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Nucleation at high pressure. I. Theoretical considerations

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A theoretical approach is presented that accounts for the influence of high pressure background gases on the vapor-to-liquid nucleation process. The key idea is to treat the carrier gas pressure as a perturbation parameter that modifies the properties of the nucleating substance. Two important mechanisms are identified in this respect: With increasing carrier gas pressure, the saturated vapor density tends to increase (enhancement effect), whereas the surface tension generally decreases. Several routes to obtain data for these pressure effects are outlined, in particular for the vapor–gas mixtures that have been studied experimentally. (The results of these expansion wave tube experiments are presented in Paper II of this paper [J. Chem. Phys. **111**, 8535 (1999), following paper.] Using classical nucleation theory, a criterion is then derived for the “pressure perturbation” approach to be valid: $x_g^{\text{eq}} \ll (S-1)/S$, where x_g^{eq} is the carrier gas solubility in the liquid phase, and S is the supersaturation ratio. For the semiphenomenological Kalikmanov–Van Dongen model, the implications of the enhancement effect and surface tension decrease are briefly discussed. We also illustrate how these two effects can be obtained from (binary) density functional theory. Results of the latter for a mixture of Lennard-Jones particles are presented, with potential parameters that are characteristic for *n*-hexane with several carrier gases. © 1999 American Institute of Physics. [S0021-9606(99)51741-8]

I. INTRODUCTION

Existing models of vapor-to-liquid nucleation describe the phase transition of one or more supersaturated vapor components. It is quite clear that this picture is incomplete for many practical circumstances: Both in nucleation rate measurements and in industrial applications, the vapors of interest are usually mixed with background (or carrier) gases. These gases were originally introduced in nucleation experiments in order to keep the nucleating vapor at isothermal conditions. One thereby assumed that the gas did not affect the nucleation process in any other way. In recent years, this assumption has often been questioned. At present, a consensus about the role of carrier gases in the nucleation process has not yet been achieved.

It is necessary to state explicitly what is meant here by a “carrier gas.” We define a carrier gas to be a *supercritical* component of a vapor phase mixture in which nucleation takes place. Since it is above its critical temperature, the carrier gas shows no tendency to condense on its own. Yet, it may affect the properties of the condensing (subcritical) component. It might even enter into the interior of the nucleating cluster; in this respect, the present definition of a carrier gas is more general than the one we used in an earlier paper on high pressure nucleation.¹

Thus far, only few papers have appeared in which the carrier gas influence on nucleation is discussed from a theoretical point of view.^{2–5} Most authors start from the virial equation of state in order to describe the interaction between the components of the vapor–gas mixture. In this way, they

conclude that the presence of the carrier gas may result in a change of the equilibrium chemical potential of the vapor, thereby changing the supersaturation ratio. The net effect on nucleation rates is found to depend mainly on the magnitude and sign of the second virial coefficients of the mixture. It is important to note that, in all of the above references, a possible dependence of surface tension on carrier gas pressure is either completely left out of consideration or argued to be insignificant.

Still, from our results on water nucleation in a carrier gas of nitrogen,¹ we concluded that a decrease of surface tension with pressure forms the key to the explanation of the observed pressure trend in the water–nitrogen mixture. In order to arrive at that conclusion, however, we first had to take into account the increased vapor phase fugacity of water with nitrogen pressure; otherwise, the pressure trend would be hidden because of a cancellation of the opposing effects involved. Moreover, such a (partial) cancellation was predicted to occur more generally, since both effects stem from mutual interactions between vapor and carrier gas molecules.

The aim of the present paper is to give the above ideas a sounder theoretical basis. We first show how the total pressure of the mixture can be treated as a “perturbation” parameter to the relevant properties of the vapor component: Saturated vapor pressure (Sec. II) and surface tension (Sec. III). In Ref. 1 we implicitly assumed that the vapor nucleation can still be modeled as a unary process; in Sec. IV we present an analysis that shows the limit of validity of this assumption, starting from a binary thermodynamic model based on the capillarity approximation.

Section V describes the implications of high carrier gas pressures for the cluster distribution in the semi-

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phenomenological Kalikmanov–Van Dongen model.⁶ Finally, in Sec. VI we present density functional calculations which clearly reveal the fugacity increase and surface tension decrease at elevated carrier gas pressures. Although we only show phase equilibrium calculations, the pressure effects could be straightforwardly implemented in a nucleation rate calculation, using binary density functional theory.⁷

II. VAPOR PRESSURE ENHANCEMENT

Consider a binary mixture of a vapor and a carrier gas, in thermodynamic equilibrium with the corresponding liquid phase at temperature T and total pressure p . From the equality of fugacities in both phases, it can be shown that the equilibrium fraction of the vapor component is given by^{1,2,8}

$$y_v^{\text{eq}} = \frac{p^s}{p} \cdot \frac{\phi^s}{\phi^{\text{eq}}} \cdot \gamma^{\text{eq}} x^{\text{eq}} \exp \int_{p^s}^p \frac{v^l(p')}{k_B T} dp'. \quad (1)$$

In the above relation, the pressure ratio is the familiar ideal gas result (no intermolecular interactions). The coefficient ϕ^s accounts for possible nonideality of the saturated pure vapor. Intermolecular interactions in the gas phase are represented by the fugacity coefficient ϕ^{eq} . Next, x^{eq} denotes the fraction of the vapor component in the liquid phase, and the activity coefficient γ^{eq} represents the nonideality of the liquid at equilibrium. Finally, the exponential factor is caused by the pressure of the gas mixture onto the liquid phase with a molecular volume v^l (Poynting effect).⁸

It is useful to rewrite Eq. (1) as

$$f_e = \frac{y_v^{\text{eq}}(p, T)p}{p^s(T)} = \frac{\phi^s}{\phi^{\text{eq}}} \cdot \gamma^{\text{eq}} x^{\text{eq}} \exp \int_{p^s}^p \frac{v^l(p')}{k_B T} dp', \quad (2)$$

where the *enhancement factor* f_e is introduced as a direct measure of the deviation from ideal gas behavior. It represents the increase of the partial saturated vapor pressure—which by definition equals the product of equilibrium molar vapor fraction and total pressure—with respect to the pure vapor state. Defining the supersaturation S as the ratio of the vapor fugacities in the nonequilibrium and equilibrium states, and assuming that vapor fractions are very small, it can be shown that S obeys the relation¹

$$S \approx \frac{y_v}{y_v^{\text{eq}}} = \frac{y_v p}{f_e(p, T)p^s(T)}, \quad (3)$$

where y_v denotes the actual vapor fraction in the mixture. Equation (3) expresses the supersaturation in experimentally accessible quantities (y_v and p), the familiar pure component saturated vapor pressure p^s , and the enhancement factor f_e . According to the first equality, S can be interpreted as a measure of the “overpopulation” of the vapor phase, even at high carrier gas pressures.

Let us now have a closer look at the saturation ratio of the carrier gas. Again using the approximation $\phi_g \approx \phi_g^{\text{eq}}$ —which is equally valid for the carrier gas, as long as vapor fractions are small—we find from Eq. (3)

$$S_g \approx \frac{y_g}{y_g^{\text{eq}}} = \frac{1 - y_v}{1 - y_v^{\text{eq}}} < 1, \quad (4)$$

indicating that the driving force for the nucleation process is provided by the vapor alone. This observation will play an important role in Sec. IV, where we describe the role of the carrier gas in classical nucleation theory.

For a particular vapor–gas mixture, numerical values of the enhancement factor f_e as a function of pressure and temperature can be obtained in several ways. The most straightforward of these is direct measurement of the saturated vapor fraction as a function of pressure and temperature. For water–vapor in air and oxygen, enhancement data were measured gravimetrically by Wylie and Fisher;^{9,10} we used their results in Ref. 1 in order to extract enhancement factors for water in nitrogen.

When enhancement data are not available in the (p, T) -range of interest, they can be extrapolated from measured data at other conditions, using an equation of state (EOS). For the n -nonane-methane mixture, equilibrium vapor fractions were calculated by Looijmans *et al.*, using the cubic Redlich–Kwong–Soave equation of state.¹¹ The resulting enhancement factors become quite large already for relatively low total pressures, which is caused by the chemical similarity (and, hence, good miscibility) of both components.¹²

A slightly different method, also based on an EOS, is the use of the virial equation to calculate the fugacity coefficients ϕ^s and ϕ^{eq} , as was done by Fisk and Katz.²

For very light gases, such as helium and hydrogen, one can neglect the interaction between vapor and carrier gas molecules. Accordingly, the vapor fugacity coefficient ϕ^{eq} can be set to unity. For insoluble gases (which again tend to be the very light ones), both x^{eq} and γ^{eq} equal unity, as does ϕ^s for sufficiently ideal vapors. The only remaining contribution in Eq. (2) is the Poynting effect. Usually the liquid is considered incompressible, in which case we have

$$f_e = \exp \left[\frac{M(p - p^s)}{\rho_l RT} \right], \quad (5)$$

M and ρ_l denoting molar mass and specific density of the liquid, respectively. Note that the Poynting factor is independent of the *kind* of pressurizing gas: Its magnitude depends only on the molar density of the pure liquid.

Finally, enhancement factors can be calculated from first principles, starting directly from molecular interaction potentials. This method will be adopted in Sec. VI, where we calculate enhancement factors for several binary mixtures of Lennard-Jones molecules.

Figure 1 shows values of f_e for water in helium and nitrogen, and for n -nonane in helium and methane, all at 240 K. Experimental nucleation data for these mixtures will be presented in Paper II of this paper.

III. HIGH PRESSURE SURFACE TENSION

The dependence of the surface tension of clusters on carrier gas pressure is usually not considered in nucleation work. Yet, it was just this effect that enabled us to account for the observed pressure trend of water nucleation rates in a carrier gas of nitrogen.¹ In the same paper, we sketched the thermodynamic background of the effect.

FIG. 1. Enhancement factors as a function of pressure, at a temperature of 240 K. Solid line: Water in helium. Dotted line: Water in nitrogen. Dashed-dotted line: *n*-nonane in helium. Dashed line: *n*-nonane in methane.

The basic mechanism of the surface tension decrease with pressure is the adsorption of gas molecules onto the liquid surface, as was already recognized by Gibbs.¹³ Measurement of surface tensions as a function of pressure has even been the common method to obtain quantitative surface adsorption data.¹⁴ However, one runs into problems when pressurized surface tensions have not or cannot be measured (for example, when the liquid is severely supercooled, as is the case for water nucleation at $T=240$ K).

In Ref. 1 we tried to extrapolate the pressure dependence of the surface tension of water in nitrogen from experimental data at room temperature, using a model for the surface adsorption. Assuming Langmuir-type adsorption, the surface coverage (the percentage of available sites that is occupied) reads

$$\vartheta = \frac{p}{p + p_L}, \quad (6)$$

where p_L is the Langmuir reference pressure. Furthermore, the ideal gas law was used to estimate the molecular volume of (free) carrier gas molecules, leading to an expression for the surface tension of the form

$$\gamma(p) = \gamma_0 - n_a k_B T \ln \left(\frac{p + p_L}{p_L} \right). \quad (7)$$

Here, γ_0 denotes the surface tension of the pure liquid, and n_a is the number of adsorption sites per unit area. Assuming a monolayer of close-packed spheres at the surface, the latter can be estimated to be near $6 \times 10^{18} \text{ m}^{-2}$, with only little variation among various liquid-gas systems.¹⁵ Equation (7) very well reproduces the $\gamma(p)$ -dependence that is generally observed in experiments: A decaying surface tension with pressure, with a positive second derivative.

What remains to be determined in the above model is the Langmuir pressure p_L , which has to be known as a function of temperature. When pressurized surface tension data are available for a given temperature range, it can simply be obtained from a best fit to experiments. For other temperatures, the $p_L(T)$ relation could then be extrapolated.

FIG. 2. Surface tension of water as a function of nitrogen pressure. Open markers: new data. Filled markers: Measurements of Massoudi and King (Ref. 14). Solid lines: Eq. (7), with $p_L = 326$ bar.

Of course, when data are only available at one single temperature, safe extrapolation is impossible, unless a one-parameter model is used for the temperature dependence of p_L . For water in nitrogen we assumed a statistical model of discrete adsorption sites,¹ with the adsorption energy E_a as a parameter. Extrapolation to nucleation temperatures of 230 and 250 K yielded quite small p_L values, and associated high surface coverages. Since the Langmuir adsorption relation is only valid up to coverages of about 30%, we concluded that our model was not applicable at the nucleation conditions of interest.

In the meantime, we have carried out new measurements of water surface tension under nitrogen pressure. To that end, a pending drop cell has been used that was developed for measurement of interfacial tensions at high temperature and pressure by Huijgens.¹⁶ After modification of this setup, allowing it to be cooled down, pressure dependent surface tensions could be measured down to the freezing point of water. Results at temperatures of 276 and 288 K are shown in Fig. 2, together with data of Massoudi and King at room temperature.¹⁴ The solid lines in the graph are curves of the form (7), but now with a fixed value of the Langmuir pressure p_L , equal to 326 bar. Apparently, this quantity is much less sensitive to temperature than was suggested by the model we used in Ref. 1.

In part II of this paper (hereafter referred to as Paper II)¹⁷ new nucleation data will be presented, and a method will be described to obtain the surface coverage of clusters directly from the observed nucleation rates. Consequently, the Langmuir pressure can be derived from Eq. (6), and the result can be regarded as an empirical value. However, this procedure is applicable only under very strict conditions, as we will point out there.

For the *n*-nonane-methane mixture, surface tension data have been measured in a broad temperature range by Deam and Maddox.¹⁸ Their data are shown in Fig. 3, together with curves of the form (7) with fitted p_L -values for each temperature. When plotted as a function of temperature, these p_L data appear to be well described by a quadratic function, see Fig. 4. It should be stressed, however, that the adsorption model is not valid for systems with appreciable carrier gas

FIG. 3. Pressure dependent surface tension of *n*-nonane in methane, according to Deam and Maddox (Ref. 18). Solid lines are fit functions of the form (7).

dissolution like the *n*-nonane-methane mixture. Hence, Figs. 3 and 4 should rather be regarded as a convenient interpolation of surface tension data.

When helium is used as a carrier gas, the pressure dependence of surface tension is always found to be very weak. For *n*-nonane in helium a very small *positive* pressure trend is found at room temperature,¹⁹ arising from the migration of *n*-nonane molecules to the surface.¹ Still, the effect is small enough to be neglected for nucleation pressures below 100 bar. For water in helium, experiments demonstrate that the surface tension does not change for pressures up to 80 bar.²⁰ (For unclear reasons, however, Eriksson¹⁵ reports a positive pressure derivative, referring to the same data.)

IV. CLASSICAL NUCLEATION THEORY

In its most concise form, the expression for the nucleation rate *J* of a single vapor substance reads, according to the kinetic variant of classical nucleation theory:

$$J = \rho_1 \rho_1^{\text{eq}} v^l \left(\frac{2\gamma}{\pi m} \right)^{1/2} \exp \left[-\frac{4}{27} \frac{\theta^3}{(\ln S)^2} \right]. \quad (8)$$

FIG. 4. Values of the Langmuir reference pressure p_L , obtained from fitting expression (7) to the experimental data in Fig. 3. The dashed line is a least-squares fit.

In this expression, the dimensionless surface tension θ is defined as

$$\theta = \frac{\gamma a_0}{k_B T}, \quad (9)$$

where $a_0 = (36\pi)^{1/3} (v^l)^{2/3}$. Furthermore, *m* is the molecular mass, and ρ_1 and ρ_1^{eq} denote the number density of single molecules (monomers) in the supersaturated and equilibrium states, respectively. The so-called internally consistent classical theory has the same form, with an extra factor e^θ .

In the preceding sections we already discussed the influence of carrier gas pressure on two essential parameters, being the supersaturation *S* and surface tension γ . Inspection of Eq. (8) shows that two more quantities might be influenced by carrier gas pressure: the molecular volume v^l of the liquid and the monomer density ρ_1 .

Although we are considering carrier gas pressures up to (typically) tens of bars, these values are still insignificant compared to the internal (Laplace) pressure in the critical cluster, which can be as large as a few thousands of bars. Compressibility effects are, therefore, not exclusively associated with high pressure nucleation, and will be neglected here.

When evaluating monomer densities, the compressibility factor of the gas phase must be taken into account. It is defined as $Z = p/\rho k_B T$, where ρ is the total number density of the gas phase. The vapor number density equals $y_v \rho = \sum n \rho_n$, where ρ_n is the number density of *n*-mers. When the cluster distribution falls off with *n* rapidly enough, the vapor density is therefore given by¹²

$$\rho_1 \approx \rho_v = \frac{y_v p}{Z k_B T}. \quad (10)$$

Under the same approximation we can write, using definition (2) of the enhancement factor

$$\rho_1^{\text{eq}} = \frac{f_e p^s}{Z k_B T}. \quad (11)$$

For small vapor fractions, the compressibility factor of the mixture equals that of the pure carrier gas with a high degree of precision.¹² Collecting the above relations, the nucleation rate according to Eq. (8) can be expressed in terms of measurable quantities

$$J = \frac{y_v p f_e p^s}{(Z_s k_B T)^2} \left(\frac{2\gamma M}{\pi N_A} \right)^{1/2} \frac{1}{\rho_l} \exp \left[-\frac{16\pi M^2}{3N_A^2 \rho_l^2 k_B^3} \frac{\gamma^3}{T^3 (\ln S)^2} \right]. \quad (12)$$

In principle, the above expression is the final result of the “pressure perturbation approach,” which assumes single component nucleation with effective properties that are modified by the presence of the carrier gas. Still, the transition from the standard formula (8) to its high pressure form (12) was done in a somewhat heuristic way. In the remainder of this section, we will examine the conditions under which Eq. (12) is applicable.

It is useful to first look briefly at the derivation of the classical result. The most general starting point is the expression resulting from elementary kinetics

$$J = \left[\int_1^\infty \frac{1}{C_n \rho_n^{\text{eq}} S^n} dn \right]^{-1}. \quad (13)$$

Assuming the sticking probability to be unity, the condensation coefficient C_n is equal to the surface area of a cluster times the impingement rate:

$$C_n = a_0 n^{2/3} \rho_1 (k_B T / 2\pi m)^{1/2}. \quad (14)$$

In the capillarity approximation, underlying classical theory, the formation energy of clusters in the equilibrium state only contains a surface term: $\Delta G_n^{\text{eq}} = \gamma a_0 n^{2/3}$. The corresponding cluster distribution obeys a Boltzmann law, resulting in $\rho_n^{\text{eq}} = \rho_1^{\text{eq}} \exp(-\theta n^{2/3})$. The product $S^n \rho_n^{\text{eq}}$ in Eq. (13) can then be written as

$$S^n \rho_n^{\text{eq}} = \rho_1^{\text{eq}} \exp(n \ln S - \theta n^{2/3}). \quad (15)$$

Subsequently, the integral in Eq. (13) is evaluated by expanding the argument of the exponential into a Taylor series around its minimum at $n = n^*$. The latter is easily found from differentiation. Equivalently, it is obtained from setting the chemical potential difference between a cluster and its surroundings to zero

$$\Delta \mu^* = v^l \Delta p - k_B T \ln S = 0, \quad (16)$$

where $\Delta p = 2\gamma/r^*$ is the Laplace pressure. Obviously, Eq. (16) is just the Kelvin relation. Finally, assuming that C_n varies only slowly with n , the integral is evaluated by standard methods, leading to the familiar result (8).

Let us now examine in what way the carrier gas alters the above arguments. To that end, consider a binary mixture of a supersaturated vapor and a (supercritical) carrier gas. The essential difference with the pure component case is that all chemical potentials now depend on pressure *and* composition. Clusters are assumed to be homogeneous liquid spheres, with molar fractions $\hat{x}_i = n_i / (n_v + n_g)$ ($i = v, g$). Besides, there may be extra carrier gas molecules (not included in n_g) adsorbed at the surface. The latter are assumed to affect the energy of cluster formation exclusively via the surface tension, i.e., they do not alter the surface area. For convenience, we assume the liquid phase to be an ideal mixture, with all activity coefficients γ_i equal to unity.

In the macroscopic equilibrium state, both components have a uniform chemical potential: $\mu_i^l(p, x_i^{\text{eq}}) = \mu_i^v(p, y_i^{\text{eq}})$, which defines the equilibrium fractions x_i^{eq} and y_i^{eq} . In the supersaturated state, the difference in chemical potential of component i between the cluster (with bulk molar fractions $\hat{x}_i$) and the vapor phase is

$$\Delta \mu_i = v_i^l \Delta p + k_B T \ln(\hat{x}_i / x_i^{\text{eq}}) - k_B T \ln S_i. \quad (17)$$

The second term on the right hand side results from mixing, whereas the last term denotes the externally imposed chemical potential difference between the saturated and equilibrium states: $k_B T \ln S_i \equiv \mu_i^l(p, y_i) - \mu_i^l(p, y_i^{\text{eq}})$.

We now use the observation that the carrier itself is *not* supersaturated, see Eq. (4). For small vapor fractions we may set $S_g = 1$. We also define $S = S_1$, the vapor supersaturation. Substituting for the Laplace pressure $\Delta p = 2\gamma/r^*$, the Kelvin relations for the vapor (further denoted with subscript v) and the carrier gas (subscript g) become

$$\frac{2\gamma v_v^l}{r^*} - k_B T \ln S + k_B T \ln \left(\frac{1 - \hat{x}_g^*}{1 - x_g^{\text{eq}}} \right) = 0, \quad (18)$$

$$\frac{2\gamma v_g^l}{r^*} + k_B T \ln(\hat{x}_g^* / x_g^{\text{eq}}) = 0. \quad (19)$$

Both were written in terms of the carrier gas fraction in the equilibrium liquid and the cluster, which facilitates the interpretation. For the vapor, an externally imposed driving force for nucleation exists, equal to $\Delta \mu_S = k_B T \ln S$; in the critical cluster this term is balanced by the Laplace pressure and a—much smaller—entropic term. The carrier gas, on the other hand, enters into the critical cluster for entropic reasons only: It dissolves until the logarithmic term balances the Laplace pressure.

We now make an important assumption. At high pressures the carrier gas is so much more abundant in the gas mixture, that it can be considered to be in (partial) equilibrium for all cluster sizes r —irrespective of their number of vapor molecules n_v . Therefore, Eq. (19) can be generalized for arbitrary r as

$$\hat{x}_g = x_g^{\text{eq}} \exp \left(- \frac{2\gamma v_g^l}{r k_B T} \right) \equiv x_g^{\text{eq}} e^{-\alpha}, \quad (20)$$

where we have introduced the parameter α (which is a function of r) for later use. The trajectory of condensation in (n_v, n_g) -space is fully determined by the above relation, since the cluster radius r obeys the geometric relation $\frac{4}{3}\pi r^3 = n_v v_v^l + n_g v_g^l$. For very small clusters ($r \rightarrow 0$), the carrier gas fraction in the liquid approaches zero; when the clusters grow larger the gas fraction increases, and finally the equilibrium solubility x_g^{eq} is reached for $r \rightarrow \infty$. Near the critical radius, α can be estimated using Eq. (18): Neglecting the mixing entropy term, we find $\alpha(r^*) = (v_g^l / v_v^l) \ln S$, and thus $\hat{x}_g^* = x_g^{\text{eq}} S^{-v_g^l / v_v^l}$.

The above assumption implies that the kinetic process of nucleation is still controlled by impingement and emission of vapor molecules, the carrier gas having a passive role. In that case the kinetic expression (13) remains valid, only with n replaced by n_v . The relevant distribution $\rho_{n_v}^{\text{eq}}$ is that of n_v -clusters in the equilibrium state; that is, clusters with n_v vapor molecules and a number of gas molecules determined by Eq. (20).

The chemical potential of component i in the cluster now contains a logarithmic mixing term, see Eq. (17). This term also enters the free energy of cluster formation, resulting in

$$\frac{\Delta G^{\text{eq}}(n_v, n_g)}{k_B T} = \theta n_t^{2/3} + n_t \sum_i \hat{x}_i \ln(\hat{x}_i / x_i^{\text{eq}}), \quad (21)$$

where $n_t = n_v + n_g$, and hence $\hat{x}_i = n_i / n_t$. Note that the above expression should contain the composition $\hat{x}_i^{\text{eq}}$ of (unstable) clusters in the macroscopic equilibrium state. However, our assumption of the carrier gas being in partial equilibrium for all cluster sizes can be made for the equilibrium state as well. Hence, the cluster composition $\hat{x}_i^{\text{eq}}$ is still determined by Eq. (20); it depends only on radius and temperature, *not* on supersaturation.

The product $S^{n_v} \rho_{n_v}^{\text{eq}}$ in the denominator of Eq. (13) can now be written as

$$S^{n_v} \rho_{n_v}^{\text{eq}} = \rho_{1,v}^{\text{eq}} \exp[n_v \ln S - \theta n_t^{2/3} - n_t \sum \hat{x}_i \ln(\hat{x}_i / x_i^{\text{eq}})], \quad (22)$$

where $\rho_{1,v}$ denotes the number density of vapor monomers. The first term in the exponent is identical to the single component case. The “molecular surface area” for the mixture follows from the assumption of ideality of the liquid, yielding $a_0 = (36\pi)^{1/3} (\sum \hat{x}_i v_i^l)^{2/3}$. Hence, the second term is proportional to $(\sum n_i v_i^l)^{2/3}$. For all but one system investigated in Paper II,¹⁷ carrier solubilities are very small; only for *n*-nonane-methane it can be appreciable, but here the molecular volume of the carrier is much smaller than that of the vapor. Therefore, we have $n_g v_g^l \ll n_v v_v^l$ in all cases; the surface area is determined by vapor molecules, and we can replace the surface energy term by $\theta n_v^{2/3}$, with a_0 equal to the pure component value.

Finally, the entropic term in Eq. (22) can be neglected with respect to the two others when $\sum \hat{x}_i \ln(\hat{x}_i / x_i^{\text{eq}}) \ll x_v \ln S$. This condition can be made more explicit using Eq. (20), which connects the cluster composition to that of the equilibrium state. Substituting Eq. (20) and the trivial relation $x_v + x_g = 1$ both for the cluster and for the equilibrium liquid, we obtain

$$\ln \left(\frac{1 - x_g^{\text{eq}} e^{-\alpha}}{1 - x_g^{\text{eq}}} \right) - \frac{x_g^{\text{eq}} \alpha e^{-\alpha}}{1 - x_g^{\text{eq}} e^{-\alpha}} \ll \ln S. \quad (23)$$

It is easily verified that the function on the left hand side increases monotonically with α for all positive values of α and x_g^{eq} , starting from zero at $\alpha=0$. Accordingly, the maximum value is reached for $\alpha \rightarrow \infty$, and the above criterion is therefore always satisfied when

$$\ln \left(\frac{1}{1 - x_g^{\text{eq}}} \right) \ll \ln S \quad (24)$$

or, equivalently,

$$x_g^{\text{eq}} \ll \frac{S-1}{S}, \quad (25)$$

which marks the limit of validity of our pressure perturbation approach, represented by expression (12).

A final remark concerns the role of the size parameter α . We only used the limit for $\alpha \rightarrow \infty$ in the derivation of criterion (25). In the evaluation of the kinetic integral, however, the relevant cluster sizes are those near the critical radius r^* . The corresponding α was found above to have a value near $(v_g^l / v_v^l) \ln S$, which can be estimated for a given experimental condition. Using Eq. (23), one can then judge whether this condition is fulfilled for the carrier gas solubility at the prevailing nucleation conditions.

V. SEMIPHENOMENOLOGICAL THEORY

Semiphenomenological models of vapor-to-liquid nucleation are generally based on the statistical-mechanical Fisher distribution of clusters, with parameters that can be adjusted to reproduce measurable vapor properties. One of the most recent models in this class is that of Kalikmanov and Van

Dongen,⁶ who tune the parameters of the cluster model to reproduce the saturated vapor pressure p^s at the prevailing nucleation temperature.

Like in other semiphenomenological models, the vapor is regarded as an ensemble of *n*-clusters, with number densities ρ_n . Assuming that the clusters do not interact, the equilibrium vapor pressure is given by Dalton's law

$$\frac{p^s}{k_B T} = \sum_{n=1}^{\infty} \rho_n^s. \quad (26)$$

The equilibrium number density of *n*-clusters ρ_n^s is again proportional to a Boltzmann factor $\exp(-\Omega_n / k_B T)$. Using the grand potential Ω_n from the Fisher model,²¹ and assuming the Tolman form for the microscopic surface tension γ_n , the result is

$$\rho_n^s = q_0 \exp[-\theta(1 + \alpha \gamma_n^{-1/3}) n^{2/3} - \tau \ln n], \quad (27)$$

where θ is again given by Eq. (9). Substitution into Eq. (26) yields

$$\frac{p^s}{k_B T} = q_0 \sum_{n=1}^{\infty} n^{-\tau} \exp[-\theta(1 + \alpha \gamma_n^{-1/3}) n^{2/3}]. \quad (28)$$

Far from the critical point the series on the right hand side rapidly converges. Equation (28) then determines $\alpha \gamma$, provided that the Fisher parameters q_0 and τ are known, which can be obtained from the critical properties of the vapor.⁶

The treatment of nucleation kinetics by Kalikmanov and Van Dongen is identical to that in classical theory, leading to Eq. (13). Again, the nucleation rate is obtained by Gaussian integration, after expanding the integrand into a Taylor series around its maximum at $n = n_c$. The functional form of the integrand is now obtained from the distribution (27), together with Eq. (14) for the *n*-dependent impingement rate C_n . The final result is

$$J = \rho_1 a_0 \left(\frac{k_B T}{2 \pi m} \right)^{1/2} \left[\frac{\theta}{9 \pi} (1 + \alpha \gamma n_c^{-1/3}) + \frac{1}{2 \pi} \left(\tau - \frac{2}{3} \right) n_c^{-2/3} \right]^{1/2} \times q_0 S^{n_c} \times \exp[-\theta(1 + \alpha \gamma n_c^{-1/3}) n_c^{2/3} - \tau \ln n_c] \quad (29)$$

with the critical cluster size n_c determined by the nonlinear equation

$$-n_c \ln S + \frac{2}{3} \theta n_c^{2/3} + \frac{1}{3} \theta \alpha \gamma n_c^{1/3} + \tau - \frac{2}{3} = 0. \quad (30)$$

Let us now consider the effect of carrier gas addition, for example at constant (partial) vapor density. As before, the carrier gas is not supersaturated, and much more abundant than the vapor component. We again assume that nucleation kinetics is fully determined by the vapor, with the carrier gas in partial equilibrium at all times. Although it has not been strictly demonstrated, it can be expected that the criterion (25) also holds for the present model: For a one-component description to be applicable, the carrier gas solubility must be sufficiently small.

The supersaturation S and macroscopic surface tension γ are independent of the nucleation model: Therefore, vapor

pressure enhancement and a possible decrease of surface tension with pressure constitute the main carrier gas effects. Liquid compressibility is again neglected, which is of importance in the evaluation of θ .

It is assumed that the vapor can still be described as a population of noninteracting clusters, whereas the carrier gas consists of monomers only. The vapor clusters are now moving in the background potential field of the carrier gas, which makes them “experience” the compressibility factor of Z_g of the carrier gas.¹² The monomer density in the supersaturated state, therefore, follows from Eq. (10), with $Z = Z_g$. The partial vapor pressure in the macroscopic equilibrium state now obeys a modified form of Dalton’s law, accounting for the above assumption

$$\frac{f_e p^s}{Z_g k_B T} = q_0 \sum_{n=1}^{\infty} n^{-\tau} \exp[-\theta(1 + \alpha_\gamma n^{-1/3})n^{2/3}]. \quad (31)$$

Mathematically, differences with the pure vapor case are the appearance of the factor f_e/Z_g and a possible change of θ , containing the surface tension. These differences result in a change of α_γ , and hence, in a modified cluster distribution.

To get a better idea of the implications for the cluster distribution, we illustrate the mathematical consequences in a first order approximation. For convenience, consider a mixture for which the surface tension is not significantly affected by the total pressure p . The shift in α_γ can be accurately specified when the departure of f_e/Z_g from unity is not too large. In that case, define

$$\frac{f_e}{Z_g} = 1 + \xi(p, T), \quad (32)$$

where ξ is positive in all cases of interest. We confine our analysis to small values of ξ , in accordance with the idea of treating the pressure effects as a perturbation to the single component case. Since the equilibrium cluster distribution falls off very rapidly with n , the value of α_γ is mainly determined by the first term of the density series. Denoting the pure component value as $\alpha_{\gamma,0}$, we obtain

$$\alpha_\gamma = -\frac{1}{\theta} \ln \left[\frac{p^s}{q_0 k_B T} (1 + \xi) \right] - 1 \approx \alpha_{\gamma,0} - \frac{\xi}{\theta}. \quad (33)$$

Substitution of this result into the cluster distribution (27) shows that

$$\rho_n^{\text{eq}}(p, T) = \rho_n^s(T) \exp(\xi n^{1/3}). \quad (34)$$

Apparently, the distribution is corrected with an n -dependent factor, the magnitude of the shift being larger at higher values of n . Still, the leading term of the exponential in Eq. (27) causes the distribution to converge rapidly.

Since the nucleation rate J is proportional to $\rho_{n_c}^{\text{eq}}$, it is tempting to conclude that it increases by a factor $\exp(\xi n_c^{1/3})$. However, the modified values of α_γ and S (due to the enhancement effect) also affect the critical size n_c . A simple analysis of first-order terms in Eq. (30) readily shows that the decrease of S is dominant. Hence, the critical size has to increase in order to keep Eq. (30) in balance. The nucleation

rate accordingly decreases; this comes up to expectations, since in the above case we only considered the enhancement effect at a fixed partial vapor density.

VI. DENSITY FUNCTIONAL THEORY

In recent years, density functional theory (DFT) has become increasingly important in the description of vapor-to-liquid nucleation. In this section we outline how the presence of a carrier gas can be accounted for in density functional theory. The idea is simple, and similar to what was done in Sec. IV. We consider a binary mixture of a vapor and a carrier gas, with all particles interacting via a Lennard-Jones 12-6 potential. The only difference between vapor and carrier gas is in the potential parameters: Phase calculations then naturally indicate that the vapor might condense, whereas the gas is supercritical.

Density functional theory for binary mixtures of Lennard-Jones particles was described in 1991 by Zeng and Oxtoby.⁷ We will follow their approach up to a certain point: We present equilibrium calculations only, whereas Zeng and Oxtoby did the full nucleation rate calculation. The reason for this restriction stems from the consideration in Sec. IV: The carrier gas significantly affects the macroscopic equilibrium properties (vapor density and surface tension), but its role in microscopic scale kinetics is only a passive one.

Consider a binary liquid–vapor system, with particles interacting via a pairwise potential which can be divided into a repulsive reference part $u_{0,ij}(r)$ and a perturbative attractive part $u'_{ij}(r)$. Using random phase approximation (RPA) and local density approximation (LDA),⁷ it can be proven that the equilibrium number density fields $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ obey

$$\mu_i = \mu_{0,i}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})] + \sum_{j=1}^2 \int d\mathbf{r}' u'_{ij}(|\mathbf{r} - \mathbf{r}'|) \rho_j(\mathbf{r}'). \quad (35)$$

Following Zeng and Oxtoby, we adopt a Lennard-Jones 12-6 potential for the pairwise interaction, which is decomposed according to the Weeks–Chandler–Andersen (WCA) scheme.²² The steeply repulsive part is then replaced by an effective hard-sphere system, with the effective diameter d calculated from the Barker–Henderson expression

$$d = \int_0^\infty dr [1 - e^{-u_0(r)/k_B T}], \quad (36)$$

which is easily evaluated numerically for the repulsive part of the Lennard-Jones potential. Analytical expressions for properties of hard sphere mixtures are available in literature.^{23–25} Continuing from here, we replace the reference state subscript “0” with “h,” denoting hard spheres.

As a boundary condition for the solution of Eq. (35), the limiting values of the number densities in the homogeneous bulk phases must be known. These are obtained from the relations

$$\mu_i = \mu_{i,h}(\rho_1, \rho_2) - \sum_{j=1}^2 a_{ij} \rho_j \quad (37)$$

and

$$p = p_h(\rho_1, \rho_2) - \frac{1}{2} \sum_{i,j=1}^2 a_{ij} \rho_i \rho_j, \quad (38)$$

where the so-called “background interaction parameter” is defined as $a_{ij} = -\int d\mathbf{r} u'_{ij}(r)$. For the attractive part of the WCA-decomposed Lennard-Jones potential, it is easily found analytically: $a_{ij} = \epsilon_{ij} \sigma_{ij}^3 (32\pi/9)\sqrt{2}$.

The condition of thermodynamic equilibrium requires the constancy of p and μ_i throughout the interface. Hence, Eqs. (37) and (38), applied to both phases, provide three relations for the four bulk densities ρ_1^v , ρ_2^v , ρ_1^l and ρ_2^l . Usually one prescribes the liquid fraction x_1^l of component 1 as a closing relation. For our purposes, however, we should fix the total pressure p . Numerically, the difference only concerns the initial guesses for the four bulk densities.

Obviously, the bulk limit calculation also yields the equilibrium values of μ_i . These play a key role in the computation of density profiles using Eq. (35). Since inhomogeneity over the plane liquid–vapor interface is only in the perpendicular z -direction, the solution can be obtained by iteration from a suitable initial guess.⁷

Once the density profiles are known, the surface tension is obtained as a one-dimensional integral over z , reading

$$\gamma = \int dz \left[p - p_h[\rho_1(z), \rho_2(z)] - \frac{1}{2} \sum_{i,j=1}^2 \rho_i(z) \int d\mathbf{r}' \rho_j(\mathbf{r}') u'_{ij}(|\mathbf{r} - \mathbf{r}'|) \right]. \quad (39)$$

As a model vapor in our calculations we have used n -hexane, for several reasons. First of all, experimental data on pressure dependent surface tensions are rather scarce. To our knowledge, the only liquids for which sufficient data exist are water and n -hexane. Due to its polarity, water vapor cannot reasonably be modeled by a Lennard-Jones potential. For non-polar substances, Lennard-Jones potentials are more appropriate: Reasonable predictions of various properties of the n -alkanes have been obtained from simulations using Lennard-Jones potentials.^{26–28}

A second advantage is that experimental (p, V, T) -data of the n -alkanes can be accurately correlated using a cubic equation of state. This provides us with an independent source of comparison for the enhancement factors resulting from DFT calculations. Finally, n -hexane is chemically similar to n -nonane, which has often been subjected to nucleation experiments.

Since the enhancement factor f_e relates the equilibrium properties of the binary mixture to that of the pure vapor, we also need information on the pure vapor equilibrium. For n -hexane, saturated vapor pressure data are readily available;²⁹ however, for a consistent treatment one should preferably calculate the pure vapor equilibrium from unary DFT. These two alternatives can be elegantly combined by fitting the potential parameters of the vapor to the experimental saturated vapor pressure p^s and liquid density ρ^l . For a given temperature T , one has to solve the three equations

FIG. 5. Density profiles of n -hexane (solid lines) and nitrogen (dashed-dotted lines) over a flat liquid–vapor interface at pressures of 10, 20, 40, and 80 bar, and $T=298.15$ K. Dashed lines represent the (dimensionless) integrand $d\gamma/dz$ of Eq. (39).

$$p_h[\rho^v, d(\sigma)] - \frac{1}{2} (\rho^v)^2 a(\epsilon, \sigma) = p_h[\rho^l(T), d(\sigma)] - \frac{1}{2} [\rho^l(T)]^2 a(\epsilon, \sigma) = p^s(T), \quad (40)$$

$$\mu_h[\rho^v, d(\sigma)] - \rho^v a(\epsilon, \sigma) = \mu_h[\rho^l(T), d(\sigma)] - \rho^l(T) a(\epsilon, \sigma), \quad (41)$$

for the three unknowns ϵ , σ , and ρ^v . Note that the latter implicitly yields the compressibility factor of the pure vapor, $Z^s = p^s / (\rho^v k_B T)$. Properties of a unary system of hard spheres were provided by Carnahan and Starling.³⁰ The effective hard sphere diameter $d(\sigma)$ is determined from Eq. (36)—where u_0 depends on σ —within the solver routine; and $a = (32\pi/9)\sqrt{2}\epsilon\sigma^3$.

At a temperature of 298.15 K (for which empirical surface tension data are available), the resulting parameter values for n -hexane are $\epsilon/k_B = 471.5$ K, and $\sigma = 5.587$ nm. We checked the temperature sensitivity of these values, which appeared to be rather small. The present method is not unique; alternative routes to obtain Lennard-Jones parameters of n -alkanes were recently published by Matyushov and Schmid.³¹

For most common carrier gases, Lennard-Jones (LJ) parameters have been correlated from viscosity data.²⁹ For simple molecules, LJ-parameters tend to be less sensitive to the property they were fitted to; therefore, we adopted these “viscosity values” for the carrier gases in our computations. For the pairwise interaction between unlike molecules, the commonly used Lorentz–Berthelot rules were applied, i.e., $\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2}$ and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$.

Obviously, the enhancement factor follows directly from the bulk limits of the density

$$f_e = \left(\frac{\rho_1^v}{\rho_1^v + \rho_2^v} \right) \frac{p}{p^s}, \quad (42)$$

FIG. 6. Normalized surface tension γ/γ_0 and enhancement factor f_e of *n*-hexane in nitrogen as a function of total pressure, for temperatures of 298.15 and 240.00 K. The main contributions to f_e are also included, see Eq. (2). Solid line: Experimental surface tension data of Ref. 20.

where ρ_i^v is the bulk vapor density of component i . The pure vapor pressure is calculated from Eq. (40). This is trivial for $T=298.15$ K, since the potential parameters of *n*-hexane were fitted to p^s and ρ^l at that temperature.

From combined binary and unary DFT calculations, it is possible to determine the individual contributions to f_e in Eq. (2). The pure vapor fugacity coefficient ϕ^s depends only on temperature. At 298 K it equals 1.009, and it is closer to unity for lower temperatures. Furthermore, the activity coefficient of component one in the liquid differs from unity by at most 2 percent for the conditions of interest. From the remaining contributions, the liquid fraction x_1^{eq} follows in a trivial manner from the bulk liquid densities. Next, the Poynting factor f_P is obtained from Eq. (5). Finally, the fugacity coefficient in the binary gas phase ϕ_1^{eq} is given by

$$\phi_1^{eq} = \frac{\phi^s p^s}{p} \left(\frac{\rho_1^v + \rho_2^v}{\rho_1^v} \right) \exp \left[\frac{\mu_1 - \mu_1^\circ}{k_B T} \right], \quad (43)$$

where the superscript ‘‘○’’ refers to the pure vapor state.

DFT calculations were performed for *n*-hexane vapor with the carrier gases helium, argon, nitrogen and methane. A temperature of 298.15 K was chosen as a reference condition. All calculations were performed at pressures of 1–100 bar, with a step size of 10 bar. In order to get an impression of how the enhancement and surface tension effects extrapolate to typical nucleation temperatures, the calculations were repeated at 240 K.

Figure 5 shows characteristic results for *n*-hexane in nitrogen at four different pressures. Beside the density profiles, the integrand of the surface tension expression (39) is represented. Obviously, the significant contributions to γ originate in the interface region. All quantities in the figure are made dimensionless with the potential parameters of *n*-hexane.

A remarkable feature is that the nitrogen number density does not increase monotonically over the interface: We are dealing with surface adsorption, indicated by the ‘‘hump’’ in ρ_2 . Moreover, the amount of surface adsorption increases with pressure. This feature was used in Sec. III to explain the pressure effect on surface tension.

The behavior of the bulk vapor density of *n*-hexane with pressure is hard to be observed in Fig. 5. Therefore, enhancement factors as a function of the total pressure p are shown in Fig. 6 for two temperatures. The most important contributing factors to f_e are also included, indicating the main mechanisms behind the enhancement effect.

Figure 7 shows the same quantities, but now computed from the Redlich–Kwong–Soave (RKS) equation of state.^{8,29} A striking resemblance between DFT and RKS predictions is observed. This is an encouraging result, since the RKS parameters are tuned to the *experimental* phase behavior of a variety of substances (among which are the *n*-alkanes). The agreement is even somewhat unexpected, in view of the simplicity of the assumed interaction potential.

Experimental surface tension data for *n*-hexane in nitro-

FIG. 7. As Fig. 6, but now obtained from the Redlich–Kwong–Soave equation of state.

FIG. 8. Normalized surface tension γ/γ_0 and enhancement factor f_e (and its main constituents) of *n*-hexane in argon as a function of total pressure, for temperatures of 298.15 and 240.0 K. Solid line: Experimental surface tension data of Ref. 32.

gen are also available at 298.15 K,²⁰ represented by the bold solid line in Figs. 6 and 7. A remarkable correspondence is found between the experimental data for the (relative) decrease of surface tension with pressure, and both DFT and RKS predictions of this decrease. The latter are obtained from the equilibrium phase compositions and densities, using the Parachor method.¹¹

Obviously, the enhancement effect is much stronger at the lower temperature of 240 K. For the surface tension, this is less clear: apparently, the decrease is not much stronger than it is at 298 K. This observation corresponds to what was found experimentally for water in nitrogen at different temperatures (see Fig. 2).

Figure 8 shows DFT results for *n*-hexane in argon, again for temperatures of 298 and 240 K. Experimental surface tension data³² at 298 K are indicated by the bold solid line in Fig. 8. In this case the experimental pressure trend is less severe than predicted by DFT. The discrepancy is probably due to the predicted too large argon fraction in the liquid.

Comparison of Figs. 6 and 8 shows that the enhancement effect is slightly stronger for argon than it is for nitrogen. The surface tension decrease is similar (experimental data show indiscernible results for argon and nitrogen). Apparently, there is no fundamental reason for the preference of argon above nitrogen as a carrier gas in nucleation experiments.

Figure 9 shows DFT results for *n*-hexane in helium. At 298.15 K, the enhancement factor is even smaller than the

Poynting factor. Since the fugacity coefficient ϕ_1^{eq} is very close to unity for all pressures, this must be caused by the increasing fraction of helium in the liquid phase, see Eq. (2). The latter is probably overestimated by the DFT calculations, since experimental helium solubilities at room temperature are generally much lower. The same argument explains why the surface tension decreases significantly with pressure: dissolution of helium reduces γ in the DFT calculation, but experimental data at 298 K indicate that there is no measurable pressure effect up to 100 bar.²⁰

At 240 K, the fugacity coefficient ϕ_1^{eq} deviates from unity with increasing pressure; the decrease nearly coincides with that of x_1^{eq} . Since Eq. (2) contains the ratio of both quantities, the enhancement factor becomes equal to its Poynting contribution. It is quite well possible that the helium solubility is still overrated at this temperature, in which case the surface tension decrease with pressure in Fig. 9(b) would be erroneous.

For reasons of brevity, the results for *n*-hexane in methane are not reproduced here. All pressure trends are much stronger in this system, which could be expected from the chemical similarity between vapor and gas. We come back to this issue in Paper II.¹⁷

VII. CONCLUSIONS

In a mixture of a condensable vapor and a supercritical carrier gas, the equilibrium properties of the subcritical com-

FIG. 9. Normalized surface tension γ/γ_0 and enhancement factor f_e (and its main constituents) of *n*-hexane in helium as a function of total pressure, for temperatures of 298.15 and 240.0 K.

ponent are affected by the presence of the carrier gas. The saturated vapor density tends to increase with total pressure, whereas the surface tension generally diminishes upon pressurization. We have outlined several methods to obtain quantitative data for these effects. New measurements were presented for the surface tension of water under nitrogen pressure at low temperatures.

The nucleation process in these mixtures is essentially a binary one, since the carrier gas may enter the nucleating clusters. Still, the single component description of the nucleation process can be preserved, provided that the carrier gas pressure is recognized as a parameter that modifies the vapor properties. This pressure perturbation approach was shown to be valid as long as the carrier gas solubility in the liquid phase is not too large: Quantitatively, the carrier gas fraction in the liquid phase should be much smaller than $(S-1)/S$, where S is the supersaturation ratio.

We have described how our pressure perturbation model can be implemented in several important classes of theoretical models. The classical expression for the steady-state nucleation rate is hardly altered, provided that the pressure dependent values of S and γ are substituted. The only other difference with the pure vapor case is the presence of a factor f_e/Z_g^2 in the kinetic prefactor, see Eq. (12).

We also demonstrated the role of carrier gases in the semiphenomenological model of Kalikmanov and Van Dongen. The enhancement effect manifests itself as a size-dependent correction to the cluster distribution, also resulting in a shift of the critical cluster size. The mathematical implementation of the enhancement effect, gas phase compressibility, and a possible surface tension effect into this model is straightforward, see Eq. (31).

Binary density functional theory was applied to calculate the enhancement effect and pressure dependent surface tensions in a mixture of Lennard-Jones molecules. We chose *n*-hexane as a model substance, mixed with nitrogen, argon, helium, and methane. The calculated pressure trends largely correspond to experimental data, with possible exception of the carrier gas solubility, which tends to be overestimated. This generally results in a small overprediction of the decrease of surface tension with pressure.

Since nucleation theory can fully be cast in terms of DFT, pressure effects could also be implemented in a nucleation rate calculation. In addition, our DFT approach for flat

surfaces could be used as a physically meaningful model for the extrapolation of pressure effects to supercooled temperatures, which are not always accessible to equilibrium measurements.

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