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Involatile nanodroplets: An asymptotic analysis

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The structure of nanometer-scale droplets of weakly volatile liquids arises through the interplay of strong intermolecular attraction, and core intermolecular repulsion, interfacial forces, and the large, negative chemical potential of the low density vapor with which it is in equilibrium. Using a van der Waals equation of state and a mesoscopic multiphase model, the structure of such nanodroplets is determined via an asymptotic analysis in terms of the ambient to critical temperature ratio. The structure of a spherical droplet is obtained as the solution of a simple "shooting" problem. The intradroplet pressure profile and a minimal droplet size are determined. The high pressure in the core of the droplet gives evidence for the preferred melting there for systems like water with a negative volume of melting. Our methodology can be generalized to multiphase droplets, as well as to composite structures wherein viruses or other nanoparticles are embedded. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2204037]

I. INTRODUCTION

Nanometer-scale droplets are of interest in a variety of health sciences, engineering, and environmental and geological contexts. These include aerosols, atmospheric and groundwater contaminants, ink jets, and migrating petroleum in the subsurface on a geological time scale. Solid nanoparticles of interest that reside in these droplets include dust (as sites of nucleation) and viruses (as they are transmitted in an airborne fashion).

The challenge addressed here is that in many of these contexts the droplets are extremely involatile or weakly soluble in the surrounding medium. Thus the manner in which equilibrium is established is at first glance difficult to understand. For example, a large atomic nucleus is often viewed as an equilibrated quantum droplet although the notion of a "vapor" with which it is in equilibrium is elusive, and similarly for oils of extremely low vapor pressure. In this study a method for solving this weakly soluble/involatile nanodroplet problem is solved via an asymptotic analysis of a mesoscopic two phase fluid model.

If the substance comprising a droplet is extremely involatile (i.e., has a very low equilibrium vapor pressure) then an apparent paradox arises. In this low vapor pressure limit, the asymptotic form of the chemical potential of the vapor has a logarithmic divergence due to the entropy ($\mathcal{R}T \ln c$) term as concentration c in the medium outside the droplet becomes vanishingly small. As the chemical potential of the fluid is constant across the system at equilibrium, the ($\ln c$) divergence at points far from the droplet must be balanced by one or more terms in the chemical potential of the liquid state. This is manifest in the present mesoscopic theory as the invariance of the functional derivative of the Helmholtz free energy with respect to c at each spatial point.

A central dimensionless parameter ε gives unity to the analysis of involatile liquids. Consider the van der Waals

equation of state $p = \mathcal{R}Tc/(1-bc) - ac^2$ for molecular concentration c. One finds that $\varepsilon = \mathcal{R}Tb/a$ is low for involatile liquids as seen in Table I wherein $\mathcal{R}Tb/a$ reduced to $8T/27T_c$ has been used. T_c values were obtained from Knovel.[1] Atomic nuclei are suggested to have a critical temperature of about 8 MeV; nuclear experiments are found to yield significant particle emission of about 5 MeV.[2–4] This suggests that $\varepsilon \approx 0.185$ for nuclei under interesting conditions.

Nanodroplets of low vapor pressure are now modeled via mesoscopic equations that are analyzed using an asymptotic method for computing their structure. Asymptotic solution methods have been used in a variety of contexts.[5–10] Here we show that the result is an estimation of minimal droplet size and an elevated core pressure that could imply inhomogeneous droplet freezing.

II. FORMULATION

Consider a droplet in a single component van der Waals fluid. At equilibrium between droplet and vapor, the chemical potential (i.e., the functional derivative of the Helmholtz free energy) is constant across the system. Adopting a simple mesoscopic model, one obtains the equilibrium condition

$$\mathcal{R}T \ln\left(\frac{c}{1-bc}\right) + \frac{\mathcal{R}T}{1-bc} - 2ac - \Lambda \nabla^2 c = \mathcal{R}T \ln c_\infty,$$

(2.1)

where a and b are van der Waals constants, Λ is a phenomenological interface parameter, and c_∞ is the concentration far from the droplet, in the vapor with which the droplet is at equilibrium. In adopting this model we have assumed that the interface parameter Λ is constant; as shall be clarified further, for the involatile fluid there is an inner core zone over which c changes smoothly, and a thin interface zone across which c changes very rapidly. In our treatment the

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TABLE I. Using critical temperature (T_c) values from Knovel[1] ε was computed via $\varepsilon = 8T/27T_c$ at a temperature of 298.15 K.

Substance	T_c (K)	ε (at 298.18 K)
Helium	5.20	17.0
Hydrogen	33.18	2.66
Nitrogen	126.19	0.70
Oxygen	158.58	0.557
Hexamethyldisiloxane	518.70	0.17
Ocatmethylcyclotetrasiloxane	585.70	0.151
Decamethylcyclopentasiloxane	617.40	0.143
Water	647.00	0.137
Diphenylamine	931.15	0.0949
Sulfur	1313.00	0.0673
Selenium	1766.00	0.05
Carbon	7020.50	0.0126

focus is on the inner zone so that the constancy of Λ is justified.

If the liquid is very involatile, then the van der Waals parameter a is large (i.e., the a term lowers free energy as c increases). To investigate this behavior we introduce a scaling parameter ($\varepsilon \ll 1$) and, in particular, $\varepsilon = \mathcal{R}Tb/a$. Note that large values of a drive c toward the limiting value b^{-1} so that it is convenient to write $c = b^{-1}(1 - \varepsilon\gamma)$ for position-dependent deviatoric concentration γ. In what follows, an analysis is developed wherein $a \to \infty$, the droplet is small, and $c_\infty \to 0$ as $\varepsilon \to 0$, all coordinates via a unifying limiting process.

The physical picture to be developed is suggested in Figs. 1(a) and 1(b). The largeness of a forces c to be near b^{-1} in the droplet. Outside the droplet, c has the very small value c_∞. There is a thin interface centered about the surface of the droplet. Integrating (2.1) across this interface, assuming a spherical droplet [for which $\nabla^2 \to \partial^2/\partial r^2 + (2/r)\partial/\partial r$], and using the fact that c is small outside the droplet, one obtains

$$\frac{\partial c}{\partial r} + \frac{2c}{r} = 0; \quad r = r_0 - 0^+ \tag{2.2}$$

for droplet radius r_0 and positive infinitesimal 0^+ to indicate evaluation just inside the droplet. This provides a boundary condition for (2.1). To complete the $\varepsilon \to 0$ computation, the

profile of c within the droplet is determined in the small ε limit as follows.

For small ε and with $\hat{\Lambda} = \Lambda/\mathcal{R}T$, (2.1) implies

$$\frac{1}{\varepsilon\gamma} - \frac{2}{\varepsilon} + \varepsilon\hat{\Lambda}\nabla^2\gamma + \cdots = \ln c_\infty, \tag{2.3}$$

where the $\cdots$ terms vanish as $\varepsilon \to 0$. Consider small droplets and take $\mathbf{r} = \varepsilon\mathbf{r}'$ for scaled spatial variable $\mathbf{r}'$, $\mathbf{r}$ being position relative to the droplet center; this ensures that both the $\partial^2 c/\partial r^2$ and the $(2/r)\partial c/\partial r$ term play a role in the $\varepsilon \to 0$ limit, a factor seen to be of interest for involatile nanodroplets as shown below. For these small droplets, the Laplacian term is comparable to the other divergent terms. With this, one arrives at the asymptotic equation

$$\frac{1}{\gamma} - 2 + \hat{\Lambda}\nabla'^2\gamma = \varepsilon \ln c_\infty. \tag{2.4}$$

Introducing an auxiliary variable A such that $c_\infty = c^* \exp(-A/\varepsilon)$ for reference concentration c^* (independent of ε), a self-consistent asymptotic equation for γ is obtained:

$$\frac{1}{\gamma} + \hat{\Lambda}\nabla'^2\gamma = 2 - A. \tag{2.5}$$

Equation (2.5) suggest that $A < 2$ so that $\gamma > 0$ as required physically.

Introducing a characteristic length $\mathbf{r}$ and value $\boldsymbol{\gamma}$ such that

$$\hat{\Lambda}\bar{\gamma}^2 = \bar{r}^2, \quad \bar{\gamma}(2 - A) = 1 \tag{2.6}$$

and letting $\gamma = \bar{\gamma}\gamma''$ and $\bar{r}' = \bar{r}\bar{r}''$ yields

$$\frac{1}{\gamma''} + \nabla''^2\gamma'' = 1. \tag{2.7}$$

This equation is to be solved inside the droplet. The boundary conditions on γ'' for the spherical droplet follows from (2.2) and the present scaling; for a droplet of radius r_0'', define β such that $r_0''^2 \beta = 1$ and $r'' = r_0''\xi$. With this the intradroplet problem for the spherical case takes the form

$$\frac{1}{\gamma''} + \beta\left(\frac{d^2\gamma''}{d\xi^2} + \frac{2}{\xi}\frac{d\gamma''}{d\xi}\right) = 1, \quad 0 \leqslant \xi < 1. \tag{2.8}$$

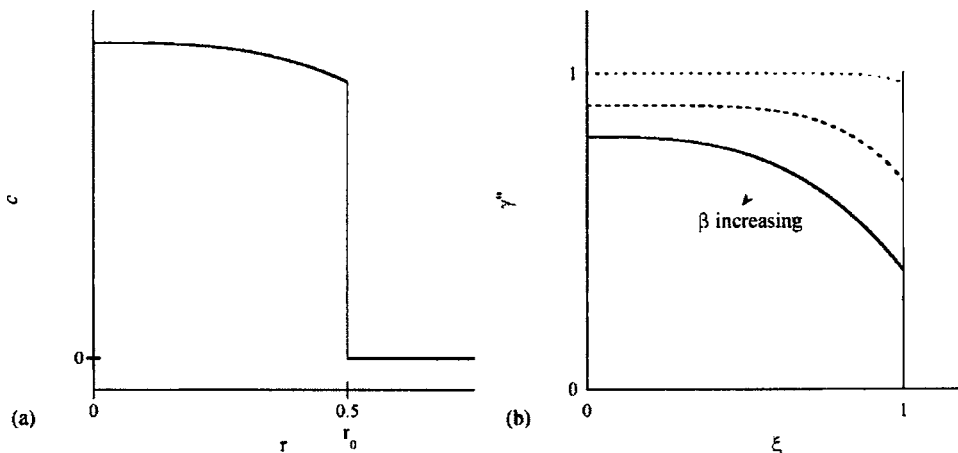In this notation, the boundary condition (2.2) implies

FIG. 1. (a) Schematic profile of density c within a spherical droplet of radius r_0. Note the quasidiscontinuity at r_0 and that c is vanishingly small beyond r_0. (b) Behavior of the c profile as β (inversely proportional to droplet radius squared) changes. For small β, c is essentially b^{-1} except for a narrow layer near the quasidiscontinuity when the dimensionless radius ξ is 1.

$$\frac{d\gamma''}{d\xi} = 2 \text{ at } \xi = 1 - 0^+. \tag{2.9}$$

Boundedness of c at the droplet center $\xi=0$ implies that $d\gamma''/d\xi=0$ there. This, with (2.8) and (2.9), completes the formulation of the asymptotic analysis for spherical droplets.

III. DROPLET STRUCTURE

Results of the asymptotic analysis show that a low vapor pressure liquid forms a nanodroplet that is an essentially uniform sphere of density just below b^{-1} for the van der Waals fluid. In the vicinity of the droplet surface, there is a narrow layer across which density drops essentially to zero or, more precisely, becomes exponentially small.

The asymptotic spherical nanodroplet equations may be solved via a shooting method. One guesses $\gamma''(1)$ and notes that from (2.9) $d\gamma''/d\xi$ at $\xi=1$ is 2. With this, one integrates (2.8) numerically from $\xi=1$ to $\xi=0$ and checks if $d\gamma''/d\xi=0$ there. One keeps changing $\gamma''(1)$ using bisection until this integration yields $d\gamma''/d\xi=0$ at $\xi=0$ to desired accuracy. For small β, $\gamma''=1$ except for a thin layer just below the droplet surface at $\xi=1$, as suggested in the c profile of Fig. 1(a).

For large β (i.e., small droplets), there is no solution to (2.8) that satisfies the boundary conditions. This implies that no droplets exist below a critical size. However, extremely small droplets require a reexamination of the full equations. In particular, the quasidiscontinuity in c across the droplet surface could have a width which is on the order of magnitude of the droplet size itself, invalidating the physical picture on which our asymptotic analysis is based. An atomistic description is more appropriate for the smallest droplets, i.e., not the continuum approach presented here. For such clusters the gradient term and the continuum approach cease to be relevant. All-atom molecular dynamics computations can be readily applied to such clusters.

A relation between c_∞ and equilibrium droplet size is implied by the above model. The total number of moles n in the droplet is given by

$$4\pi \int_0^{r_0} r^2 dr c = n. \tag{3.1}$$

This, and using $c=b^{-1}(1-\varepsilon\gamma)$, implies a relationship between droplet size, mass, and interfacial and attraction versus hard core repulsion effects.

It has been assumed in deriving the boundary condition on c at the droplet surface that the interface was very narrow. This is likely to be the case for small ε fluids where the intermolecular attraction is strong. Thus we expect the interface is only a few molecular diameters in width. In that case the gradient expression for the free energy should be replaced by an integral expression of the form $\int d^3r d^3r' \phi(\mathbf{r}-\mathbf{r}')c(\mathbf{r})c(\mathbf{r}')$ for interaction kernel ϕ. Thus while resolving the extremely narrow interface of interest and the density variations within the droplet, the gradient approximation suffices.
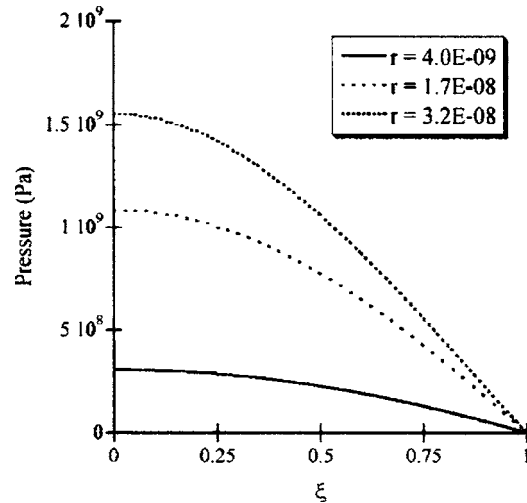

FIG. 2. Effect of nanodroplet radius r on the pressure profile along the dimensionless radius ξ calculated using (4.3) and the van der Waals constants a and b for water.

IV. DROPLET PRESSURE

The profile of pressure yields further insight into nanodroplet structure. To address this we made the ansatz that the pressure generalizes from its classical thermodynamic relation to the free energy density f and chemical potential μ, i.e.,

$$p = c\mu - f. \tag{4.1}$$

Within the pressure model $f=f^{cl}+\frac{1}{2}\Lambda|\bar{\nabla}c|^2$ and $\mu=\mu^{cl}-\Lambda\nabla^2 c$ so that

$$p = p^{cl} - c\Lambda\nabla^2 c + \tfrac{1}{2}\Lambda|\bar{\nabla}c|^2. \tag{4.2}$$

While the first two terms on the right-hand side are $O(\varepsilon^{-1})$ as $\varepsilon \to 0$, the last is $O(\varepsilon^0)$ so it will be dropped henceforth. Using the changes of variables from Sec. II and (2.8) to eliminate the Laplacian term, we find

$$p(\xi) = \frac{\mathcal{R}T}{\varepsilon b}\left[\frac{(2-A)}{\gamma''} - 1 + \frac{1}{(2-A)}\left(\frac{\gamma''-1}{\gamma''}\right)\right],$$
$$0 \leq \xi < 1. \tag{4.3}$$

For physically relevant solutions $p(\xi)\geq0$ for $0\leq\xi<1$ (see Fig. 2). For stress continuity with the outside medium, the lowest order pressure at the droplet surface must vanish. Hence

$$p(\xi=1) = 0, \tag{4.4}$$

which, upon finding $\gamma''(1)$, yields a condition on A.

Consider now an approximate solution $\gamma''=\Gamma(\xi,\lambda)$ for variational parameter λ. We define the error $E(\lambda)$ via

$$E(\lambda) \equiv \int_0^1 \xi^2 d\xi\left[1 - \Gamma + \beta\Gamma\left(\frac{d^2\Gamma}{d\xi^2} + \frac{2}{\xi}\frac{d\Gamma}{d\xi}\right)\right]^2. \tag{4.5}$$

We take the best choice of λ to be that which minimizes E.

A simple trial solution that satisfies the boundary conditions at zero ($d\gamma''/d\xi=0$) and at $\xi=1$ ($d\gamma''/d\xi=2$) is $\Gamma=\lambda+\xi^2$. With this we find

$$\lambda(\beta) = \frac{4 + 25\beta}{10(1 - 6\beta)}. \tag{4.6}$$

Using this solution with the pressure boundary condition $p(\xi=1)=0$ yields a unique physically relevant solution (i.e., for which $p>0$):

$$A = 3 - \gamma''(1), \tag{4.7}$$

With this solution p monotonically decreases from a maximum value at $\xi=0$ to zero at the droplet surface $\xi=1$. The number of moles in the droplet is given by

$$n = \frac{4\pi r_0^3}{b} \int_0^1 \xi^2 d\xi (1 - \varepsilon \gamma), \tag{4.8}$$

and hence the mass deviation $\Delta n = n - 4\pi r_0^3/3b$ becomes

$$\Delta n = -\frac{4\pi r_0^3 \varepsilon \bar{\gamma}}{3b} \left(\lambda + \frac{3}{5} \right). \tag{4.9}$$

Thus $|\Delta n|$ increases with r_0.

V. CONCLUSIONS

The asymptotic approach to nanodroplets of weakly volatile fluids yields insights into how their equilibrium is attained, i.e., as a balance between strong intramolecular attraction, hard core repulsion, and interfacial forces. The result of the analysis is a novel nonlinear differential equation that can be solved via a shooting method and which implies a minimal size below which droplets can exist, as well as a unique spherical equilibrium droplet size for a given vapor pressure. As droplet structure for involatile fluids is driven by the large value of the van der Waals parameter a, the existence of a critical droplet size appears to be a manifestation of cooperativity—i.e., the binding energy of a given molecule increases with the density of its neighbors. Significant variation in pressure between the surface and the core of a nanodroplet can lead to inhomogeneous melting—i.e., core melting first with temperature increase with water. A measure of the mass deviation can be used to estimate the phenomenological surface parameter Λ. The asymptotic analysis presented can be generalized to multicomponent fluids and the nonspherical droplet geometries they may support when two intradroplet, compositional-distinct phases exist.

APPENDIX: PRESSURE COMPUTATIONS

The pressure as analyzed in Sec. IV is obtained as follows. Keeping only leading terms one obtains

$$p^{\text{cl}} = \frac{\mathcal{R}T}{\varepsilon b \gamma} - \frac{a}{b^2}. \tag{A1}$$

Since $a = RTb/\varepsilon$,

$$p^{\text{cl}} = \frac{\mathcal{R}T}{\varepsilon b} \left(\frac{1}{\gamma} - 1 \right). \tag{A2}$$

But $\gamma = \bar{\gamma}\gamma''$ so that

$$p^{\text{cl}} = \frac{\mathcal{R}T}{\varepsilon b} \left(\frac{1}{\bar{\gamma}\gamma''} - 1 \right). \tag{A3}$$

Let $\Delta p = p - p^{\text{cl}}$. Neglecting the higher order $|\bar{\nabla}_c|^2$ term,

$$\Delta p = -\Lambda \nabla^2 c = \frac{\varepsilon \Lambda}{b} \nabla^2 \gamma, \tag{A4}$$

Further changes of variables introduced in Sec. II yield

$$\Delta p = \frac{\Lambda \bar{\gamma}\beta}{\varepsilon b^2 \bar{r}^2} \left(\frac{d^2\gamma''}{d\xi^2} + \frac{2}{\xi} \frac{d\gamma''}{d\xi} \right). \tag{A5}$$

With (2.8) to eliminate the derivative terms, one obtains

$$\Delta p = \frac{\mathcal{R}T(2 - A)}{\varepsilon b} \left(1 - \frac{1}{\gamma''} \right). \tag{A6}$$

Using $\Lambda = \mathcal{R}T\hat{\Lambda}$, $\bar{\gamma} = (2 - A)^{-1}$ and $\bar{r}^2 = \hat{\Lambda}/(2 - A)^2$ we obtain

$$\Delta p = \frac{\mathcal{R}T(2 - A)\beta}{\varepsilon b} \left(\frac{d^2\gamma''}{d\xi^2} + \frac{2}{\xi} \frac{d\gamma''}{d\xi} \right). \tag{A7}$$

Combining this with (A2) we find

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