritical cluster in order that the complete nucleation kinetics can be evaluated. Finally, we computed the nucleation rate by adaptation of the standard steady state

nucleation kinetics and compared the theoretical prediction to the experimental data. The prediction is not yet fully quantitative for several reasons. First, the performance of the Peng-Robinson equation of state at low temperatures (with respect to the critical point) is poor. Second, unresolved problem is the exact magnitude of the prefactor of Eq. (58), representing the translational degrees of freedom of the cluster. Upon the condition that a sufficiently accurate mean-field equation of state is available, the gradient theory is, with certainty, superior to the capillarity approximation, assuming a constant surface tension. On the other hand, it is to be realized that the gradient theory itself contains approximations. It is to be expected that the gradient theory performs well if the gradient length of the density profile is large in comparison with the range of the intermolecular forces. For the examples considered in this paper, this condition is only marginally met.

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APPENDIX A: SOME DERIVATIONS

In this appendix we derive several results of the gradient theory important for the present paper. Some analogous equations found in the literature⁵ are based on the pressure tensor. In this paper we avoided the introduction of the pressure tensor.

We first derive the formulas Eq. (27) and Eq. (28) suitable for the computation of the work of formation $\Delta\Omega$ for a given density profile $\rho(r)$. We make use of the fact that $d\Delta\omega_{\text{hom}}/dr = \Delta\mu \cdot d\rho/dr$. Using the Euler-Lagrange equation [Eq. (24)], we obtain

$$\frac{d\Delta\omega_{\text{hom}}}{dr} = \frac{c}{2} \frac{d}{dr} \left(\frac{d\rho}{dr} \right)^2 + \frac{2c}{r} \left(\frac{d\rho}{dr} \right)^2. \quad (\text{A1})$$

By integration from r to ∞ and using the fact that $\Delta\omega_{\text{hom}}$ vanishes in the limit $r \rightarrow \infty$, we obtain

$$\Delta\omega_{\text{hom}} = \frac{c}{2} \left(\frac{d\rho}{dr} \right)^2 - Q(r), \quad (\text{A2})$$

where

$$Q(r) \equiv \int_r^\infty \frac{2c}{r'} \left(\frac{d\rho}{dr'} \right)^2 dr'. \quad (\text{A3})$$

From Eq. (A2) we see that the quantity $Q(r)$ as the following limits:

$$Q(0) = -\Delta\omega_{\text{hom}}[\rho(0)], \quad Q(\infty) = 0. \quad (\text{A4})$$

We also note the following identity obtained by integration by parts:

$$\int_0^\infty Q(r) 4\pi r^2 dr = \frac{2}{3} \int_0^\infty c \left(\frac{d\rho}{dr} \right)^2 4\pi r^2 dr. \quad (\text{A5})$$

Now we substitute $\Delta\omega$ given by Eq. (A2) into the original expression Eq. (17) for the work of formation. Using further Eq. (A5) we obtain immediately Eq. (27), where the integrand is the square gradient only. Further, by a linear combination of $3\Delta\Omega$ given by Eq. (A5) and $-2\Delta\Omega$ given by Eq. (17), we recover expression (28) for the work of formation, where the integrand is $\Delta\omega_{\text{hom}}$.

We utilize function $Q(r)$ once more to derive a formula for the computation of the radius of the surface of tension r_s , which will be particularly useful for proving Eq. (32) used to determine the position of the surface of tension for the planar phase interface. For a large cluster (a droplet) whose center is not affected by the phase interface, the density at $r=0$ is equal to the density of the bulk liquid phase ρ_L corresponding to a given chemical potential $\mu_L = \mu_G$. Consequently, realizing that the grand potential density of a homogeneous system equals $-p$, the excess grand potential density reduces to the negative of the pressure difference,

$$\Delta\omega_{\text{hom}}(\rho_L) = [\phi_{\text{hom}}(\rho_L) - \mu_L \rho_L] + p_G = -\Delta p. \quad (\text{A6})$$

Because of the properties (A4) of function $Q(r)$, we have

$$\Delta p = Q(0) = \int_0^\infty \frac{2c}{r} \left(\frac{d\rho}{dr} \right)^2 dr. \quad (\text{A7})$$

We express the radius of the surface of tension, r_s , using Eq. (4) and use Eq. (27) for $\Delta\Omega$ and Eq. (A7) for Δp ,

$$r_s'^3 = \frac{\int_0^\infty c(d\rho/dr)^2 r^2 dr}{\int_0^\infty c(d\rho/dr)^2 r^{-1} dr}. \quad (\text{A8})$$

This expression gives an approximation r_s' of the radius of tension r_s . The approximation consists in the assumption that the density in the center reaches the bulk density ρ_L corresponding to the given chemical potential. This assumption is certainly met for macroscopic droplets. The present results (cf. Fig. 11) indicate that the convergence of $r_s' \rightarrow r_s$ as $r_s \rightarrow \infty$ is extremely fast: Already when the radius is about the same as the thickness of the phase interface [represented with L_1 , Eq. (40)], the relative difference is 1×10^{-4} ; for a radius which is twice the thickness, the difference is smaller than 1×10^{-7} , reaching the numerical accuracy. The observed relative deviations $(r_s'/r_s - 1)$ can be approximated with a function $6 \times 10^{-4} \cdot (L_1/r_s')^{17.0}$. We note the extreme value of the exponent. For clusters whose center is significantly influenced by the phase interface, r_s' is a more rational definition of the radius; it stays in the neighborhood of the inflection point of the phase interface, whereas r_s is too small. Figure 11 shows that r_s' has a minimum value of about $0.6L_1$. This is a general feature of the mean-field theory close to the spinodal.³⁹ The spatial extent of the cluster increases (diverges at the spinodal), whereas the amplitude (density difference) decreases. In the whole range, we observe $r_s' > r_s$; this indicates that Δp evaluated with Eq. (A7) is smaller than the exact value given by equality of chemical potentials Eq. (2).

FIG. 11. Relative deviation of the radius of the surface tension r'_s computed with Eq. (A8) from r_s determined with Eq. (4) as a function of the ratio of the width of the phase interface L_1 and the radius r'_s . (Solid line) Empirical correlation $(r'_s/r_s - 1) \approx 6 \times 10^{-4} (L_1/r'_s)^{17.0}$.

We will proceed now to the analysis of the position of the surface of tension for low curvature, including the flat phase interface. We chose a coordinate system (z, ρ) with origin located within (or close to) the phase interface, at a distance r_x from the center of the cluster. We substitute $r_x + z$ for r in the right-hand side of Eq. (A8), and $r_x + z'_s$ for r'_s in the left-hand side,

$$(r_x + z'_s)^3 = \frac{\int_{-r_x}^{\infty} c(d\rho/dz)^2 (r_x + z)^2 dz}{\int_{-r_x}^{\infty} c(d\rho/dz)^2 (r_x + z)^{-1} dz}. \quad (\text{A9})$$

In the denominator we use a Taylor series

$$(r_x + z)^{-1} = r_x^{-1} \left[1 + \sum_{k=1}^{\infty} (-1)^k (z/r_x)^k \right]. \quad (\text{A10})$$

Series Eq. (A10) only converges for $|z| < r_x$. Therefore, we limit the integrations to the interval $(-r_x, r_x)$. This limitation is not restrictive as far as we consider sufficiently large clusters. Performing the integration on the members of the series and denoting $q_x \equiv 1/r_x$, we obtain

$$1 + 3z'_s q_x + 3z'^2_s q^2_x + z'^3_s q^3_x = \frac{1 + 2s_1 q_x + s_2 q^2_x}{1 + \sum_{k=1}^{\infty} (-1)^k s_k q^k_x}, \quad (\text{A11})$$

where

$$s_k \equiv S_k/S_0, \quad S_k \equiv \int_{-r_x}^{r_x} c(\partial\rho/\partial z)^2 z^k dz. \quad (\text{A12})$$

The position of the surface of tension z'_s can be obtained by solving Eq. (A11). For small curvatures we expand the solution in the form of a series,

$$z'_s = s_1 + \left(-s_1 s_2 + \frac{1}{3} s_3 + \frac{2}{3} s_1^3\right) q^2_x + \left(\frac{2}{3} s_1 s_3 - \frac{1}{3} s_1^4 - \frac{1}{3} s_4\right) q^3_x + \dots \quad (\text{A13})$$

We see immediately that, for a flat phase interface, $z'_s = s_1$, which is a proof of Eq. (32).

Further, we note that a term linear in curvature is missing. Therefore, the surface of tension remains close to the position given by Eq. (32) even for quite small clusters (high curvatures). This is a special feature of the radius of the surface of tension. The equimolar surface shifts from the planar position by a distance proportional to curvature. The observation that the surface of tension stays associated with the density profile was used to construct the approximate density profile of the cluster given by Eqs. (35) and (36).

APPENDIX B: THERMOPHYSICAL PROPERTIES OF *n*-NONANE

Surface tension. The surface tension for *n*-nonane has been measured by Jasper *et al.*^{38,54} Orthobaric⁵⁷ data³⁸ span over the range of 0–60 °C and has been correlated by the authors to a linear form $\sigma(\text{mN m}^{-1}) = 24.84 - 0.09417(T/K - 273.15)$. Isobaric measurements⁵⁴ were taken in a dry nitrogen atmosphere at a total pressure of 760 Torr (101 325 Pa) in the range of 0–100 °C. The data have been correlated by the authors as $\sigma(\text{mN m}^{-1}) = 24.72 - 0.09347(T/K - 273.15)$. Adsorbed nitrogen decreases the surface tension. This effect is more pronounced at lower temperatures because the gas molecules with lower thermal energy adsorb more easily. Consequently, both the surface tension at 273.15 K and the slope have somewhat lower values for the isobaric case than for the orthobaric case. The determination of the influence parameter was based on the orthobaric data.³⁸

Liquid density. Density of the liquid *n*-nonane was computed from the fundamental equation of state by Lemmon and Span.⁵³ This equation provides a superior representation of density and other thermodynamic properties in both liquid and gas phases. The computed liquid densities are in a good agreement with earlier correlations.⁵⁵

Vapor pressure. The vapor pressure of saturated *n*-nonane has been discussed in detail by Hung *et al.*²⁴ These authors recommended equation by King and Al-Najjar,⁴⁹ although a different correlation was used in a later study by Rudek *et al.*²⁷ More recently, a generalized vapor pressure equation has been obtained by Lemmon and Goodwin⁵⁶ [their Eq. (12)]. Also, the vapor pressure can be computed from the fundamental equation of state by Lemmon and Span.⁵³ We chose the correlation by King and Al-Najjar, which seems most safe for the necessary extrapolation to low temperatures.

Equation of state. The Peng-Robinson³³ equation of state was used for the gradient theory computations. Accurate correlations of by Lemmon and Goodwin⁵⁶ were used for the critical temperature, critical pressure, and the acentric factor of *n*-nonane [their Eqs. (20), (21), and (24), respectively].

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