

Analytical density functional theory of homogeneous vapor condensation

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Starting from an exact gradient transcription of the perturbative density functional theory of homogeneous vapor condensation, we propose an analytical approximation that reproduces the density profile and free energy of critical fluctuations to high accuracy. For a broad variety of substances, including nonpolar, weakly polar, and metallic liquids, the method predicts nucleation rates that are orders of magnitude closer to experiment than those from the classical approach. The present treatment incorporates detailed molecular theory into macroscopic modeling.

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Vapor-liquid nucleation plays an essential role in phenomena of scientific and practical interest including cloud formation [1], climatic changes [2], and various technological procedures. Analogous processes take place during crystallization [3], phase separation [4], boiling [5], and the first-order phase transitions associated with the early history of the universe [6]. The molecular models based on the *density functional theory* (DFT) clarified important aspects of nucleation such as the formation of metastable phases [7], nucleation in the presence of a metastable critical point [8], condensation of polar substances [9], and the magnitude of nucleation prefactor for condensation [10] and crystallization [11], and results that either accord with computer simulations [12] or are complementary to them.

Starting from molecular interactions, the density functional theory of vapor condensation [13] accounts for much of the discrepancy between experiment and classical theory, and predicts nucleation rates improved by orders of magnitude [14]. In this approach, the attractive part of the molecular interaction appears as a perturbation relative to a repulsive hard-sphere (HS) contribution. The work of formation of the inhomogeneous system is

$$W = \int \phi[\rho(\mathbf{r})] d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) w(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (1)$$

where $\phi = f_h - \mu_0 \rho + p_0$, f_h is the Helmholtz free energy density of the HS fluid given by the Carnahan-Starling (CS) equation, ρ is the number density of molecules, μ_0 and p_0 are the chemical potential and pressure of the supersaturated vapor, while $w(|\mathbf{r} - \mathbf{r}'|)$ is the attractive part of the potential, assumed to be of the Yukawa form. The extremum of this functional corresponds to the nucleus, for which the density distribution is obtained as the solution of the (integral) Euler-Lagrange equation

$$\mu_0 = \mu_h + \int_0^\infty \psi(r, r') dr' \quad (2)$$

where μ_h is the local chemical potential of the HS fluid, $\psi = -(\alpha \lambda r'/2r) \{ \exp[-\lambda|r - r'|] - \exp[-\lambda(r + r')] \} \rho(r')$, while α and λ are the integral strength and the range parameter of the Yukawa potential [13]. The iterative determination of the unstable solution of Eq. (2) is time consuming,

thus, the inclusion of the DFT into macroscopic scale modeling has been considered unfeasible. In this paper we present a highly accurate analytical approximation, that resolves this difficulty.

Our starting point is an exact transcription of Eq. (1) into a gradient theory proposed recently by Iwamatsu and Horii for Yukawa attraction [15] that introduces the HS chemical potential μ_h as the order parameter. For spherical droplets,

$$W = \int_0^\infty \left[\Delta \omega(\mu_h) + \frac{A}{2} \left(\frac{d\mu_h}{dr} \right)^2 \right] 4\pi r^2 dr, \quad (3)$$

where the local deviation of the effective free energy density ω from the value for the homogeneous system is expressed in terms of the potential V introduced in [15]: $\Delta \omega = \omega - \omega_\infty = V(\mu_h) + p_0$. The coefficient A is related to the surface tension γ via the planar version of Eq. (3),

$$\gamma = \int_{\rho_v}^{\rho_l} A \lambda [2\Delta I(\rho, \rho_v)]^{1/2} \left(\frac{d\mu_h}{d\rho} \right) d\rho, \quad (4)$$

where $\Delta I(\rho, \rho_v) = \int_{\rho_v}^{\rho} (\mu_h - \mu_e - \alpha \rho) (d\mu_h/d\rho) d\rho$ [16]; ρ_v and ρ_l are the equilibrium vapor and liquid densities, and μ_e is the chemical potential of the saturated vapor.

We approximate the free energy-order parameter relationship by a triple parabola expansion: $\omega = \frac{1}{2} \lambda_i (m - m_i)^2 - \beta m + \delta_{i,1} \omega_0$. Here $m = (\mu_h - \mu_{h,v}) / (\mu_{h,l} - \mu_{h,v})$ is a normalized order parameter, m_i are the positions of the tips of the parabolas for the vapor and liquid minima ($i=0$ and 2) and the maximum in between ($i=1$), $\lambda_{0,2} > 0$ and $\lambda_1 < 0$ are the respective curvatures, $\mu_{h,l}$ and $\mu_{h,v}$ are the HS chemical potentials for the equilibrium liquid and vapor phases, β is the free energy difference, $\delta_{i,1}$ is the Kronecker's delta, while ω_0 is the height of the free energy barrier in equilibrium. For fixed λ_i , m_0 , and m_2 , continuity of the free energy and its first derivative at the matching points m_A and m_B (see Fig. 1) requires that $m_A = (\lambda_0 m_0 + |\lambda_1| m_1) / (\lambda_0 + |\lambda_1|)$, $m_B = (\lambda_2 m_2 + |\lambda_1| m_1) / (\lambda_2 + |\lambda_1|)$, and $\omega_0 = \frac{1}{2} \lambda_0 (m_A - m_0)^2 + 1/2 |\lambda_1| (m_A - m_1)^2$, where $m_1 = [-q + (pq)^{1/2}] / (p - q)$, while $p = \lambda_0 |\lambda_1| / (\lambda_0 + |\lambda_1|)$ and $q = \lambda_2 |\lambda_1| / (\lambda_2 + |\lambda_1|)$.

To accurately reproduce the free energy curve for the practically important small supersaturations, the curvatures for the vapor and liquid branches ($i=0$ and 2) are evaluated in equilibrium as

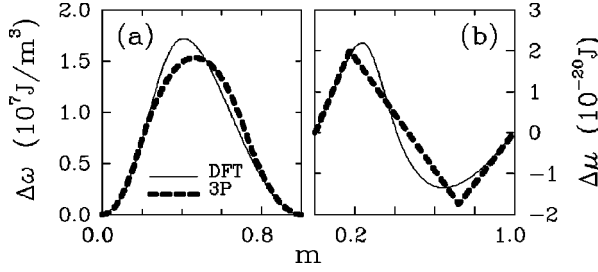


FIG. 1. Equilibrium thermodynamics for nonane at $T=315$ K in the density functional theory (DFT) and the triple-parabola approximation (3P): (a) The free energy density and (b) the chemical potential relative to the saturated vapor as a function of the order parameter m .

$$\lambda_i = A(\mu_{h,l} - \mu_{h,v})^2 \frac{\left. \frac{d\mu_h}{d\rho} \right|_{\rho_i} - \alpha}{\left. \frac{d\mu_h}{d\rho} \right|_{\rho_i}}. \quad (5)$$

We set λ_1 so as to recover exactly the surface tension of the full DFT.

This triple parabola approximation linearizes the respective Euler-Lagrange equations yielding

$$M_i'' + \frac{2}{r} M_i' \pm \Gamma_i^2 M_i = 0, \quad (6)$$

where the prime stands for differentiation with respect to r , $\Gamma_i = (\lambda_i/2c)^{1/2}$ for $i=0$ and 2 , $\Gamma_1 = (|\lambda_1|/2c)^{1/2}$, and $c = \frac{1}{2} A(\mu_{h,l} - \mu_{h,v})^2$, while the positive sign of the third term applies for $i=1$. Equations (6) have the piecewise analytical solutions [17]

$$\begin{aligned} M_0 &= \{a_0 \exp(\Gamma_0 r) + b_0 \exp(-\Gamma_0 r)\} r^{-1}, \\ M_1 &= \{a_1 \sin(\Gamma_1 r) + b_1 \cos(\Gamma_1 r)\} r^{-1}, \\ M_2 &= \{a_2 \sinh(-\Gamma_2 r) + b_2 \cosh(-\Gamma_2 r)\} r^{-1}, \end{aligned} \quad (7)$$

for the reduced order parameter profiles $M_i = m - m_i - \beta/\lambda_i$, an approach similar to that we explored in Ref. [17]. Considering the boundary conditions $m \rightarrow m_\infty$ for $r \rightarrow \infty$ and $m' \rightarrow 0$ for $r \rightarrow 0$, and the continuity of the order parameter profile, the coefficients a_i and b_i can be expressed in terms of the coordinates r_A , r_B , m_A , and m_B of the matching points between the piecewise solutions. The condition of continuity of m' yields transcendental equations for r_A and r_B :

$$0 = M_{1,A}[\Gamma_1 \cot(\Gamma_1 r_A) - r_A^{-1}] + M_{0,A}[\Gamma_0 + r_A^{-1}] - b_1 \Gamma_1 [r_A \sin(\Gamma_1 r_A)]^{-1}, \quad (8)$$

$$\begin{aligned} 0 &= M_{1,B}[\Gamma_1 \cot(\Gamma_1 r_B) - r_B^{-1}] + M_{2,B} \\ &\times [r_B^{-1} + \Gamma_2 \coth(-\Gamma_2 r_B)] - b_1 \Gamma_1 [r_B \sin(\Gamma_1 r_B)]^{-1}, \end{aligned} \quad (9)$$

where $b_1 = [M_{1,B} r_B \sin(\Gamma_1 r_A) - M_{1,A} r_A \sin(\Gamma_1 r_B)] / \sin[\Gamma_1(r_A - r_B)]$, $M_{i,A} = M_i(m_A)$, and $M_{i,B} = M_i(m_B)$.

Having determined r_A and r_B numerically, the work of formation is evaluated by integrating the right-hand side of Eq. (3) piecewise, yielding $W = W_0 + W_1 + W_2$, where

$$W_0 = 2\pi\lambda_0 M_{0,A}^2 \left(\frac{r_A}{\Gamma_0}\right)^2 [\Gamma_0 + r_A^{-1}], \quad (10)$$

$$\begin{aligned} W_1 &= \frac{4\pi}{3} \left[\omega_0 + \frac{\beta^2}{2} \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) + \beta(m_0 - m_1) \right] \\ &\times (r_A^3 - r_B^3) + \frac{2\pi\lambda_1}{\Gamma_1^2} (M_{1,A}^2 r_A - M_{1,B}^2 r_B) \\ &+ \frac{2\pi\lambda_1}{\Gamma_1} \left\{ \frac{2M_{1,B} r_B M_{1,A} r_A}{\sin[\Gamma_1(r_A - r_B)]} - (M_{1,A}^2 r_A^2 \right. \\ &\left. + M_{1,B}^2 r_B^2) \cot[\Gamma_1(r_A - r_B)] \right\}, \end{aligned} \quad (11)$$

$$\begin{aligned} W_2 &= \frac{4\pi}{3} \left[\frac{\beta^2}{2} \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_2} \right) + \beta(m_0 - m_2) \right] r_B^3 \\ &+ 2\pi\lambda_2 M_{2,B}^2 \left(\frac{r_B}{\Gamma_2}\right)^2 \left[\Gamma_2 \frac{\sinh(2\Gamma_2 r_B)}{\cosh(2\Gamma_2 r_B) - 1} - r_B^{-1} \right]. \end{aligned} \quad (12)$$

The nucleation rate is calculated as

$$J = J_0 \exp\{-W/kT\}, \quad (13)$$

where the classical nucleation prefactor

$$J_0 = \rho_0^2 \rho_l^{-1} (2\gamma/\pi m)^{1/2}$$

is used [14,18], with ρ_0 as the density of the supersaturated vapor, and m as the molecular mass. A full dynamical treatment of the DFT gives results almost indistinguishable from this simple choice of J_0 [10].

In applying the present model to the condensation of real substances, we first set the values of α and the HS radius d so that they reproduce the equilibrium vapor pressure (p_e) and density of the liquid. Then, the planar version of Eq. (1)

$$\gamma = \frac{1}{\lambda} \int_{\rho_v}^{\rho_l} \frac{(p_e - p_h) - \frac{1}{2} \rho (\mu_e - \mu_h)}{[2\Delta I(\rho, \rho_v)]^{1/2}} \left(\frac{d\mu_h}{d\rho} \right) d\rho, \quad (14)$$

is used to evaluate the range parameter λ from the measured surface tension, where $p_h(\rho)$ and $\mu_h(\rho)$ are the CS relationships for pressure and chemical potential. Note that α , d , and λ depend on temperature [14]. Having fixed these parameters, A and λ_i are determined via Eqs. (4) and (5), while β is chosen so that the free energy difference between the vapor and liquid minima (that shift relative to m_0 and m_2 for $\beta \neq 0$) is equal to the bulk chemical potential difference [$\Delta\mu \approx kT \ln(S)$, where S is the supersaturation].

The free energy and chemical potential curves predicted by the DFT and the triple parabola approximation are compared in Fig. 1. At small supersaturations, the triple parabola expansion reproduces the thermodynamic properties of the

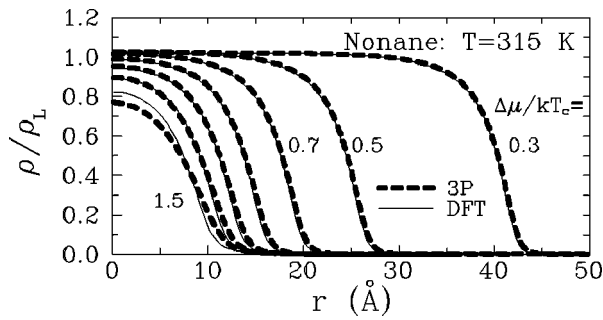


FIG. 2. Radial density profiles as predicted for nonane at $T = 315$ K by the density functional theory (DFT) and the analytical approximation (3P).

HS-Yukawa system with a high accuracy. Deviations are only seen for extreme supersaturations that are out of the typical range of experiments. Accordingly, below a limiting supersaturation ($\Delta\mu \approx 1.3kT_c$, where T_c is the critical temperature determined by λ , α , and d), the predicted density profiles (Fig. 2) and nucleation rates (Fig. 3) are in an excellent agreement with the numerical results from the DFT. Similar agreement has been found for the condensation of various substances (Fig. 4). Note that the DFT predictions are insensitive to the form of the attractive potential (comparable results were obtained for Yukawa and Lennard-Jones type attraction) [14], and that by incorporating microscopic features the DFT predictions are significantly closer to the experiments [19–23] than those from the classical theory [18] (see Figs. 3 and 4).

The success of the present model stems from using the HS chemical potential as the order parameter. Previous gradient theories of condensation, that rely on density as the order parameter, proved less successful [24]. The essential difference is that $A = \text{const}$ in Eq. (3) translates to a strongly density-dependent coefficient of the gradient term when density is introduced as the order parameter.

Summarizing, we demonstrated that the analytical model presented here can be used with confidence to reproduce the DFT predictions for both the density profile and the nucle-

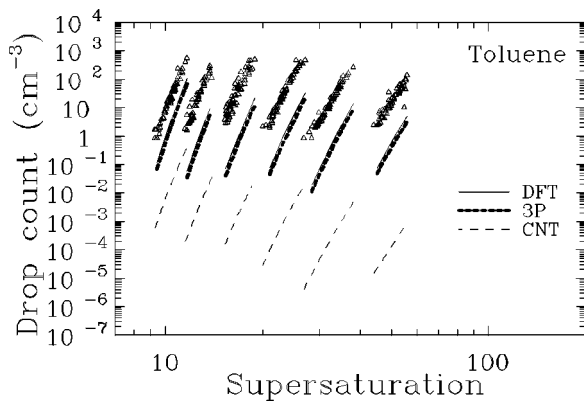


FIG. 3. Drop count (proportional to nucleation rate) as predicted by the density functional theory (DFT) and the triple-parabola approximation (3P) for toluene. Experimental results (triangles, Ref. [19]), and the classical predictions (CNT) are also shown. Data sets from left to right correspond to pre-expansion temperatures of 45, 35, 25, 15, 5, and -5 °C. (The uncertainty of drop count due to the error of input data is about an order of magnitude.)

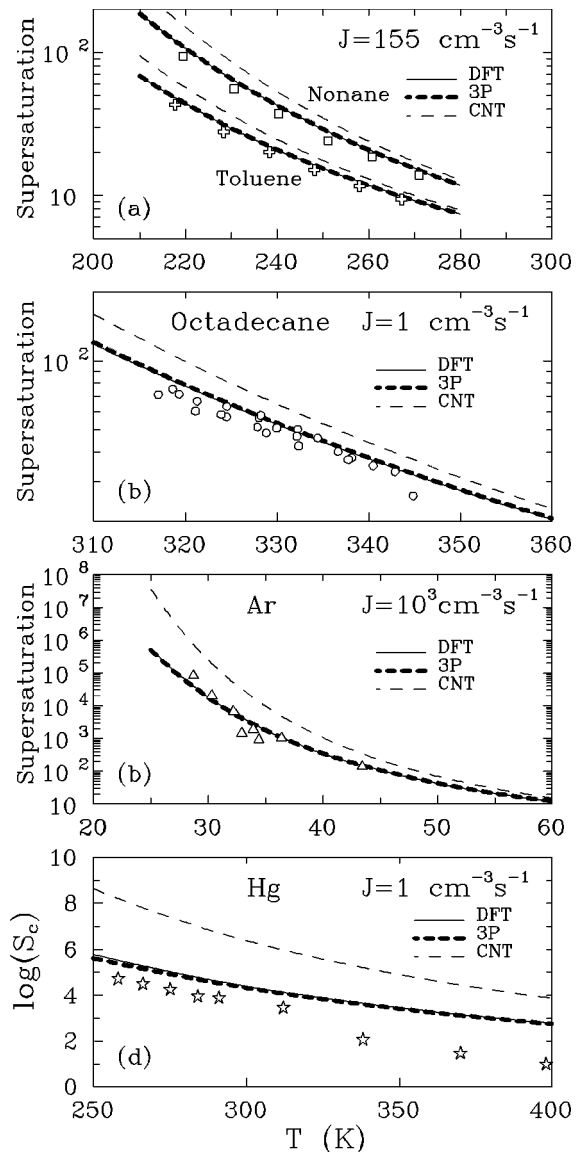


FIG. 4. Comparison of the predicted critical supersaturations (S_c) that correspond to fixed nucleation rates with experiments on (a) nonane and toluene [$J = 155 \text{ cm}^{-3} \text{ s}^{-1}$ corresponds to a drop count of $\sim 1 \text{ cm}^{-3}$ (Ref. [20])], (b) octadecane (Ref. [21]), (c) Ar (Ref. [22]), and (d) Hg (Ref. [23]). Note that a small deviation in S_c may correspond to orders of magnitude difference in the nucleation rate [cf. panel (a) and Fig. 3]. The larger deviations seen for Hg are associated with a metal-nonmetal transition taking place in small clusters (Ref. [23]). Log stands for base 10 logarithm.

ation rate. This is done at substantially lowered computational costs, opening the way for incorporating the detailed molecular theory into macroscopic scale modeling. Such an approach may be of importance in diverse fields including the evaluation of laboratory experiments on condensation (supersonic nozzle, laminar flow cloud chamber) and atmospheric sciences.

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