Phase separation kinetics in compressible polymer solutions: computer simulation of the early stages

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Abstract. A coarse-grained model for solutions of polymers in supercritical fluids is introduced and applied to the system of hexadecane and carbon dioxide as a representative example. Fitting parameters of the model to the gas–liquid critical point properties of the pure systems, and allowing for a suitably chosen parameter that describes the deviation from the Lorentz–Berthelot mixing rule, we model the liquid–gas and fluid–fluid unmixing transitions of this system over a wide range of temperatures and pressures in reasonable agreement with experiment. Interfaces between the polymer-rich phase and the gas can be studied at temperatures both above and below the end point of the triple line where liquid and vapour carbon dioxide and a polymer-rich phase coexist. In the first case interfacial adsorption of fluid carbon dioxide can be demonstrated. Our model can also be used to simulate quenches from the one-phase to the two-phase region. A short animation and a series of snapshots help to visualize the early stages of bubble nucleation and spinodal decomposition. Furthermore we discuss deviations from classical nucleation theory for small nuclei.
1. Introduction

The phase behaviour of polymer–solvent systems has important applications in industry for the production and processing of many kinds of plastic materials [1]–[6]. An example is the formation of solid polystyrene foams [3]–[6]. In addition, both the understanding of the equilibrium phase diagram of these systems and the kinetic mechanism of phase separation are challenging problems in statistical mechanics. On the one hand, variation of the molecular weight of the polymer (i.e. the ‘chain length’ of the flexible linear macromolecule, \( N \)) offers a control parameter that leaves intermolecular forces invariant, and hence allows a more stringent test of the theory than would be possible for small-molecule systems. On the other hand, it is crucial to take the compressibility of the system fully into account, since for practical reasons one normally wishes to use supercritical fluids (e.g. \( \text{CO}_2 \)) as solvent [1]–[6]. Then small changes of the pressure result in a large variation of the solvent density, and this fact obviously facilitates applications. While for an incompressible polymer solution (as modelled, for instance, by the well-known Flory–Huggins lattice theory [7]–[10]) the early stages of phase separation can only be studied if one realizes a rapid temperature quench from a state in the one-phase region into the miscibility gap (cf figure 1(a)), for compressible polymer solutions it is possible to induce phase separation by an (experimentally much more convenient) pressure jump (cf figure 1(b)). Of course, in figure 1 we have made the tacit assumption that including the pressure does not change the qualitative form of the phase diagram, i.e. the point \((T_c, x_c)\) in \((T, x, p)\)-space becomes a line \((T_c(p), x_c(p))\) or, expressed in the appropriate inverse functions, \((p_c(T), x_c(T))\), respectively (figure 1(b)). In reality, the situation is more complicated, since one must treat both the densities of \( \text{CO}_2 \) and hexadecane as two coupled order parameters, which both play a crucial role in the possible phase transitions (remember that for the pure solvent at its critical point, gas–liquid phase separation starts). As a result, it can happen that both gas–liquid and liquid–liquid phase separation are present in the phase diagram, leading to the occurrence of a triple line (figure 2) [11]. As will be discussed below, the presence of the triple line has a profound influence on the interface properties and hence the nucleation behaviour of the system.

The present paper is devoted to a study of the early stages of phase separation kinetics in such systems by computer simulation. We use a coarse-grained model for mixtures of hexadecane and carbon dioxide as an archetypical example. The reason for the choice of this particular system is the fact that recently extensive experiments on nucleation in this system have been performed [12]. In section 2, we shall briefly describe the model and the simulation techniques. Section 3 presents the relevant static equilibrium properties, in particular the phase diagram and the properties of planar interfaces separating coexisting phases. Section 4 describes the
Figure 1. (a) Schematic phase diagram of an incompressible polymer solution. Temperature $T$ and molar fraction $x$ of the solvent are variables, pressure $p$ is constant. The position of the critical point is shown by •. We indicate how a sudden decrease of temperature from a state in the one-phase region to a state in the two-phase region is carried out. Note that the molar fraction $x_c$ of the critical point tends to unity when the chain length $N$ of the macromolecule becomes large. (b) Schematic isothermal slice of a phase diagram of a compressible polymer solution, using pressure $p$ and molar fraction $x$ of the solvent as variables. We indicate how a pressure jump experiment could be performed. In both cases (a) and (b) it is assumed that the state after the jump is in the unstable region of the phase diagram, i.e. underneath the spinodal curve. If the quench ends in between the spinodal curve and the coexistence curve, phase separation will start by homogeneous nucleation.
Figure 2. Isotherms of a simple model system obtained from self-consistent field calculations [11]. At \( T = 343.7 \) K the phase diagram is like the schematic diagram in figure 1(b). However, at temperatures close to the critical point of pure CO₂ we observe liquid–liquid immiscibility for a type III system. A three-phase line and a second critical point occur.

Simulations of quenching experiments under different conditions that lead either to nucleation and growth or to spinodal decomposition. Section 5 summarizes our conclusions.

2. Model and simulation techniques

A fully atomistic simulation of mixtures of hexadecane (C₁₆H₃₄) and carbon dioxide (CO₂), which aims at both establishing phase diagrams as a function of the three variables \( T, p \) and \( x \) and the study of phase transition kinetics under various conditions, would be an extremely formidable problem. The potentials for the length of the covalent bonds in these molecules (as well as the potentials for bond angles) are very stiff. Hence, an extremely short time step (of the order of about 1 fs) would be required in a molecular dynamics (MD) simulation. In a corresponding Monte Carlo (MC) simulation only very small random displacements of atoms would be admissible. Thus, for liquid alkanes it is a quite common and well-established practice to integrate CH₂ groups (as well as the CH₃ end groups) into ‘united atoms’ [13], and also to work with a fixed C–C bond length. These simplifications already reduce the necessary computer time by a factor of 100. However, we have estimated that even for such a simplified model computer resources as they are available today are still not yet sufficient. Thus it was decided to simplify the model even further, representing CO₂ by a single pseudo-atom, and representing C₁₆H₃₄ by a flexible chain of five subsequent effective segments, each of which then contains roughly three successive C–C bonds. All such effective monomeric units interact with a truncated and shifted Lennard-Jones (LJ) potential

\[
V_{LJ}(r) = 4\epsilon_{hh} \left[ \left( \frac{\sigma_{hh}}{r} \right)^{12} - \left( \frac{\sigma_{hh}}{r} \right)^6 + \frac{127}{16384} \right], \quad r \leq r_c = 2 \times 2^{1/6} \sigma, \tag{1}
\]
while \( V_{\text{LJ}}(r > r_c) = 0 \). Subsequent effective monomers along a chain are exposed in addition to a finitely extensible non-linear elastic (FENE) potential \([14]\)

\[
V_{\text{FENE}}(r) = -33.75 \epsilon_{hh} \ln \left[1 - \left(\frac{r}{1.5 \sigma_{hh}}\right)^2\right].
\]

(2)

The constants in this potential are chosen such that the most favourable distance between bonded neighbours is 0.96\( \sigma_{hh} \), while the preferred distance between non-bonded effective monomers is \(2^{1/6} \sigma_{hh} \approx 1.12 \sigma_{hh} \). This mismatch is desirable to prevent crystallization at high densities \([15]\), which is appropriate for glass-forming polymers \([3]–[6]\).

The parameters \( \sigma_{hh}, \epsilon_{hh} \) set the scales for energy and length of our hexadecane model. Since we want our model to fit the thermodynamic properties of this material in the fluid phase as faithfully as possible, we have adjusted them such that the critical temperature \( T_c = 723 \text{ K} \) and the critical density \( \rho_c = 0.21 \text{ g cm}^{-3} \) of hexadecane are correctly reproduced. In simulations, a critical point can be computed by a finite-size scaling study of the liquid–gas transition along the lines of the techniques proposed by Wilding et al \([16]\). A comparison of critical temperature and density in LJ units with the experimental values yields \( \epsilon_{hh} = 5.787 \times 10^{-21} \text{ J}, \sigma_{hh} = 4.523 \times 10^{-10} \text{ m} \) \([17, 18]\).

Since the description of hexadecane is thus already reduced to a crude coarse-grained model, it would not make sense to keep all atomistic detail for carbon dioxide. Thus the CO\(_2\) molecule is also coarse-grained into a point particle, and we require an interaction potential between CO\(_2\) molecules of exactly the same LJ form as in equation (1), but with parameters \( \epsilon_{cc}, \sigma_{cc} \). Requiring once more that the critical temperature and density of real CO\(_2\) are correctly reproduced we obtain \([17]\) \( \epsilon_{cc} = 4.201 \times 10^{-21} \text{ J} \) and \( \sigma_{cc} = 3.693 \times 10^{-10} \text{ m} \). It is clear that this procedure ignores some physical effects, e.g. the fact that the CO\(_2\) molecules carry electrical multipole moments is completely neglected. Nevertheless our model describes not only the gas–liquid coexistence curve of hexadecane and CO\(_2\) over a reasonable temperature range \([17]\), but also other data (like the critical pressure, or the temperature dependence of the surface tension near \( T_c \) \([18]\)).

Of course, the choice of interaction parameters between CO\(_2\) and hexadecane is more subtle. We model the interaction between the pseudo-atoms representing CO\(_2\) and the pseudo-atoms representing three subsequent CH\(_2\) groups again by an LJ potential of the form as in equation (1), but now with parameters \( \epsilon_{hc}, \sigma_{hc} \). It then remains to find an optimal choice for these parameters. The simplest choice would be the well-known Lorentz–Berthelot mixing rule \([19]\):

\[
\epsilon_{hc} = \sqrt{\epsilon_{hh} \epsilon_{cc}}, \quad \sigma_{hc} = (\sigma_{hh} + \sigma_{cc})/2.
\]

(3)

However, when one tries the choice of equation (3) the resulting phase diagram of our model system is of type I in the classification scheme of Van Konynenburg and Scott \([20, 21]\) (i.e. the critical points of pure hexadecane and CO\(_2\) are connected by a critical line of the mixture system; liquid–liquid phase separation does not exist and thus there is no three-phase coexistence). However, experimentally it is known \([22]\) that alkane–CO\(_2\) mixtures exhibit a type I phase behaviour only for very short alkanes, while for hexadecane–CO\(_2\) mixtures the phase diagram is of type III. Instead of a connecting line we rather observe a topology as shown in figure 3 \([17, 23]\). In the \((p, T)\) projection of the phase diagram, a critical line emerges from the critical point of hexadecane and does not end at the critical point of CO\(_2\). In addition we observe liquid–liquid immiscibility and a three-phase line. When we want to obtain this behaviour from our coarse-grained model we must allow for a deviation from the first equation of equation (3), assuming rather

\[
\epsilon_{hc} = \xi \sqrt{\epsilon_{hh}, \epsilon_{cc}}, \quad \xi < 1.
\]

(4)
Figure 3. Projection of the hexadecane–CO₂ phase diagram \((p, T, x)\) onto the pressure–temperature plane. Black curves, + and •: simulations (for \(\xi = 0.886\)); red curves: analytic calculations from TPT1 based on the same model \([23]\); blue curves: experimental data. Gas–liquid coexistence curves are from \([44, 45]\), the two critical curves are from \([39]\) and \([22, 46]\) (dashed blue) and differ considerably. Experiments are in qualitative agreement with both simulations and analytic calculations. Three features can be identified: gas–liquid coexistence lines (+) of pure CO₂ and hexadecane both end at the corresponding critical point (at \(T = 304\) and 723 K, respectively). A curve of critical points (•) emerges from the critical point of pure hexadecane and gradually changes its composition from gas–liquid hexadecane to liquid CO₂–liquid hexadecane. The red dotted three-phase curve (TPT1) lies slightly below the corresponding CO₂ coexistence curve, but only above the critical point of CO₂ can it be distinguished in this plot. The critical point of CO₂ and the end point of the three-phase line are connected by another short critical line which also cannot be distinguished.

It turns out that a suitable choice for the parameter \(\xi\) which characterizes the deviation from the Lorentz–Berthelot mixing rule is \([17, 18, 23]\) \(\xi = 0.886\). Equation (4) with this choice of \(\xi\) was in fact used to compute the phase diagram shown in figure 3. However, experimental measurements of the critical line vary considerably and a small modification in \(\xi\) raises or lowers the critical line. Details about how such phase diagrams are in fact estimated from the simulation are given elsewhere \([18]\).

For a study of the phase diagram (figure 3) as well as for a study of the interfacial free energy between coexisting gas and liquid phases \([17, 18]\) the grand canonical ensemble is used, where volume \(V\), temperature \(T\) and the chemical potentials \(\mu_c, \mu_h\) are fixed. Both the particle numbers \(N_c\) and \(N_h\) of CO₂ and hexadecane and the pressure \(p\) are then (fluctuating) observables ‘measured’ in the simulation \([18]\). Figure 4 shows an isothermal slice through the phase diagram at \(T = 486\) K. This temperature is higher than the temperature of the critical end point where the critical line ending at the critical point of CO₂ and the line of triple points \(p_{\text{trip}}(T)\) in the \((p, T)\) phase diagram (figure 3) meet. Therefore, unlike figure 2, there is no triple point in the

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Figure 4. Isothermal slice through the phase diagram in figure 3 at temperature $T = 486$ K. The black curve with circles shows the simulated coexistence curve, red curves are corresponding predictions from TPT1 theory [23] for the coexistence (full) and spinodal curve (dotted), respectively. The positions of the critical points are denoted by •. ♦ indicate the phase diagram positions of the nucleation movie in figure 6 and the snapshot series in figure 7. Inset: surface tension as a function of pressure.

phase diagram, and the qualitative features are the same as in figure 1(b). We shall examine the kinetics of the phase separation at this temperature in section 4.

In order to observe the kinetics of bubble nucleation in the vicinity of the coexistence curve we control the undersaturation of the system by fixing the chemical potential of both species. As a starting configuration we use a homogeneous state equilibrated at a higher temperature. This situation corresponds to a simulation cell in contact with a much larger reservoir which is held at constant undersaturation. As the number of particles in the simulation cell is not conserved, and the particles do not move according to a realistic dynamics, we do not obtain information about the timescale of bubble nucleation. The kinetics of phase separation in the vicinity of the coexistence curve is, however, chiefly determined by the free energy barrier the system encounters on its path towards the equilibrium state. Hence, we expect the relaxation path to be similar to a simulation with realistic dynamics. The most natural choice would be to apply MD methods [24]–[26]. However, if the number of particles was conserved we would need prohibitively large simulation cells for the undersaturation not to decrease substantially even in the very early stages of nucleation. The simulation of spinodal decomposition took place in the canonical ensemble. Again, a homogeneous starting configuration was equilibrated at a higher temperature and quenched to a state below a critical point of the mixture system. We only allowed for local MC displacements, which should yield kinetics comparable to that obtained in MD.

3. Static equilibrium properties

First we return to the phase diagrams in figures 3 and 4 and discuss their properties more closely. Note that at the temperature chosen in figure 4 ($T = 486$ K) we are very far below the critical
point of pure hexadecane (which is at $T_c = 723 \text{ K}$). Therefore the hexadecane melt (with some dissolved carbon dioxide) coexists with almost pure CO$_2$, the composition of which gradually changes from gas- to liquid-like with increasing pressure. In both cases there is almost no hexadecane present. This is reflected in the coexistence curve which rapidly approaches the CO$_2$ molar fraction $x = 1$.

We have also included the results of an analytical approximation for the phase diagram of our model, obtained from a thermodynamic perturbation theory [23] called TPT1, developed along the lines of Wertheim et al [27]. It is seen that this theory describes the coexistence curve in figure 4 at pressures that are much smaller than the critical pressure $p_{\text{crit}}(T)$ almost quantitatively, while the critical pressure itself is clearly overestimated. Of course, such an overestimation of the critical parameters $p_{\text{crit}}(T)$, $x_{\text{crit}}(T)$ is quite typical of all theories that invoke a mean field description of the critical behaviour, as TPT1 does. A similar analytical study for more alkane–CO$_2$ systems has been performed recently [28]. Note also that the TPT1 theory readily yields a spinodal curve, which has the standard meaning of separating ‘metastable states’ from ‘unstable states’ in the phase diagram [29]–[31]. The naive (mean field) description implies that in the metastable region of the phase diagram the initial stages of phase separation kinetics are described by nucleation and growth [29, 30], while in the unstable region the decay mechanism is spinodal decomposition [30, 31]. In systems with short-range forces there is no well-defined sharp spinodal line: the actual transition between both decay mechanisms occurs rather gradually in a broad transition region, and this region is not centred around the mean field spinodal line but occurs closer to the coexistence curve [31]. However, for the quenching experiment performed at $T = 486 \text{ K}$ and $x = 0.60$, where the final state corresponds to a pressure of about $p \approx 130 \text{ bar}$, we are so close to the coexistence curve and so far from the mean field spinodal line that classical nucleation-type behaviour [29, 30] should be observable. In order to demonstrate the mechanism of spinodal decomposition, we quenched into the unstable region as defined by the mean-field spinodal line (compare with figure 4).

Classical nucleation theory assumes (in our case) the formation of spherical gas bubbles of essentially pure CO$_2$ within a hexadecane matrix. For a quantitative understanding of the free energy barrier against homogeneous nucleation, clearly the understanding of the interface between macroscopic coexisting phases is a prerequisite. As discussed elsewhere [17, 18], such interfaces are most conveniently studied in the grand canonical ensemble in conjunction with a multicanonical preweighting scheme that generates mixed-phase configurations. Choosing a simulation box of rectangular shape $L \times L \times cL$ with a constant $c = 2$ or larger and periodic boundary conditions, one generates system configurations where the two coexisting phases are separated by two parallel $L \times L$ interfaces (compare figure 5(a)). ‘Measuring’ the canonical probability of these two-phase configurations relative to the probability of the pure phases is a standard method for the estimation of interfacial free energies [16]–[18], [32]–[37]. The results for $T = 486 \text{ K}$ are shown in the inset of figure 4. In addition, this method can be used to generate well-equilibrated configurations of interfaces allowing a study of the interfacial structure. Figure 5 shows, as an example, two snapshot pictures of such states containing interfaces, one at $T = 486 \text{ K}$ and the other at $T = 243 \text{ K}$. The size of the particles is enlarged (radii shown are $\sigma_{cc}, \sigma_{hh}$ rather than $\sigma_{cc}/2, \sigma_{hh}/2$), for the sake of a clearer view. The temperature $T = 243 \text{ K}$ is slightly lower than the temperature of the critical point of pure CO$_2$, and thus the system possesses a triple point where a polymer-rich phase coexists with two CO$_2$-rich phases, one being liquid CO$_2$ and the other the gas. Consequently, when we study the interface between the polymer-rich phase and gaseous CO$_2$, a layer of the third phase
Figure 5. Snapshot pictures of systems in the centre of the two-phase coexistence region for $T = 243$ and $486$ K. The snapshots show a $2\sigma_{\text{hh}}$ slice through a box with dimensions $L_x \times L_y \times L_z = 18\sigma_{\text{hh}} \times 18\sigma_{\text{hh}} \times 54\sigma_{\text{hh}}$. The positions of particles are projected onto the $xz$ plane. CO$_2$ particles are shown as yellow circles of radius $\sigma_{\text{cc}}$, while effective monomers of hexadecane are shown as red circles of radius $\sigma_{\text{hh}}$ (we choose $\sigma_{\text{hh}} = 1$ as our unit of length, which then implies $\sigma_{\text{cc}} = 0.816$); the background is blue. For $T = 243$ K interfacial wetting can be observed.

(liquid CO$_2$) intrudes at this interface. The thickness of this layer is expected to diverge when the pressure approaches the value of the triple point pressure. For higher pressures, we then have a coexistence between the polymer rich-phase and the liquid-like dense CO$_2$, similar to the situation that occurs at the higher temperature (figure 5(a)). At low enough temperatures, where a triple point occurs, one already expects a strong decrease of the interfacial tension when the triple point pressure is approached [11]: the interfacial tension between the polymer-rich phase and liquid-like CO$_2$ is much smaller than the interfacial tension between the polymer-rich phase and the gas. The barrier against nucleation also decreases when one approaches the spinodal curve from the metastable region. This fact facilitates the nucleation of relatively large droplets observable on the timescales of our MC simulation.

4. Monte Carlo simulation of bubble nucleation

The animation in figure 6 visualizes how phase separation in polymer solutions proceeds via nucleation. In the beginning the system fluctuates around a metastable free energy minimum. One observes the ‘birth and death’ of small density fluctuations in the hexadecane matrix (displayed as red spheres) which become visible whenever the blue background shines through the slice. These irregular voids are too small, however, to lead to an immediate decay of the initial metastable state. Usually the voids also contain a few CO$_2$ molecules (displayed as small yellow spheres). Only after some time lag does a void manage to grow to critical size and overcome the free energy barrier which separates the metastable from the homogeneous equilibrium state.

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Figure 6. A short animation showing the time evolution of a quenching experiment in the metastable region ($T = 486$ K, $x = 0.60$ and (final) pressure $p \approx 130$ bar—compare with figure 4). Phase separation occurs via nucleation. The linear dimension of the simulation box is $22.5 \sigma_{hh}$. The movie is generated from subsequent snapshot pictures of a grand canonical MC simulation. For clarity, not the whole simulation but only a slice of thickness $2 \sigma_{hh}$ is shown. The colour coding is the same as in figure 5.
Figure 7. A series of snapshots visualizing the early stages of spinodal decomposition after a quenching experiment in the unstable region ($T = 486$ K, $x = 0.833$ and (final) pressure $p \approx 52$ bar—compare with figure 4). Phase separation occurs via spinodal decomposition. The size of the box is $91.21\sigma_{hh} \times 91.21\sigma_{hh} \times 17.53\sigma_{hh}$, but only a slice of $10\sigma_{hh}$ is shown. The system is actually more dilute than the one shown in figure 6. (a) Starting configuration, (b) after 125,000 and (c) after 500,000 local displacements ($0–0.3\sigma_5$) per particle. The colour coding is the same as in figure 5.

From now on the bubble will grow until it fills the whole simulation box. As expected, the critical void is also filled with CO$_2$ molecules, thus decreasing the supersaturation of the remaining polymer-rich phase. Remarkably, this filling of the bubble does not occur homogeneously: at the interface between the gas and the polymer, i.e. at the surface of the bubble, the CO$_2$ density is clearly higher than it is in the centre of the bubble. This surface enrichment effect may be interpreted as a precursor to interfacial wetting of the fluid CO$_2$ predicted when one approaches the triple point [11]. A quantitative analysis of this phenomena is in preparation [40].

Of course, the observation of a nucleation event displayed in figure 6 is by no means the first observation of nucleation phenomena by computer simulations: for example, [29] contains a series of snapshot pictures illustrating nucleation in the two-dimensional lattice gas model. Since then many more elaborate studies have appeared. However, the present work deals with nucleation in a system of industrial relevance, namely bubble nucleation in metastable polymer melts supersaturated with supercritical CO$_2$. In addition, the nucleation mechanism here is quite non-trivial, since the ‘critical bubble’ (which just has the size to be at the nucleation barrier, where there is a 50% chance of growth or decay) is characterized by two variables, its size and the number of CO$_2$ molecules it contains. Similarly, the interface is described by the non-trivial profiles of two variables, the total density and the relative concentration of CO$_2$. Such a non-trivial coupling between two order parameters has also been predicted by recent self-consistent field calculations based on a qualitatively similar model [11]. Since these mean field descriptions do not take into account the effects of fluctuations, a check by computer simulation methods is clearly warranted.

When we quench to a position below the critical point (figure 7), the behaviour is rather different: fluctuations in the relative concentration of CO$_2$ become gradually more pronounced everywhere. These fluctuations are not localized, however, in the form of identifiable
Figure 8. Free energy as a function of droplet size for $T = 486$ K and $p = 0.5 p_{\text{crit}}$ and $p \approx 0$ (coexistence pressure of pure hexadecane—compare with figures 3 and 4). Red curve: a simple estimate for the free energy: $\Delta F = 4\pi \gamma R^2$; surface tension $\gamma$ is taken from figure 4 (inset) (flat surface). Black: results from simulations of different system sizes. Only the envelope of the curves is relevant. Other parts of the curves belong to regions of the distribution where no nucleation is expected. For small droplets the free energy is smaller than expected. Differences decrease with increasing radius and decreasing distance from the critical point of the isotherm.

bubbles, but rather form an irregular percolating network. This is the hallmark of spinodal decomposition [30, 31]. Since the linear theory of spinodal decomposition only holds for systems with long-range forces in the very early stages [31], we do not attempt a more quantitative analysis of these data. Note also that the build-up of these concentration fluctuations is relatively faster than the nucleation of bubbles. Hence the separation of timescales between the structural relaxation and the rate constant of spinodal decomposition is less well established. In the intermediate stages of spinodal decomposition, we also expect hydrodynamic mechanisms to prevail [30, 31], which are not captured by MC moves.

Returning now to the simulation of nucleation phenomena, we ask how one can quantify these observations. A straightforward but tedious method would be to repeat dynamic simulations as shown in figure 6 many times in order to extract an estimate of the nucleation rate from the average time it takes to form a bubble or a droplet. Of course, since the nucleation rate is expected to increase dramatically if the quench depth is decreased slightly, such a direct method hardly works in practice. An indirect method to obtain information on the surface free energy of clusters as a function of cluster size simply uses the final equilibrium states of simulations. If we assume that bubbles (or droplets) are spherical, filled with gas and surrounded by a homogeneous liquid of coexistence density (or vice versa) we can assign a radius to each density:

$$\frac{4}{3}\pi R^3 \rho_l + (V - \frac{4}{3}\pi R^3)\rho_g = \rho V.$$  

Indices l and g denote liquid and gas coexistence properties. An estimate for the free energy as a function of density can be obtained directly from the probability distribution. In this context
special care has to be taken of finite-size effects to identify regions of densities which correspond to a single cluster \([41, 42]\). Together with (5) we get \(F(R)\). Figure 8 compares the results from simulations with a simple estimate for the free energy:

\[
F = -p_l V_l - p_g V_g + \mu_g n_g + \mu_l n_l + 4\pi \gamma R^2 \approx F(n_{g,l}) + 4\pi \gamma R^2
\]  

(6)

if we set \(\mu_{g,l} = \mu_{coex}\) and \(p_{g,l} = p_{coex}\). In the so-called ‘capillarity approximation’, \(\gamma\) is given by the interfacial tension of flat interfaces as shown in figure 5 and derived in figure 4. Figure 8 indicates that the excess free energy \(\Delta F = 4\pi \gamma R^2\) constitutes an upper bound for simulation estimates. Differences decrease with increasing cluster size and distance to the critical point of the mixture. At this stage, however, the findings are still somewhat preliminary and more work will be necessary to improve the model \([43]\). The liquid–vapour interface has a finite width and different definitions of the interface location can be envisaged which result in different radii. This effect is particularly important for small cluster sizes. The approximations \(\mu_{g,l} = \mu_{coex}\) and \(p_{g,l} = p_{coex}\) are only valid for large clusters, and the dependence of \(\gamma\) on the curvature of the cluster needs to be investigated in more detail, too.

5. Concluding remarks

In summary, we have presented a simple model and computational tools which allow us to examine the equilibrium properties and kinetics of phase separation in systems of industrial relevance. We were able to produce a two-component mixture phase diagram with a complete critical line which is in qualitative agreement with experiments. For a system at \(T = 486\) K we determined the isotherm and interfacial tension of a flat surface as a function of pressure. In a series of small animations and snapshots we visualized bubble nucleation and spinodal decomposition for this specific system. For the first case we found a precursor of interfacial wetting which was also observed on a flat surface in the vicinity of the three-phase coexistence line. Finally, we found evidence that for small bubbles the interfacial tension is smaller than expected.

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