

PHASE TRANSITIONS IN MULTICOMPONENT SYSTEMS AT THE NANO-SCALE: THE EXISTENCE OF A MINIMAL BUBBLE SIZE

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ABSTRACT

The formation of nanoscale droplets/bubbles from a metastable bulk phase is still connected to many unresolved scientific questions. In this work, we analyze the stability of multicomponent liquid droplets and bubbles in closed $N_{\text{tot},i}$, V_{tot} , T systems (total mass of components, total volume and temperature). To investigate this problem, square gradient theory combined with an accurate equation of state is used. To give further insight into how the state of the fluid affects the formation of droplets and bubbles, we compare the results from the square gradient model to a modified bubble/drop model which gives a macroscopic capillary description of the system. We discuss under which conditions the square gradient model or the modified bubble models predict a finite threshold size for bubbles and their stability in terms of the reversible work of bubble formation. The work reveals a metastable region close to the minimal bubble radius. We find that the liquid compressibility is crucial for the existence of this minimum threshold size for bubble formation in $N_{\text{tot},i}$, V_{tot} , T systems.

INTRODUCTION

Small systems receive now increasing attention, not only in academia, but also in industry. Fabrication of novel nano materials for instance, requires insight into phase transitions such as condensation, evaporation and crystallization at the nanoscale [1; 2]. The first and important step in a typical phase transition is the formation of a nucleus from a metastable bulk phase. Recent experimental developments have made it possible to observe formation of tiny droplets and crystals consisting of only a few molecules. The experiments have evidenced the limitations of current theories, including classical nucleation theory, to describe some of the observations [3]. These systems challenge our current understanding and they motivate the development and use of new tools. In this work, we will give insight into the stability of multicomponent bubbles/droplets in systems with constant $N_{\text{tot},i}$, V_{tot} , T (total mass of components, total volume and temperature). Special attention will be given to the conditions under which very small stable or critical-sized bubbles cannot be formed [4].

For nanoscale bubbles or droplets, the thickness of their interfaces can be of the same order of magnitude as their size. Models which do not specifically take into account surface gradients, such as classical nucleation theory and discontinuous excess formulations, might then be insufficient. We will thus use a square gradient theory for curved systems coupled with a qualitatively accurate cubic equation of state [5; 6] to investigate the system. In the square gradient theory, the Helmholtz energy density has contributions up to second order in the gradients of the densities. The functional minimization of the total Helmholtz energy keeping $N_{\text{tot},i}$ and T constant, gives the equilibrium density and concentration distributions in the canonical ensemble [7]. The advantage of this approach is that continuous profiles across the interface can be found. Square gradient theory combined with an accurate equation of state and suitable models for the pure components has been able to reproduce ex-

perimental results for the surface tension of planar interfaces of multicomponent mixtures [8]. We will use it here to describe the formation of bubbles and liquid droplets. To give further insight into how the size of the system and the composition of the fluid affect the formation of small bubbles and drops, we will compare the results from the square gradient model to a modified bubble model which gives a macroscopic capillary description for different models of the bulk phases [9]. While previous work on this topic has focused on single-component systems [4], we formulate our problem for several components. In addition, we show that a thermodynamic stability analysis is crucial to capture the behavior of the system near the threshold size, an asset which was not discussed in detail earlier [4].

The paper is structured as follows. First, the theoretical framework used will be presented. A short introduction will be given to the use of a quantitatively accurate cubic equation of state coupled with either the square gradient theory (mesoscopic approach), or the capillary approach (macroscopic approach) to describe the formation of bubbles and liquid droplets of interest for nucleation processes. We will then show that the capillary approach is able to reproduce results from the square gradient theory remarkably well for a binary mixture, using hexane-cyclohexane as an example. This observation is used to explain the behavior of very small bubbles, based on a thermodynamic stability analysis. Both approaches will be used to analyze the stability of small bubbles and the existence of a threshold size below which no stable or critical-sized bubbles can be formed. Finally, some concluding remarks are provided.

THEORY

We consider a spherical container with volume, V_{tot} , temperature T and a fixed number of molecules of each component i , $N_{\text{tot},i}$. We assume that a perfectly spherical bubble or droplet is placed at the center of the container. At equilibrium, we know that the state of this system should be at a global minimum in the

total Helmholtz energy. Both the square gradient model and the capillary approach rely on an equation of state which is capable of capturing the thermodynamic behavior of both the liquid and the vapor at different compositions. In this work, we will use the cubic equation of state, Peng Robinson, which has proven to give accurate predictions of the density in both gas and liquid regions for non-polar mixtures. In addition, it captures the vapor-liquid equilibrium behavior of multicomponent mixtures, if proper interaction parameters are used, as demonstrated for CO₂-rich fluids by several authors [5; 6]. In general, most two-parameter cubic equation of state may be represented as:

$$P = \frac{R_g T}{v-b} + \frac{a\alpha(T)}{(v-bm_1)(v-bm_2)} \quad (1)$$

Here, P is the pressure, R_g the universal gas constant, v the molar volume, and a , α , and b are parameters of the equation of state. The constants m_1 and m_2 represent the biggest difference between the various two-parameter cubic equations of state. For the Peng-Robinson equation of state, $m = -1 \pm \sqrt{2}$. Provided that $m_1 \neq m_2$, Eq. 1 can be integrated with respect to the volume to give the residual Helmholtz energy (i.e. the difference between the Helmholtz energy of the homogeneous phase and that of an ideal gas) :

$$\frac{F_{\text{eos, res}}}{R_g T} = N \ln \left(\frac{v}{v-b} \right) - \frac{a\alpha(T)}{(m_1 - m_2)bR_g T} \ln \left(\frac{v - m_2 b}{v - m_1 b} \right) \quad (2)$$

This expression can be differentiated to give the first and second order derivatives of the Helmholtz energy, which are the building blocks for residuals of the other thermodynamic variables such as the chemical potentials, the entropy, the enthalpy and the internal energy. To obtain a complete thermodynamic description of the system, the residual values must be linked to the ideal gas state. Accurate heat capacity polynomials for each component, standard values for enthalpy of formation and entropy have been used to create a thermodynamic framework which gives values for the state functions that follow SI-standards. To verify that the framework is indeed thermodynamically consistent and correctly implemented, a comprehensive consistency check as described by Michelsen and Mollerup was applied [10].

The square gradient model

A rigorous introduction to the square gradient model both at equilibrium and outside equilibrium has been given by Glavatskiy [7]. The functional minimization of the total Helmholtz energy of the square gradient model keeping the total mass of each component constant gives the equilibrium molar concentration distributions, c_i , in the canonical ensemble. The local specific Helmholtz energy is given by:

$$F_{\text{sgm}} = F_{\text{eos}} + \sum_{i,j}^{N_c} \frac{\kappa_{ij}}{c_i} \nabla c_i \cdot \nabla c_j \quad (3)$$

Where the subscript "sgm" refers to the square gradient model. Assuming that the square gradient parameters κ_{ij} are constant and symmetrical, the chemical potentials of the multicomponent

square gradient model are:

$$\begin{aligned} \mu_{\text{sgm},k} &= \mu_{\text{eos},k} - \sum_{i=1}^{N_c} \kappa_{ik} \nabla \cdot \nabla c_i \\ &= \mu_{\text{eos},k} - \sum_{i=1}^{N_c} \kappa_{ik} \left(\frac{2}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial r^2} \right) \end{aligned} \quad (4)$$

Here, the second line is a simplified expression valid for a system with spherical symmetry around the center, N_c is the number of components and r is the distance from the center. This can be rewritten in matrix form:

$$\mathbf{M}_\kappa \nabla \cdot \nabla \mathbf{c} = \boldsymbol{\mu}_{\text{eos}} - \boldsymbol{\mu}_{\text{sgm},k} \quad (5)$$

The matrix \mathbf{M}_κ is such that each index (i,j) equals κ_{ij} . Bold face variables refer to tensors of rank > 0 . If the mixing rule for the square gradient constants is defined according to the most common expression $\kappa_{ij} = \sqrt{\kappa_i \kappa_j}$, the matrix is singular with row rank 1, since row i equals row j times $\sqrt{\kappa_i/\kappa_j}$. This allows us to define the variables from the multicomponent square gradient model using the structure parameters κ , ε_i and q . We then define the following variables:

$$\kappa = \kappa_s \quad (6)$$

$$\varepsilon_i = \sqrt{\frac{\kappa_i}{\kappa}} \quad (7)$$

$$q = \sum_{i=1}^{N_c} \varepsilon_i c_i \quad (8)$$

We choose the component with subscript s , as the one with the largest $N_{\text{tot},i}$. Moreover, by introducing the definitions of κ , ε and q in Eq. 5 one obtains the following system of partial differential equations:

$$\mu_{\text{eos},k} - \mu_{\text{sgm},k} = \kappa \varepsilon_k \nabla \cdot \nabla q \quad (9)$$

Since the coefficient matrix \mathbf{M}_κ has row rank 1, the system of differential equations above can be reduced to one second order differential equations and (N_c-1) algebraic equations:

$$(\boldsymbol{\mu}_{\text{eos}} - \boldsymbol{\mu}_{\text{sgm}}) - \boldsymbol{\varepsilon} (\mu_{\text{eos},s} - \mu_{\text{sgm},s}) = 0 \quad (10)$$

In terms of the new order parameter, q , the state functions and pressures can be represented as follows:

$$F_{\text{sgm}} = F_{\text{eos}} + \frac{\kappa}{2c} (\nabla q)^2 \quad (11)$$

$$U_{\text{sgm}} = U_{\text{eos}} + \frac{\kappa}{2c} (\nabla q)^2 \quad (12)$$

$$S_{\text{sgm}} = S_{\text{eos}} \quad (13)$$

$$H_{\text{sgm}} = H_{\text{eos}} - \frac{\kappa q}{c} \nabla^2 q \quad (14)$$

$$G_{\text{sgm}} = G_{\text{eos}} - \frac{\kappa q}{c} \nabla^2 q \quad (15)$$

$$P_{\text{sgm}} = P_{\text{sgm},\parallel} = P_{\text{eos}} - \frac{1}{2} \kappa (\nabla q)^2 - \kappa q \nabla^2 q \quad (16)$$

$$P_{\text{sgm},\perp} = P_{\text{eos}} + \frac{1}{2} \kappa (\nabla q)^2 - \kappa q \nabla^2 q \quad (17)$$

Details in derivations of the state functions will not be provided in this paper. A more detailed discussion of for instance the parallel and perpendicular pressures can be found in [7]. In addition to the second order partial differential equation, Eq. 9, which can be represented as two first order differential equations, the cumulative mass, $\overline{N_{\text{tot},i}}(r)=4\pi\int_0^r r^2 c_i dr$, is used as additional variable, satisfying:

$$\frac{\partial \overline{N_{\text{tot},i}}}{\partial r} = 4\pi r^2 c_i \quad (18)$$

The combined system of differential and algebraic equations was solved using the "bvp4c" solver in Matlab, coupled with a multidimensional Newton-Raphson approach to solve the system of algebraic equations at each iteration. The Jacobian matrix of the Newton-Raphson approach was constructed based on the Hessian matrix of the Helmholtz energy. In addition to the temperature and the total volume, the following $(2+N_c)$ boundary conditions are necessary to fully specify the boundary value problem:

$$\left. \frac{\partial q}{\partial r} \right|_{r=R_{\text{tot}}} = \left. \frac{\partial q}{\partial r} \right|_{r=0} = 0 \quad (19)$$

$$\overline{N_{\text{tot},i}} \Big|_{r=R_{\text{tot}}} = N_{\text{tot},i} \quad (20)$$

The capillary model

Based on previous work on small bubbles and droplets described in Refs. [9; 11] we define a modified bubble/droplet model, also called the capillary model, to be able to compare the square gradient model to a macroscopic approach. Assuming that the bubble/droplet and the exterior both have homogeneous thermodynamic properties separated by a discontinuous interface at the radius, R , the changes in the Helmholtz energies of the gas and the liquid phases are:

$$dF_g = -P_g dV_g + \sum_{i=1}^{N_c} \mu_{g,i} dN_{g,i} \quad (21)$$

$$dF_l = -P_l dV_l + \sum_{i=1}^{N_c} \mu_{l,i} dN_{l,i} + \sigma d\Omega \quad (22)$$

Here, the surface has been assigned to the liquid phase. In addition, the total number of moles of each component and the total volume are constant. This means that $dV_l = -dV_g$ and that $dN_{g,i} = -dN_{l,i}$. We will use the subscript "n" to denote both a liquid droplet and a bubble at the center of the container, and "e" for the exterior. Assuming that the bubbles/droplets are perfectly spherical, $d\Omega = 2dV_n/R$, is the link between the surface area, Ω and their radius. The change in the Helmholtz energy valid for both the liquid droplet and the bubble is then:

$$dF_{\text{sys}} = - \left(P_n - P_e - \frac{2\sigma}{R} \right) dV_n + \sum_{i=1}^{N_c} (\mu_{n,i} - \mu_{e,i}) dN_{n,i} \quad (23)$$

Equilibrium at constant mole numbers and volume is characterized by a global minimum in the Helmholtz energy, at which a necessary condition is $dF_{\text{sys}} = 0$. This leads to equality of

the chemical potentials of both phases and the famous Laplace relation:

$$P_n - P_e = \frac{2\sigma}{R} \quad (24)$$

The Laplace relation and equality of the chemical potentials are necessary conditions for a minimum, but maxima and saddle points satisfy the same conditions, since they are also extrema of the Helmholtz energy of the system. We have to investigate the second derivative matrix, H , namely the Hessian of the Helmholtz energy to resolve whether the solution is thermodynamically stable, i.e. a minimum. A minimum is characterized by a positive definite Hessian matrix (positive eigenvalues), a maximum by a negative definite matrix (negative eigenvalues) and a saddle point is characterized by a non-singular Hessian matrix which is neither positive nor negative definite. A singular Hessian means that higher derivatives have to be investigated. The component mass balances for the system give additional algebraic equations to be satisfied:

$$\frac{4\pi}{3} (c_{n,i} R^3 + c_{e,i} (R_{\text{tot}}^3 - R^3)) = N_{\text{tot},i} \quad (25)$$

Equality of the chemical potential for each component through the system, together with the mass balances and the Laplace equation gives a total of $2N_c+1$ equations, which fully specify the composition in the interior and exterior of the bubble/droplet together with the unknown radius. We will investigate two different models in the capillary approach:

Capillary Model 1: Here, we assume that the liquid is compressible and its pressure and volume are given by the cubic equation of state.

Capillary Model 2: In this approach, we assume that the liquid is incompressible and behaves as an ideal mixture. The gas is ideal.

For an incompressible ideal mixture, the chemical potential of component i is given by:

$$\mu_i(T, P) = \mu_i(T, P_{i,\text{sat}}) + RT \ln x_i + v_{i,\text{sat}} (P - P_{i,\text{sat}}) \quad (26)$$

Here, subscript "sat" refers to a saturated quantity, x_i is the mole fraction, and v_i is the partial molar volume. The two different capillary models will be used to investigate the role of compressibility of the liquid in the stability of bubbles in a multi-component system.

RESULTS AND DISCUSSION

Results are presented for the binary system, hexane-cyclohexane, since it has been a popular mixture in the literature [7; 12]. Parameters used in the models can be found in Tab. 1. Here, the square gradient parameters, κ_1 and κ_2 , were chosen such that they reproduce exactly the surface tension reported for the single-component systems hexane and cyclohexane at 300 K [13]. The surface tension used in the capillary models, reported in Tab. 1, is the one predicted by the square gradient model for a planar surface. The overall composition for the simulations was constant, and close to the liquid phase composition. It was thus not necessary to consider a composition dependent surface

tension in the capillary models. We will first show how the capillary models compare with the square gradient model in terms of quantitative results for key-parameters, such as composition and pressure. Given that the surface tension is calculated by the excess of the parallel pressure in the square gradient model, both capillary models reproduce well results from the square gradient model for small bubbles and droplets (Fig. 1. and 2) From the

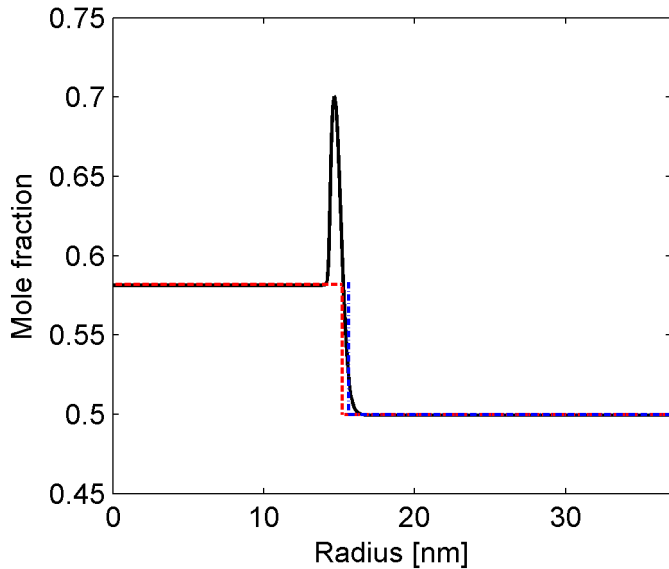


Figure 1. Bubble; mole fraction of hexane, predicted by the square gradient model (solid line), Capillary Model 1 (red dashed line) and Capillary Model 2 (blue dash-dot line)

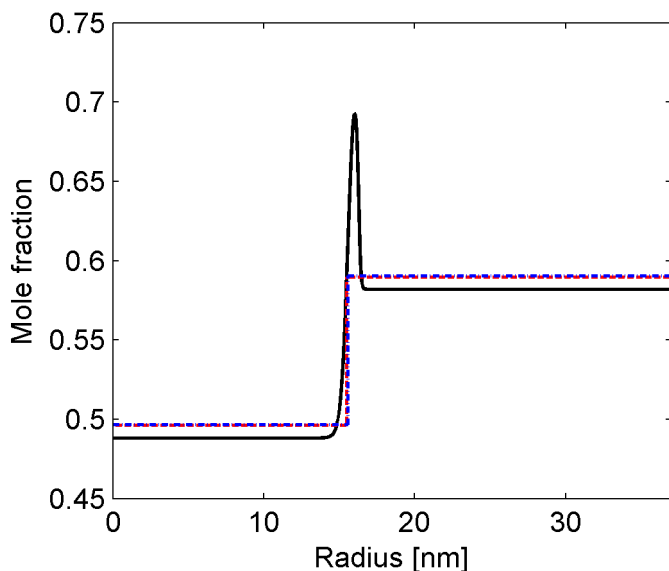


Figure 2. Droplet; Mole fraction of hexane, predicted by the square gradient model (solid line), Capillary Model 1 (red dashed line) and Capillary Model 2 (blue dash-dot line)

figures, one can see that the thickness of the surface, coarsely defined as the zone where the composition deviates from those of the two homogeneous phases, is significant compared to the

Table 1. Data used in the simulations. Component 1 is hexane, component 2 is cyclohexane. Surface tension is calculated by the square gradient model for a flat surface, for the mixture at the temperature and composition considered

Variable	Value
Temperature	330 K
κ_1	$4.2 \cdot 10^{-13} \text{ Jm}^5/\text{kmol}^2$
κ_2	$3.4 \cdot 10^{-13} \text{ Jm}^5/\text{kmol}^2$
Mole fractions	0.5
Surface tension	0.162 N/m
Container radius	38 nm

radius. Even if the capillary models are obviously not capable of reproducing the behavior of the square gradient model at the surface, the compositions, pressures and densities in the homogeneous regions are reproduced well, both for the single component systems, and for the binary system. This is surprising since the excess of mass of both components is 0 in the capillary models, when it is clearly different from 0 in the square gradient model. The location of the equimolar surface (overall density) in the square gradient model gives the radius of the bubble/droplet. The radii predicted by the capillary models deviate from this by less than one percent. The difference between the gas and the liquid pressure in the two cases, also known as the Laplace pressure, is even less. These observations are true, even if the liquid is assumed to be incompressible. This shows that a capillary model can be used as a tool to understand the behavior of the more detailed square gradient model, and to reveal the behavior and stability of bubbles and droplets at small sizes, as we shall see.

The minimal bubble radius

In this section, we discuss how assumptions about the liquid-phase will affect the smallest possible bubble-size in a system in the canonical ensemble. We also discuss the stability of the different extrema of the Helmholtz energy in terms of the Hessian and of the work of formation. The difference in Helmholtz energy between a system with a bubble or a droplet and a supersaturated gas or undersaturated liquid is known as the reversible work of formation, ΔW [9; 14]. If this quantity is positive, it indicates that the bubble is unstable or metastable with respect to the homogeneous liquid solution. In particular, one can show that there exists a region where a bubble is metastable, which means that the total Helmholtz energy of the system is at a local minimum, but ΔW is positive. We define the minimal radius of a bubble as the smallest radius for which it will form spontaneously, i.e. the state where $\Delta W = 0$, $dF_{\text{sys}}=0$ and F_{sys} is convex (positive eigenvalues of the Hessian matrix). Fig 3 shows how the radii corresponding to the extrema of the Helmholtz energy of the system change with the scaled total mass. The reference point for mass is the mass corresponding to the homogeneous liquid at the equilibrium density. It is evident that with a specified total mass in the system, Capillary model 1 predicts two possible bubble radii, one large and one small, both representing extrema of the Helmholtz energy in the capillary models. The radii of the large bubbles in both capillary models

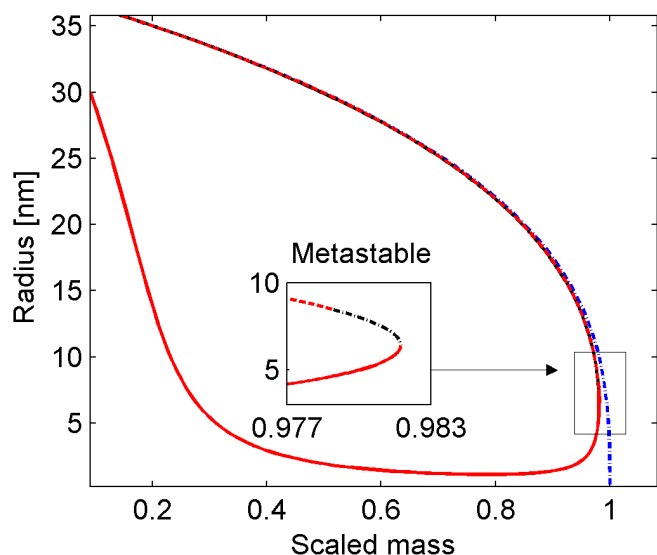


Figure 3. The square gradient model (black solid line) compared with Capillary Model 1 in the stable (dashed line) and the unstable (solid line) region, and Capillary Model 2 (dash-dot lines) for two component bubbles at 330 K.

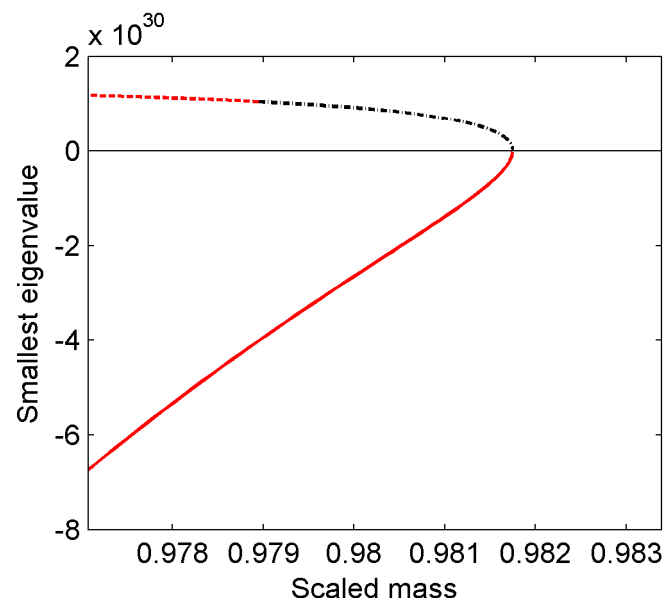


Figure 4. The smallest eigenvalue of the hessian, $H_{m,n}$, in the Capillary Model 1 describing two component bubbles at 330 K, for the stable (dashed line), the unstable (solid line) and the metastable region (dash-dot line). The solid line corresponds to small bubbles, and the upper line is the large bubbles.

are almost identical to the radii predicted by the square gradient model. In fact, they are so similar that they can hardly be distinguished from each other in Fig. 3. Since we have two components in this system, there are three possible eigenvalues of the Hessian, associated with the number of moles of the components and the volume of the bubble. Fig. 4 shows that the large bubbles give only positive eigenvalues of the Hessian, which proves that these solutions are minima, and locally stable bubbles. The small bubbles (dot-dashed lines) have one negative and two positive eigenvalues. This means that these solutions are unstable saddle-points of the Helmholtz energy, corresponding to the critical bubble of interest for nucleation. The same behavior was observed for the single-component systems, hexane and cyclohexane (not shown here).

We would like to give some attention to the region close to where the stable and unstable solutions of Capillary Model 1 merge. From Fig. 5 we observe that there exists locally stable minima of the Helmholtz energy of the bubbles, where it is energetically favorable for the system to have a homogeneous density and no bubble. We make this observation for both Capillary Model 1 and the square gradient model, and refer to this region as metastable. The minimal radius for a stable bubble is reached at 8.4 nm, but it is actually possible to have a metastable bubble down to 6.5 nm in this system (see Fig. 3). The minimal stable radius is found by identifying the radius at which $\Delta W = 0$, and the minimal metastable radius is found by locating the point where the smallest eigenvalue is close to zero. We have done the same analysis for the single-components, hexane and cyclohexane and found the same behavior. Metastable behavior can also be observed for hexane-cyclohexane droplets near the minimum density, as already discussed in Ref. [11]. These observations show that one should be careful to distinguish between metastable and unstable bubbles, since they are all extremal states of the total Helmholtz energy.

Another interesting observation is that Capillary Model 2, where the liquid surrounding the bubble is incompressible, has only one possible bubble solution at a specified total mass of

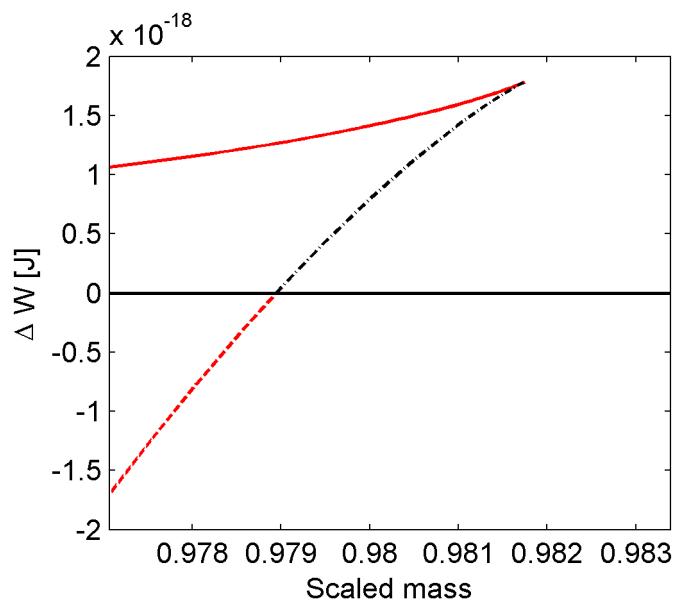


Figure 5. The reversible work of formation of Capillary Model 1 for two component bubbles at 330 K for the stable (dashed line), the unstable (solid line) and the metastable region (dash-dot line)

the system (Fig. 3). This means that assumptions about the compressibility of the liquid will have a large impact on estimates of minimal radii. In the limiting case of an incompressible liquid, there is no minimal radius of the bubble, but when the liquid is compressible there is a minimal radius. We can address the stability of Capillary Model 2, through evaluation of ΔW , with homogeneous ideal gas as the only possible reference state. Then the bubbles are always stable. A more detailed analysis is needed to see if the minimal radius decreases monotonically with the compressibility. For small drops, the assumption of an incompressible liquid did not change the minimal radius of the drop to a significant extent (not shown).

CONCLUSION

In this paper, we have investigated how the formation of nanoscale bubbles are limited by a minimal size in systems with constant $N_{\text{tot},i}$, V_{tot} , T (total mass of components, total volume and temperature). We used the square gradient model for curved systems combined with the cubic equation of state, Peng Robinson, to analyze the system from a mesoscopic point of view, and compared the results to those obtained from the capillary model, which addresses the problem from a macroscopic point of view. For the hexane-cyclohexane mixture, we observed that the capillary model was able to reproduce the results from the square gradient model in the homogeneous regions well, if the value for the surface tension obtained from the square gradient model was used. The minimal radius for a stable bubble in a 38 nm container in this binary system was found to be 8.4 nm, but a thermodynamic stability analysis showed that it was possible to have metastable bubbles down to 6.5 nm. No threshold radius, and only one possible bubble solution corresponding to a stable bubble was found using the capillary model with the liquid assumed to be incompressible. The assumption of incompressible liquid had little effect on the minimal droplet radius. This indicates that a more detailed analysis should be done regarding the role of the compressibility in determining the stability and size of nano bubbles in binary systems.

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NOMENCLATURE

α	Parameter in EoS
a	Parameter in EoS [Pam^6]
b	Parameter in EoS [m^3/mol]
c	Concentration [mol/m^3]
\mathbf{c}	Concentration vector [mol/m^3]
ε	Structure parameter
F	Helmholtz energy [J/mol]
H	Hessian matrix of Helmholtz energy
κ	Square gradient parameter [Jm^5/mol^2]
\mathbf{M}	Matrix with kappas [Jm^5/mol^2]
m	Constants in EoS
μ	Chemical potential [J/mol]
N	Number of moles, capillary model [mol]
\mathbf{n}	Composition vector [mol]
n_i	Moles of component i [mol]
Ω	Surface area [m^2]
P	Pressure [Pa]
q	Order parameter
r	Radial position in container [m]
σ	Surface tension [N/m]
R	Radius bubble/droplet [m]
R_{tot}	Radius of container [m]
R_g	Universal gas constant [$\text{J}/\text{K mol}$]
U	Internal energy [J/mol]
v	Molar volume [m^3/mol]
V	Volume [m^3]
x_i	Mole fractions

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