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Inverse-range-parameter dependence of gas–liquid nucleation in a Yukawa fluid
A density functional approach

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We studied the gas–liquid nucleation in Yukawa fluids by employing the density functional theory (DFT) and considering variable-range interaction forces between the particles of a one-component fluid. As a result, some interfacial quantities are sensitive in this kind of interaction (density profiles, principal tensors, mechanical surface tension and dividing radius), while some are not (pressure difference, density at the drop centre, equimolar surface tension).

Key words: *nucleation; density functional; Yukawa fluid; inverse-range-parameter; density profile*

1. Introduction

The nucleation process is one of the most universal phenomena found in various areas in physics, providing the mechanism for the onset of first-order transitions. A stable phase is formed in an otherwise homogeneous background of a metastable phase; such a process is the formation of a liquid drop inside a bulk vapour phase, wherein in a sufficiently supersaturated vapour phase spontaneous density fluctuations cause condensation, that is, they act as condensation nuclei (homogeneous nucleation) otherwise it is heterogeneous in the presence of a solid substrate. The gas –liquid nucleation has been subjected to intensive research because of its importance in atmospheric and industrial processes, thus considerable attention has been paid to the formulation of phenomenological theories to predict the nucleation rates from measurable quantities. A consistent theoretical description of nucleation should provide knowledge into the processes leading to the formation of the embryo-nucleus of the new phase as well as its size down to the very beginning two-particle clusters.

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The nucleation of a liquid drop from a bulk vapour phase was initially developed by Volmer, Farkas, Becker, Döring and Zeldovich, within the framework of thermodynamics, considering that even very small drops behave as macroscopic (classical nucleation theory CNT), thus having a well-defined radius and enclosing a bulk liquid phase of density corresponding to the exterior bulk vapour phase at the same temperature; also the respective surface tension is that of a planar dividing surface at equilibrium and the same temperature and the interface is narrow compared to the size of the nucleus. The free energy ΔG of cluster-formation in a supersaturated vapour consists of a bulk and a surface term, $\Delta G = -\Delta G_b + \Delta G_s$; the bulk term, ΔG_b, is due to the free energy gain of the condensing particles, while the surface term, ΔG_s, to the free energy loss because of the formation of the dividing interface of the cluster. Recent experimental results revealed that the conclusions of CNT are in error [1], especially in the case of small drops containing few particles; CNT underestimates the homogeneous nucleation rate, but accounts correctly for the main trends and provides a qualitative description. Its predictions however are to be taken with reservations, thus making necessary the reconsideration of this model. The initial attempt to correct CNT was the square gradient approximation (SGA), generalized by the density functional theory (DFT). The SGA was the first microscopic model; it was proposed by van der Waals and generalized by Cahn and Hilliard [2], according to which, the average density varies slowly over atomic distances and may not be valid away from the critical point. DFT is a rigorous statistical-mechanical approach in which the grand potential of a nonequilibrium inhomogeneous system being expressed as a functional of system's density and divided into intrinsic and extrinsic contributions, taking into account the interactions between particles, those with external fields and separating the various force fields into repulsive and attractive, the former ones are taken to be hard-sphere-like [3–5]. The equilibrium density of the inhomogeneous system extremizes the grand potential functional and results as a solution of a variational principle [3–5]. In the current research, the nucleation in a one-component system is studied via DFT for a Yukawa fluid, since it yields universal results that can serve as prototypes of various fluid systems and is computationally simpler.

2. Theory

The DFT of inhomogeneous fluids relies on a proper choice of the grand potential functional $\Omega_V(\rho(\boldsymbol{r}))$ [3–5]

$$\Omega_V\left(\rho(\vec{r})\right) = \int_V \left[f_{hs}\left(\rho(\vec{r})\right) + \frac{1}{2}\rho(\vec{r}) \int_V \rho(\vec{r}\,')\Phi_{FF}\left(\left|\vec{r}-\vec{r}\,'\right|\right) d\vec{r}\,' - \mu\rho(\vec{r}) \right] d\vec{r} \qquad (1)$$

in the absence of an external field; μ is the bulk vapour chemical potential and V the volume of the system. The term $f_{hs}\left(\rho(\vec{r})\right)$ is the Helmholtz free energy density of a uniform hard-sphere fluid at density $\rho(\vec{r})$, which accounts for the repulsive force contribution; $\Phi_{FF}(\vec{r})$ is the attractive part of the pairwise potential between two fluid molecules $r = |\vec{r}|$ distant apart, which is chosen to be of the form

$$\Phi_{FF}(r) = -\frac{\alpha\lambda^3}{4\pi}\frac{e^{-\lambda r}}{\lambda r} \tag{2}$$

α and λ being constants; the latter is the inverse-range parameter, usually chosen as $\lambda d = 1$, where d is the hard-sphere diameter. The equilibrium density $\rho(\vec{r})$ of the inhomogeneous fluid is obtained by minimizing Eq. (1) through the variational principle

$$\frac{\partial\Omega_V[\rho(\vec{r})]}{\partial\rho(\vec{r})} = 0$$

yielding

$$\mu = \mu_{hs}(\rho(\vec{r})) + \int_V \rho(\vec{r}')\Phi_{FF}(|\vec{r}-\vec{r}'|)d\vec{r}' \tag{3}$$

where

$$\mu_{hs}(\rho(\vec{r})) = \frac{\partial f_{hs}(\rho(\vec{r}))}{\partial\rho(\vec{r})}$$

is the hard-sphere chemical potential.

For the sake of simplicity, all quantities are transformed to dimensionless units, $\mu^* \equiv \beta\mu$, $p^* \equiv \beta d^3 p$, $r^* \equiv \lambda r$, $\rho^* \equiv \rho d^3$, $\alpha^* \equiv \beta\alpha/d^3 = 11.102/T^*$; ($T^* = T/T_c$ where T_c is critical temperature) although the asterisks will be suppressed.

Substituting the attractive potential (Eq. (2)) into Eq. (3) and differentiating the resulting equation twice with respect to $u \equiv \lambda r$ yield

$$\mu''_{hs}(\rho(u)) + \frac{2}{u}\mu'_{hs}(\rho(u)) - \mu_{hs}(\rho(u)) + \mu = -\alpha\rho(u) \tag{4}$$

The prime denotes derivative with respect to u. In the limit $u \to 0$, the solution is less well-behaved, since at the origin $u = 0$ it is singular unless $\mu'_{hs}(u)$ vanishes in that limit

$$\lim_{u\to 0}\frac{\mu'_{hs}(u)}{u} = \lim_{u\to 0}\frac{\frac{d\mu'_{hs}(u)}{du}}{\frac{du}{du}} = \lim_{u\to 0}\mu''_{hs}(u) \tag{5}$$

according to de l’Hopital rule, therefore, in the neighbourhood of the origin, Eq. (4) becomes

$$\lim_{u\to 0}\mu''_{hs}(u)=\frac{1}{3}\left(\mu_{hs}(u)-\mu-\alpha\rho(u)\right) \tag{6}$$

Thus, the first boundary condition is $\mu'_{hs}(0)=0$. The other one is related to the behaviour of the solution at infinity as $u\to\infty$. As u gets larger, the contribution of the term $\left(2\mu'_{hs}(u)/u\right)$ becomes less significant and the behaviour of $\rho(u)$ is similar to that for a one-dimensional planar interface at the same temperature; hence, $\mu_{hs}(u)$ approaches the hard-sphere chemical potential of the bulk vapour phase $\mu_{hs}^{vs}\equiv\mu_{hs}(\rho_{vs})$ and $\mu'_{hs}(u)=0$ as $u\to\infty$.

The differential equation (4), with the boundary conditions

$$\mu'_{hs}(0)=0,\quad \mu_{hs}(\rho_{vs})=\mu_{hs}^{vs},\qquad \mu'_{hs}(\rho_{vs})=0$$

constitutes the problem under consideration, which will be solved numerically. The potential between two particles depends on the parameter λ, which is now considered to vary, control parameter. The spatial variable u transforms into $u\equiv\lambda r=(\lambda d)(r/d)=Lv$; v is the new spatial variable and L the new reduced inverse range parameter. As a result of this transformation, Eq. (4) becomes

$$\mu''_{hs}(v)+\frac{2}{v}\mu'_{hs}(v)+L^2\left(\mu-\mu_{hs}(v)\right)=-\alpha L^2\rho(v) \tag{7}$$

The calculation will be based on the Carnahan–Starling approximation for the hard spheres,

$$\beta p_{hs}(\rho)=\rho\frac{1+c+c^2-c^3}{(1-c)^3},\qquad \beta\mu_{hs}(\rho)=\ln c+\frac{8c-9c^2+3c^3}{(1-c)^3} \tag{8}$$

where $c=\pi\rho d^3/6$, the packing fraction (called density for clarity); considering it as the dependent variable instead of $\mu_{hs}(v)$ or $\rho(v)$, Eq. (7) yields,

$$c''(v)=-\frac{2}{v}c'(v)-B_1(v)c'^2(v)-L^2\left(B_2(c)+B_3(c)c(v)\right) \tag{9a}$$

subject to the boundary conditions

$$c'(0)=0,\qquad c(\infty)=c_{vs},\qquad c'(\infty)=0$$

and

$$A_1(\eta)=\frac{\partial(\beta\mu_{hs})}{\partial\eta}=\frac{1}{\eta}+\frac{8-2\eta}{(1-\eta)^4},\qquad A_2(\eta)=\frac{\partial A_1(\eta)}{\partial\eta}=-\frac{1}{\eta^2}+\frac{30-6\eta}{(1-\eta)^5} \tag{9b}$$

$$B_1(\eta)=\frac{A_2(\eta)}{A_1(\eta)},\qquad B_2(\eta)=\frac{\beta\mu-\beta\mu_{hs}(\eta)}{A_1(\eta)},\qquad B_3(\eta)=\frac{6\alpha\beta}{\pi A_1(\eta)} \tag{9c}$$

Because of the existence of the singularity at the origin, the solution is expanded in a power series about $v = 0$,

$$c(v) = q + \frac{v^2}{2!}c^{(2)}(0) + \frac{v^4}{4!}c^{(4)}(0) \qquad \text{as } v \to 0 \tag{10}$$

where $q \equiv c(0)$ and

$$c^2(0) = -\frac{1}{3}\left[B_2(q) + qB_3(q)\right]$$

$$c^{(4)}(0) = -\frac{3}{5}\left\{2B_1(q)\left[c^{(2)}(0)\right]^2 + c^{(2)}(0)\left[\left(\frac{dB_2(c)}{dc}\right)_{v=0} + q\left(\frac{dB_3(c)}{dc}\right)_{v=0} + B_3(q)\right]\right\} \tag{11}$$

The interaction potential takes the form due to the transformation

$$\Phi_{FF}(L,v) = -\frac{\alpha_c L^3 \mathrm{e}^{-Lv}}{Lv}$$

$\alpha = 11.102 k_B T_c / 4\pi$ and possesses a minimum at $Lv = 2$ as a function of L.

The surface tension $\gamma(R_\gamma; \Delta p)$, the work for the formation of the unit surface, in reduced units is

$$\gamma\left(R_\gamma; \Delta p\right) = \frac{1}{3\alpha L R_\gamma^2}\int_0^\infty \left(v\mu_{hs}'(v)\right)^2 dv + \frac{1}{3}LR_\gamma \Delta p \tag{12}$$

R_γ stands for the mechanical R_s or equimolar R_e dividing radii and Δp is the pressure difference

$$\Delta p = \int_{\text{inside}}^{\text{outside}} \frac{2}{\alpha L^2 v}\mu_{hs}'^2(v)\,dv = \frac{2\gamma_s}{R_s} \tag{13}$$

for the mechanical dividing surface [5].

Another important quantity is the nucleation work W for the formation of a nucleus, the difference between the grand potentials for the inhomogeneous and homogeneous systems

$$W = \Omega_V\left(\rho(\vec{r})\right) - \Omega_V\left(\rho_{VS}\right) = \Omega_V\left(\rho(\vec{r})\right) + p_B V$$

p_B the bulk pressure; taking into account (1)

$$W = \int_V \left\{\tfrac{1}{2}\rho(r)\left[\mu_{hs}(\rho) - \mu\right] - p_{hs}(\rho) + p_B\right\} d\vec{r}$$

3. Results and conclusions

In an inhomogeneous system, the common route followed for the study of its structure is in terms of temperature and bulk density, neglecting any other parameter that can affect it; such a parameter is the inverse range parameter L that changes the range of the intermolecular forces and affecting, in general, some of the system's parameters. The latter route is followed in the current case, the boundary value problem in hand is solved numerically by an iterative way; its solution provides the equilibrium density profile as a function of the radial distance from the centre of the drop, for specific values of the bulk vapour density c_{VS}, L and $T = 0.7$. From the numerical solution, it was found that $R_T(L) = R_T(L = 1)/L$, where $R_T(L)$ is the radial distance from the origin of the drop where $c(r,L)$ attains its bulk value c_{VS}, thus if $R_T(L = 1)$ is known [5], $R_T(L)$ can be calculated for any L for the same c_{VS}; the larger the L the smaller the $R_T(L)$, since on increasing L the attractive fluid/fluid interaction decreases, forming smaller drops, while the opposite is true on increasing L. Consequently, L and $R_T(L)$ cannot vary simultaneously.

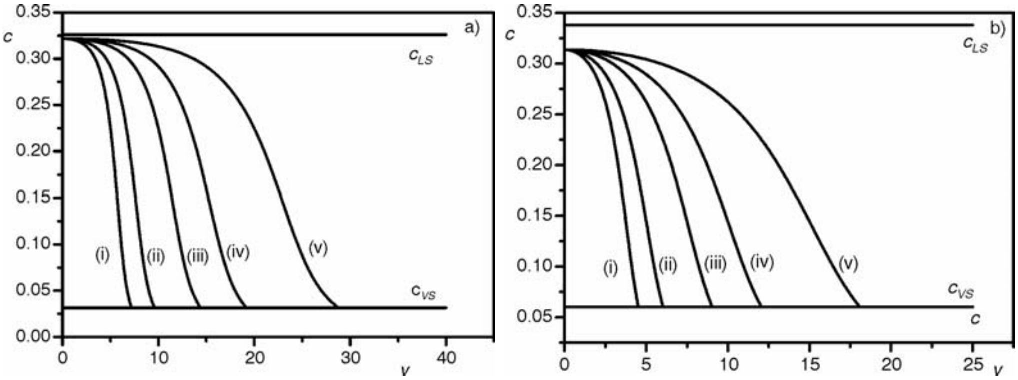

Fig. 1. Density profiles $c(v,L)$ vs. reduced distance v for various values of L : (i) 2.0, (ii) 1.5, (iii) 1.0, (iv) 0.75, (v) 0.5: a – $c_{vs} = 0.03142$ ($\rho_{vs}= 0.06$), b – $c_{vs} = 0.06021$ ($\rho_{vs}= 0.115$). The corresponding liquid densities, $c_{Ls} = 0.326134$ and $c_{Ls} = 0.338244$, respectively, at the same temperature are also indicated

The value of $R_T(L)$ can also be considered as an estimation of the physical radius of the drop without anticipating the structure of the enclosed fluid phase. For a specific value of c_{VS}, Eq. (9) was solved by considering L as independent variable assuming the values 0.5, 0.75, 1.0, 1.5, 2.0; the corresponding density profiles appear in Figures 1a, b for different bulk densities ($c_{VS} = 0.0314159$ ($\rho_{VS} = 0.06$) and $c_{VS} = 0.0602139$ ($\rho_{VS} = 0.116$); we observe that the structure of the density profile for any value of L is unaffected in comparison to that for $L = 1$, except that it is either broadened for $L < 1$ (larger radii) or shrunk for $L > 1$ (smaller radii). In addition, in Figure 1a, small supersaturation, the plots (iv) and (v) corresponding to smaller values of L possess a flat part close to the drop centre implying the existence of a homogeneous phase inside the drop with higher density than the corresponding c_{VS}.

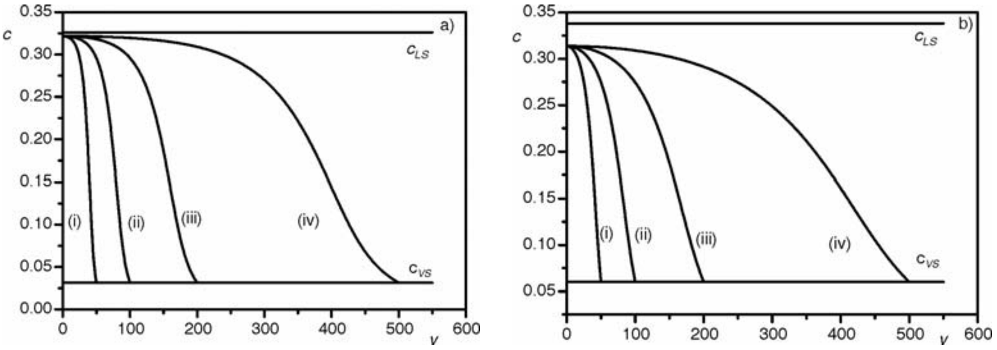

Fig. 2. Density profiles $c(v,L)$ vs. reduced distance v for various values of $R_T(L)$: (i) 50.0, (ii) 100.0, (iii) 200.0, (iv) 500.0: a) $c_{vs} = 0.03142$ (ρ_{vs}=0.06), b) $c_{vs} = 0.06021$ (ρ_{vs}=0.115). The corresponding liquid densities, $c_{Ls} = 0.326134$ and $c_{Ls} = 0.338244$, respectively, at the same temperature are also indicated

In order to make the broadening and shrinking of drops more obvious, $R_T(L)$ is now chosen as control parameter instead of L. The respective plots are given in Figures 2a, b. For small supersaturations, $c_{VS} = 0.0314159$ and high values of $R_T(L)$, the corresponding drop encompasses a liquid-like phase, evidenced by the straight line in Figure 2a (iii, iv), implying the existence of a homogeneous phase of constant density inside the drop while for smaller values of $R_T(L)$ the extent of the enclosed homogeneous phase is barely perceptible, thus Figure 2a (i, ii) are examples of highly inhomogeneous systems. However, for higher supesaturations, $c_{VS} = 0.0602139$ and higher values of $R_T(L)$, the extent of the homogeneous phase is much smaller than for the smaller supersaturations, Figure 2b. These examples indicate that a large drop cannot always enclose a homogeneous phase (a necessary ingredient of the Laplacian thermodynamics) for any value of c_{VS} but depends significantly on supersaturation.

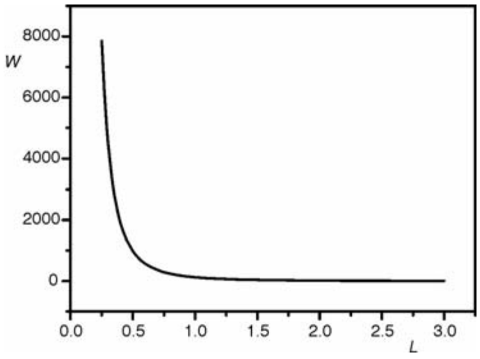

Fig. 3. The work of formation W *vs.* the scaled inverse-range parameter L

The work W for the formation of a nucleus in terms of L is shown in Figure 3, a decreasing function of L. For large values of L ($L >> 1$) the range of the fluid–fluid interactions is short, thus the formed clusters consist of a small number of particles (small drops) and the required work is small although, ultimately, they cannot survive because of the strong hard sphere forces which dominate in short distances. On the contrary, for a small value of L (L <<1) the range of the fluid–fluid interactions is large, resulting in forming drops of large radii and the required work is larger. A similar behaviour is shown by the surface tension, the work for the formation of the unit surface. For a given value of the bulk vapour density, the quantities left unaffected on varying L are the density at drop centre, pressure difference Δp and the equimolar surface tension [5].

Concluding, the existence of a homogeneous phase inside a drop, whatever large it might be, is independent of L and depends only on supersaturation, since the attractive forces behave as a uniform background without affecting the structure of the system which is dominated only by the hard-sphere forces; the direct influence of L is to broad or shrink the density profile only. The effect of the attractive forces is to accommodate the particles of the interior phase into the available space without changing the structure.

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