Diffuse Interface Approach to Vapour Condensation

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Abstract. – A diffuse interface approach to nucleation based on a parameterization of the cross-interfacial enthalpy and entropy profiles has been applied for vapour condensation in non-polar systems. Without introducing adjustable parameters, the model describes the experiments remarkably better than the classical theory.

Introduction. – First-order phase transformations (vapour condensation, boiling, freezing, melting, liquid-phase separation, precipitation, etc.) begin with nucleation, *i.e.* the new phase forms with the growth of heterophase fluctuations that are larger than a critical size below which the fluctuations are destabilized by the excess free energy from the interface region[1]. This process may be assisted by heterogeneities (container walls, impurities, foreign particles—heterogeneous nucleation). Although computer simulations[2] and molecular theories[3] are particularly useful in exploring the microscopic aspects of nucleation, at present they cannot be used for quantitative predictions in real systems. As a consequence, the experiments[4] are often interpreted in terms of a simple and flexible phenomenological model—known as the classical nucleation theory (CNT)—developed for vapour condensation by Becker and Döring[5] and modified for condensed matter-condensed matter transformations by Turnbull and Fisher[6]. Based on the «capillarity» approximation, the CNT views the nuclei as spherical particles characterized by bulk properties (Gibbs free energy and interface free energy)—a picture strictly valid if the thickness of the interface region is negligible compared to the size of the nucleus, which is hardly true for nuclei containing 30 to few 100 molecules obtained in most cases[1a, 2a, 7a]. Computer simulations[2] and microscopic models[3] show that the nuclei are nearly «all interface» and that the respective correction to CNT may be substantial. This conclusion accords with a failure of the CNT to describe vapour condensation in various systems[8].

That a modification of the CNT might be necessary in case of an extended («diffuse») interface has been recognized for some time. It has been suggested[9] that under such conditions the interface free energy is size dependent, $\gamma(R) = \gamma_\infty \{1 - 2\delta_T/R + O(R^{-2})\}$, where γ_∞ is the free energy of the planar interface, δ_T is the Tolman length (distance of the equimolar surface and the surface of tension), while R is the radius of the fluctuation. Despite

efforts to evaluate δ_T, both the magnitude and the sign of the Tolman length are uncertain [2b]. Using the ansatz $\gamma = \gamma_\infty (1 + \alpha_1 i^{-1/3} + \alpha_2 i^{-2/3})$, where i is the number of molecules in the heterophase fluctuation, Dillmann and Meier determined $\alpha_1 (\sim \delta_T)$ and α_2 from the equation of state of the vapour [10]. Except for highly polar substances [8f] the predicted strongly size-dependent interface free energy leads to a good agreement with experiments. Thus, it is somewhat puzzling that i) according to a recent computer simulation δ_T cannot be distinguished from zero within error [2b], and ii) an analysis based on the Irwing-Kirkwood theory of microscopic pressure tensor implies that for the symmetric density profile the Tolman length is zero [11].

In other extensions of the CNT [12] the classical expression for the free energy of fluctuations, W_{CNT}, is replaced by a «self-consistent» formula $W(i) = W_{CNT}(i) - W_{CNT}(1)$, giving the proper value at the monomer limit: $W(1) = 0$. Although this modification is rather arbitrary (a variety of correction functions $\Delta W(i)$ satisfying $\Delta W(1) = - W_{CNT}(1)$ and $\lim_{i \to \infty} \{\Delta W(i) / W_{CNT}(i)\} = 0$ could be chosen), in some cases [12c] a remarkable agreement with experiments has been reported.

In the light of these uncertainties neither the size-dependent interface free energy nor the «self-consistent W» concept can be fully accepted without further verification. An essentially different diffuse interface approach to nucleation has been proposed recently [13]. Parameterizing the cross-interfacial enthalpy and entropy profiles, a size-dependent interface free energy similar in form to the ansatz of Dillmann and Meyer has been obtained. The model is consistent with experiments on crystal nucleation in glassy $Li_2O \cdot 2SiO_2$. From the temperature dependence of the nucleation rate, the parameter δ corresponding formally to $2\delta_T$ (although with a different physical meaning to be described below) is (2.41 ± 0.01) Å, resulting in a substantial correction to the CNT.

In the present letter this new approach is applied for vapour condensation. The high-precision experimental data (nucleation rate, surface tension and vapour pressure), unparalleled in case of other phase transformations, make a thorough test possible. It will be shown that for non-polar substances the predictions are in fair agreement with experiments.

Model. – As pointed out by Turnbull [14], the variation of the local physical state in the interface region can be characterized by cross-interfacial enthalpy and entropy distributions (see fig. 1). Assuming spherical symmetry, the Gibbs free energy of formation of a heterophase fluctuation reads as

$$W = \int_0^\infty (\Delta h - T \cdot \Delta s) \cdot 4\pi r^2 \cdot dr \,, \tag{1}$$

where $\Delta h = N(r)\{H(r) - H_1\}$, $\Delta s = N(r)\{S(r) - S_1\}$, $N(r)$ is the local number density of molecules, $H(r)$ and $S(r)$ are the local enthalpy and entropy per molecule, while subscript 1 denotes the parent phase. Replacing Δh and Δs in eq. (1) with $\Delta h_{eff} = \Delta h_0 \{1 - \theta(r - R_H)\}$ and $\Delta s_{eff} = \Delta s_0 \{1 - \theta(r - R_S)\}$, W can be expressed in terms of the position of the «enthalpy» and «entropy» surfaces R_H and R_S as

$$W = \kappa \cdot (R_H^3 \cdot \Delta h_0 - R_S^3 \cdot T \cdot \Delta s_0) \,, \tag{2}$$

where $\kappa = 4\pi/3$, $\Delta h_0 = \Delta h(0)$ and $\Delta s_0 = \Delta s(0)$, θ is the step function, while R_H and R_S can be
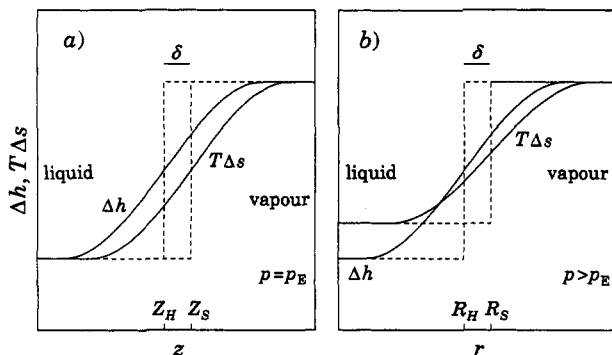
Fig. 1. – Schematic cross-interfacial enthalpy (Δh) and entropy (Δs) profiles a) for planar geometry in equilibrium and b) for a curved interface between liquid and supersaturated vapour. The «rectangularized» distributions (dashed lines), the position of the «enthalpy» (Z_H, R_H) and «entropy» (Z_S, R_S) surfaces, and the definition of the interface parameter δ are also shown. (z, r: spatial coordinates perpendicular to the interface.)

obtained by inserting $\Delta f = \Delta h$ and $\Delta f = \Delta s$ into

$$\int_0^{R_F} [\Delta f(r) - \Delta f_{\text{eff}}] \, 4\pi r^2 \, \mathrm{d}r = \int_{R_F}^{\infty} [\Delta f_{\text{eff}} - \Delta f(r)] \, 4\pi r^2 \, \mathrm{d}r \,, \tag{3}$$

respectively. W can be evaluated if R_H and R_S are known from, $e.g.$, a microscopic model. A different route is chosen here. For planar interface between phases in equilibrium the interface free energy γ_∞ is equal to the area A enclosed by curves Δh and $T\Delta s$ [14]. Evidently, the area enclosed by Δh_{eff} and $T\Delta s_{\text{eff}}$ is equal to A, thus $Z_S - Z_H = \delta = -\gamma_\infty / \Delta h_0$, where Z_H and Z_S are the positions of the planar «enthalpy» and «entropy» surfaces (see fig. 1a)), defined by the planar analogue of eq. (3). For γ_∞ to be positive, the curve Δh must lie higher than $T\Delta s$ [14], $i.e.$ $\delta > 0$. Note that δ is expressed in terms of macroscopic quantities (interface free energy and heat of transformation) known for vapour condensation in various systems. For particles much larger than the interface thickness it can safely be assumed that i) $R_S - R_H \approx \delta$ and ii) $\Delta h_0 = N_2(H_2 - H_1)$ and $\Delta s_0 = N_2(S_2 - S_1)$, where the subscript 2 denotes the new phase. Clearly, these assumptions break down for small clusters. However, a validity range wider than for the CNT may be expected, since a) macroscopic properties are assumed in only the centre of the fluctuation, and b) the corresponding size dependence of γ is consistent with experiments for another nucleation problem [13]. Postulating $R_S - R_H = \delta$, a simple nucleation theory can be obtained. Expressing R_H in terms of δ and R_S, then, maximizing W with respect to R_S, the size and Gibbs free energy of the critical fluctuation are $R_S^* = \delta(1 + q)\eta^{-1}$ and

$$W^* = -\kappa \cdot \delta^3 \cdot \Delta g_0 \cdot \psi(\eta) \,, \tag{4}$$

respectively, where $q = (1 - \eta)^{1/2}$, $\eta = \Delta g_0 / \Delta h_0$, $\Delta g_0 = \Delta h_0 - T\Delta s_0$, while $\psi = 2(1 + q)\eta^{-3} - (3 + 2q)\eta^{-2} + \eta^{-1}$. The volumetric Gibbs free-energy difference between the liquid and the supersaturated vapour can be expressed as $\Delta g_0 = -kT \ln(p/p_E)/v_m^L$, where k, p, p_E and v_m^L are Boltzmann's constant, the vapour pressure, the equilibrium vapour pressure and the molecular volume of the liquid, respectively. Assuming ideal-gas behaviour (a realiable

approximation in the temperature range of experiments) Δh_0 can be determined from the Clausius-Clapeyron equation as $\Delta h_0 = - kT^2 (\mathrm{d} \ln p_\mathrm{E} / \mathrm{d}T) / v_\mathrm{m}^\mathrm{L}$.

Following the classical procedure and assuming $i \approx \kappa R_S^3 / v_\mathrm{m}^\mathrm{L}$, the nucleation rate for vapour condensation can be given as $I = I_0 \exp [- W^* / kT]$, where $I_0 = N_\mathrm{v} A^* p \cdot$ $\cdot (2\pi m k T)^{-1/2} Z$, $N_\mathrm{v} = p / kT$, $A^* \approx 4\pi R_S^{*2}$ and $Z = (v_\mathrm{m}^\mathrm{L} / 2\pi R_S^{*2}) \{ | \Delta g_0 | (R_S^* - \delta/\eta) / kT \}^{1/2}$, while m is the molecular mass. Note that i) the nucleation rate can be evaluated from the same input data as in the case of the CNT, and ii) the present model—like the CNT—*does not contain adjustable parameters.*

Testing materials. – Since in the present approach δ is evaluated from the surface tension measured on macroscopic drops (approximately planar geometry) possible curvaturedependent contributions from the dipole-dipole interaction [7b] or from breaking-up of an ordered planar interface [7c] are not taken into account. To avoid such effects, non-polar substances of weakly
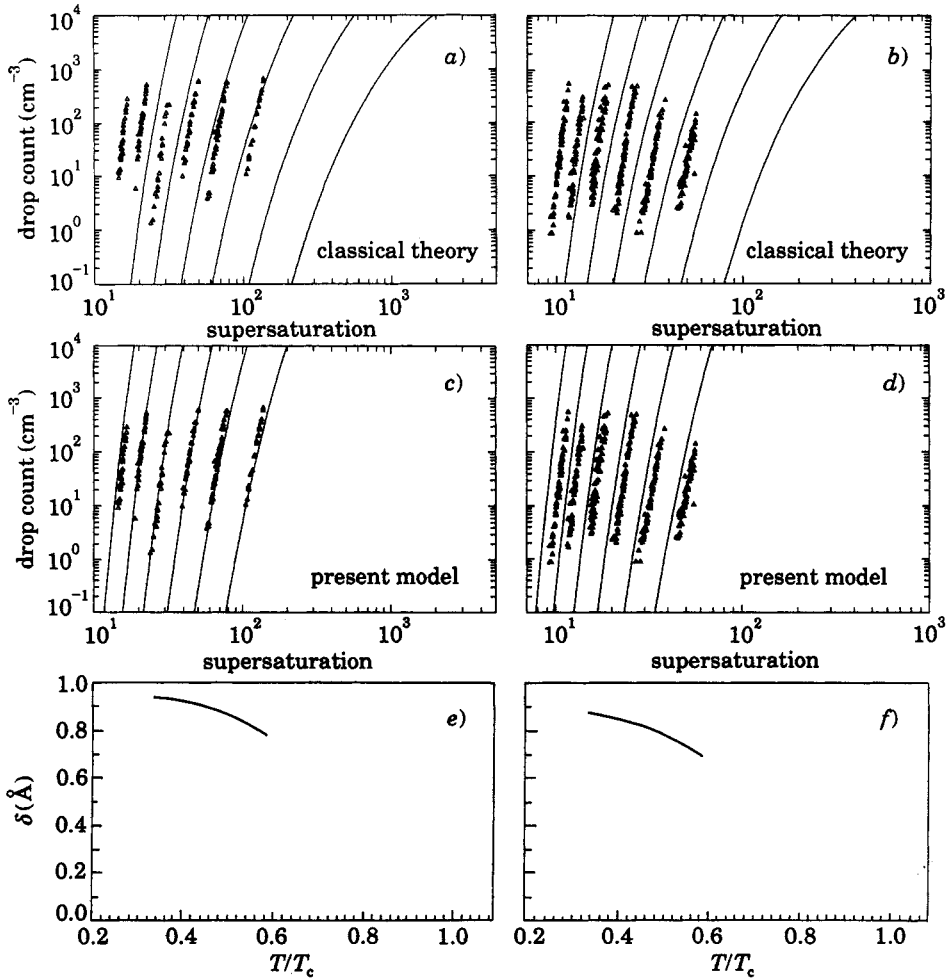

Fig. 2. – Comparison of predictions (——) by the CNT and the present model to experimental results ($\triangle$) on nonane (left) and toluene (right). In a)-d) from left to right experimental data sets and calculated curves correspond to pre-expansion temperatures 45, 35, 25, 15, 5, and $-5\,°\mathrm{C}$, respectively. The temperature dependence of the interface parameter δ is shown in e), f).

interacting large molecules (nonane and toluene) have been chosen for the test. Drop count, temperature and supersaturation ($S_p = p/p_E$) data communicated to the author by Schmitt have been used. These data originate from expansion cloud chamber experiments described in ref. [8a] and [8c] and are identical to those used in ref. [15]. Since in expansion cloud chambers the temperature and supersaturation are not independent, the temperature corresponding to a certain supersaturation has been calculated as $T = a \ln S_p + b$, where coefficients a and b have been obtained for every pre-expansion temperatures by a least-square fit to the experimental $\{T, S_p\}$ pairs. Physical properties taken from ref. [8a] and [8d] have been used in the calculations. The computed nucleation rates were transformed to drop count using the conversion factor given in ref. [15] (155 drops $\cdot$ cm^{-3} s^{-1} corresponds to 1 drop $\cdot$ cm^{-3}).

Results and discussion. – The predictions of the CNT and the present model are compared to the experiments in fig. 2. While in the case of CNT several orders of magnitude deviation from experimental data can be observed (fig. 2a), b)), drop counts from measurements and the present model are in a fair agreement for both substances (fig. 2c), d)). Approaching the trend $\delta \sim \tau^{\mu - \beta}$ expected from the critical behaviour of the heat of evaporation ($\sim \tau^\beta$) and surface tension ($\sim \tau^\mu$), where $\tau = 1 - T/T_c$, T_c is the critical temperature, while $\beta = 0.32 \div 0.36$ and $\mu = 1.26 \div 1.3$ (measured on pure liquids), the interface parameter δ varies between about $(0.7 \div 0.9)$ Å in the temperature range of experiments (fig. 2e), f)). Under such conditions eq. (4) can be well approximated by inserting $\gamma' = \gamma_\infty (1 - \delta/R_{CNT}^*)$ into the classical formula $W_{CNT}^* = 4\kappa \gamma'^3 \Delta g_0^{-2}$, where $R_{CNT}^* = -2\gamma_\infty/\Delta g_0$, corresponding to a $(5 \div 9)\%$ reduction of γ_∞.

Condensation of nonane has been studied at significantly higher [8b] and lower [8d] nucleation rates by other methods. While data from a two-piston expansion cloud chamber [8b] are essentially coherent with the results of Schmitt [15] and the present theory, the nucleation rates measured in a diffusion cloud chamber [8d] do not fit to the extrapolation of the Schmitt data to low nucleation rates, or to the predictions from either the CNT or the present model. Further experimental and/or theoretical work is needed to clarify the origin of this discrepancy.

To test whether the present model indeed breaks down for polar substances, nucleation rates computed with physical properties taken from ref. [10] have been compared to experiments on alcohols [8c] and water [16]. As expected in the presence of a strong dipole-dipole interaction, the predicted nucleation rates are significantly larger than the measured values. Assuming dipole moments perpendicular to the interface, Abraham estimated the excess dipole-dipole potential energy due to interface curvature for water [7b]. The corresponding reduction of the nucleation rate is, however, far too large (about 15% of this correction to γ would be enough to reach agreement with experiments). A possible explanation could be that a significant fraction of dipoles decline from the assumed orientation, as suggested by recent optical measurements [17]. Extension of the present model for polar substances could be attempted by determining the size dependence of $R_S - R_H$ from either the equation of state of vapour or from a microscopic model. A more detailed comparison to experiments will be presented elsewhere.

Summary. – A diffuse interface approach to nucleation based on a parameterization of the cross-interfacial enthalpy and entropy profiles has been applied for vapour condensation in non-polar systems. By evaluating the distance of the «enthalpy» and «entropy» surfaces from the macroscopic interface free energy, a fair agreement with experiments has been obtained.

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