Nucleation and Growth of Droplets in Vapor-Liquid Transition

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Results for the kinetics of vapor-liquid transitions, following temperature quenches with different densities, are presented from the molecular dynamics simulations of a Lennard-Jones system. For critical density, bicontinuous liquid and vapor domains are observed which grow with time obeying the prediction of hydrodynamic mechanism. On the other hand, for quenches with density significantly below the critical one, phase separation progresses via nucleation and growth of liquid droplets. In the latter case, Brownian diffusion and collision mechanism for the droplet growth is confirmed. We also discuss the possibility of inter-droplet interaction leading to a different amplitude in the growth law. Arguments for faster growth, observed at early time, are also provided.

The subject of nucleation and growth is of significant importance in many branches of physics, chemistry and engineering [1, 2]. In spite of that, answers to many fundamental questions in this area still remain challenging [3]. The phenomena of growth is understood in some detail in simple situations, e.g., late time non-equilibrium dynamics in bulk solid mixtures with critical (symmetric) compositions (which belongs to the so-called category of spinodal decomposition), via simple Ising model or Cahn-Hilliard equation [1, 3]. In this case one obtains interconnected domain morphology. Even for such simple situations our knowledge appears rather incomplete when one considers dynamics at early time [4, 7] or when one puts the systems in confinement [8, 9]. Both these examples are related to nanoscopic length scales. The situation is far worse in fluids where one encounters greater complexity due to the influence of hydrodynamics [10–12]. In this work we address the problem of vapor-liquid phase separation in extreme off-critical situation that gives rise to droplet morphology and thus related to the nucleation phenomena. This, of course, has direct relevance in nanoscience and technology. For the ease of a precise definition of the problem, below we give a brief introduction to the field in the context of a binary mixture (A + B).

When a homogeneously mixed system is quenched inside the coexistence curve, the system phase separates via formation and growth of A-rich and B-rich domains. Typically, this phase separation is a self-similar phenomena [1, 3, 4], viz., the morphology at different times (t) are similar except for a change of length scale, ℓ(t), which is the average size of domains. This fact is reflected in the scaling behavior of functions that characterize the pattern formation. E.g., the two-point equal time correlation function C(r, t) (r being the scalar distance between two points) exhibit the scaling form [1, 3] C(r, t) = C(ℓ/t). It has remained a challenge [1, 4] to obtain the analytical form for C when the order-parameter is a conserved quantity, as it is in the present context. The growth of ℓ(t) typically follows a power-law [4]

\[ ℓ(t) \sim t^\alpha, \]

where the exponent α depends upon the system and order-parameter dimensionality, conservation of order-parameter as well as hydrodynamic effects. Here we confine ourselves to conserved scalar order-parameter in space dimensionality d = 3.

For diffusive transport, which is true for the entire growth dynamics in solid binary mixtures, the rate of change of ℓ(t) is related to the chemical potential (μ) gradient as [1]

\[ \frac{d\ell(t)}{dt} \sim \frac{1}{\ell(t)} \frac{\partial C}{\partial \ell} = \frac{1}{\ell(t)} \frac{\gamma}{\ell(t)}, \]

where γ is the interfacial tension. The solution of Eq.(2) provides α = 1/3. The original derivation due to Lifshitz and Slyozov (LS) [13], obtained for off-critical situation, is much more involved. However, as can be judged from the general nature of the derivation in Eq.(2), α = 1/3 is expected to hold for compositions critical as well as off-critical. On the other hand, the hydrodynamic effects cause a faster growth at late times for fluids as well as polymers. Typically, for a critical quench in a fluid binary mixture one expects three distinct regimes of domain coarsening [10, 12], viz., diffusive, viscous hydrodynamic and inertial hydrodynamic, with exponents 1/3, 1 and 2/3, respectively. Essentially, at late time the tube-like interconnected structure facilitates advective transport in fluids. However, this picture is not true when one has disconnected droplet morphology which geometrically has to be the case for an off-critical quench, if the principle of interfacial free energy minimization is accepted.

In the off-critical situation, Binder and Stauffer (BS) [14, 15] proposed a Brownian droplet diffusion and collision mechanism. There, the time dependence of ℓ(t) can be obtained from [10] (C being a constant)

\[ \frac{dn}{dt} = CD\ell n^2, \]

where the droplet density n ∝ φ/ℓ^3, φ being the volume fraction of the minority species and D is the droplet diffusion constant. Treating Dt as a constant (according to Stokes-Einstein-Sutherland relation [16]), from (3) one obtains α = 1/3 [10], same as the LS value. It has been pointed out that the ratio of amplitudes A_{BS} and A_{LS}, in the BS and LS cases, respectively, is [10, 17, 18]

\[ A_{BS}/A_{LS} = K \phi^{1/3}; \quad K \approx 6. \]

Possibility for K ≈ 4.84 has also been argued [17, 18]. It is claimed that the BS scenario will be valid only in the low droplet density, for φ < 0.06 [17, 18]. For high droplet density, inter-droplet interaction mechanism, due to concentration gradient, may be important [17, 20]. This latter mechanism, though leads to the same exponent, gives amplitude higher than the BS value.
Even though we confined our discussion to binary liquids, all the above pictures, we believe, should apply to vapor-liquid phase separation as well. For off-critical case, this was, in fact, confirmed by an experimental study \cite{21}. On the other hand, for critical quenches the effect of hydrodynamics was observed in molecular dynamics (MD) simulations of both liquid-liquid \cite{22} and vapor-liquid \cite{23} phase separations. However, to the best of our knowledge, there exists no such computational study with atomistic models to verify the predictions in the off-critical case, be it a vapor-liquid transition or a liquid-liquid one. In this work, we present extensive results from MD simulations \cite{25} to address this important issue of nucleation and growth. We confirm that the off-critical case, be it a vapor-liquid transition or a liquid-liquid one. In this work, we present extensive results related to Eq. (4) and provide arguments for early time fast dynamics.

We use a model where particles of equal mass \((m)\) at positions \(\vec{r}_i\) and \(\vec{r}_j\) interact, for \(r < r_c\), via \cite{24}

\[
u(r = |\vec{r}_i - \vec{r}_j|) = U(r) - U(r_c) - (r - r_c)(dU/dr)_{r=r_c},
\]

with \(U(r)\) being the standard Lennard-Jones (LJ) pair potential with inter-particle interaction strength \(\epsilon\) and \(\sigma\) being the particle diameter. The cut-off distance \(r_c(= 2.5\sigma, \sigma\) being the particle diameter) was introduced to facilitate faster computation. We obtained the values for \(T_c\) and \(\rho_c\), the latter being the critical value of the density \((\rho = N\sigma^3/L^3)\), to be approximately \(0.9\epsilon/k_B\) and 0.3. We use following units for various relevant quantities. Lengths are expressed in units of \(\sigma\), temperature in \(\epsilon/k_B\) and time in \(m\sigma^2/\epsilon\). For the sake of convenience we set \(\sigma = 1, \epsilon = 1, k_B = 1\) and \(m = 1\). Homogeneous systems with different overall densities were prepared at very high temperatures before quenching them to \(T = 0.6\), inside the coexistence curve. Unless otherwise mentioned, a Nosé-Hoover thermostat (NHT) \cite{25}, known for its ability to preserve hydrodynamics, was implemented to control the temperature in the MD simulations that used integration time step \(\Delta t = 0.005\). Periodic boundary conditions were applied in all directions.

In Fig.(a) we show the evolution snapshots for \(\rho = 0.3\). It is seen that the phase separation started at a very early time, as expected for spinodal decomposition, and the domain structures are interconnected. Since the results for the hydrodynamic effects on the growth of \(\ell(t)\) for this density, though at a slightly different temperature, was already presented elsewhere \cite{24}, for the sake of brevity, we avoid it here. Next we focus on the snapshots for \(\rho = 0.05\), shown in Fig.(b). Note that the binodal density for the vapor branch at this temperature is \(\approx 0.01\). Considering that, we are well inside the metastable region. So, here the phase separation progresses via nucleation and growth of droplets. Compared to Fig.(a), where it is a spontaneous phase separation, the nucleation of droplets in Fig.(b) is significantly delayed due to less super saturation. Our objective in this work is to study the time dependence of the growth of these droplets once they are formed.

**FIG. 1.** (a) Snapshots from the evolution of the single component Lennard-Jones system that exhibits vapor-liquid phase transition. An initial configuration with homogeneous density, prepared at a temperature far above the critical value with the overall density \(\rho \approx 0.3\), was quenched to the temperature 0.6. The linear dimension of the cubic box is \(L = 64\). The dots represent location of particles. (b) Same as (a) but for \(\rho = 0.05\).

**FIG. 2.** The left panels represent two dimensional cross-sections of the evolution snapshots at two different times. Here \(\rho = 0.05\), \(L = 100\) and \(T = 0.6\). The right panels correspond to the corresponding pictures after mapping onto a simple cubic lattice following a method described in the text.

It is indeed difficult to calculate the droplet radius \(\ell(t)\) from the continuum configurations seen in Fig.1 To facilitate such calculation, in Fig.2 we describe a simple procedure 3. The left panels on this figure are \(2-d\) slices of the snapshots for \(\rho = 0.05\). The right panels, which look very similar to the original ones, are corresponding mapped configurations where the particles are moved to the nearest sites of an \(L^3\) simple cubic lattice. Further, in these mapped configurations, all sites
around which the density is higher than the critical number have been assigned a spin value \( S_i = +1 \) and the rest got \(-1\). Then the collections of up spins constitute liquid droplets. Essentially, we are left with a two component Ising model for which \( C(r, t) \) can be calculated as \( C(r, t) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle; \ r = |i - j| \). From the number of +1 spins in the system one can calculate the fraction of volume occupied by liquid droplets. In analogy with a symmetric binary liquid, this corresponds to \( \phi \) for which we obtain a value \( \simeq 0.054 \). This provides \( A_{BS}/A_{LS} \simeq 2.3 \).

From Fig 1(b) it is quite clear that the densities in the liquid and vapor domains take significantly long time to equilibrate. For a quantitative picture we have plotted the liquid domain density, \( \rho_l \), in the main frame of Fig 3 as a function of time. The inset of this figure shows the scaling plots of \( C(r, t) \) vs \( r/\ell(t) \) for five different times. The value of \( \ell(t) \) was obtained from the distance at which \( C(r, t) \) decays to \( 1/4^{th} \) its maximum value. Starting from \( t = 2000 \) onwards, the data collapse is excellent. The poor scaling at early time could be appreciated from the fact that during this period \( \rho_l \) (and so \( \rho_v \)) is changing very fast. Note that in addition to computing \( \ell(t) \) from the decay of \( C(r, t) \), we have obtained it directly as well. In this direct method \( \ell(t) \) one sweeps through the whole system in different directions to find out number of domains at different sizes from which the average value can be calculated in a straight forward manner.

![Figure 3](image3.png)

**FIG. 3.** Plot of the density, \( \rho_l \), inside the liquid droplets as a function of time. Inset: Scaling plot of the correlation function \( C(r, t) \) as a function of \( r/\ell(t) \). Data from five different times are used. The values of \( \ell(t) \) were obtained from the decay of \( C(r, t) \) to \( 1/4^{th} \) its maximum value. The results correspond to \( \rho = 0.05, L = 100 \) and \( T = 0.6 \) and on averaging over 10 independent initial configurations.

![Figure 4](image4.png)

**FIG. 4.** Trajectory of the centre of mass of a droplet in the NHT-MD. Only a part of the box is shown, for clarity.

In Fig 4 we depict a typical trajectory of a droplet starting from \( t = 1000 \) to \( t = 5000 \). This looks reasonably Brownian. One can also try to calculate the mean squared displacement from such trajectories. However, because of limited number of droplets as well as availability of limited time before they collide, it is extremely difficult to obtain data of presentable quality. Having been convinced about the Brownian motion of droplets, in Fig 5(a) we present the plot of \( \ell(t) \) vs \( t \), on log scale, from both types of calculation as described above. While there is overall consistency between the two methods, noticeable discrepancy at early time is due to the non-scaling behavior of \( C(r, t) \) for \( t < 2000 \). Almost constant value of \( \ell(t) \) up till approximately \( t = 100 \) is indicative of the delayed formation of nucleus of critical size as one moves closer to the coexistence curve. On the other hand, at late times (when the domain densities “almost” equilibrated) the data are very consistent with the predicted BS value \( \alpha = 1/3 \). Note that in this regime we deal with stable droplets whose sizes change only after collision. In this context, however, calculation of critical nucleus size could be useful, a good discussion of which is provided in Ref. \[26\]. Here one may ask the question:
how to distinguish this from the LS law that also predicts same value for $\alpha$. In fact, the same system we have studied via application of an Andersen thermostat (AT) \cite{25}. Note that in AT the particles collide randomly with the heat reservoir and so stochastic in nature. In that situation, the local conservation of momentum is not maintained as required in hydrodynamics. In such a case, the domains should grow due to diffusion of density leading to the LS value of the exponent. This is different from the droplet diffusion in the BS mechanism. Indeed we observe that the centre of masses of droplets are static in the AT case as expected for LS mechanism. In Fig.5(b) we presented a comparison between the two cases. For the AT, clearly the amplitude of growth is much smaller than the NHT. The amplitudes obtained from Fig.5(b) is $A_{BS}/A_{LS} \approx 3.4$ which differs from the theoretical estimate by a factor $\approx 1.5$ (it becomes closer to 2 if we take $K = 4.84$). This discrepancy could be attributed to the fact that possibly there is inter-droplet interaction mechanism in addition to the BS one.

Next we focus on the part of the plot in Fig.5(a) where, immediately after the nucleation of droplets, there is a rapid rise of $\ell(t)$. There have been arguments for linear growth in line of viscous hydrodynamics, for early time dynamics. This is \cite{17} keeping with the fact that at this early stage, when there is high density of droplets, one has nearly interconnected domain structure as in case of critical quench. However, our result is more consistent with inertial hydrodynamic growth ($\alpha = 2/3$), the last scaling regime for critical quench. In this latter case one expects a competition between growth and break-up of interconnected structures. Indeed, in the present case, even though the domains are connected in the time regime of discussion, they break up fast due to rapid equilibration of density. Nevertheless, we caution the reader that this early time result should not be taken seriously due to lack of scaling as seen in the inset of Fig.5.

In summary, we studied kinetics of vapor-liquid phase separation in a single component Lennard-Jones system. For quenches close to the critical density, we observe a percolating structure of vapor and liquid domains which grows very rapidly because of the hydrodynamic effects. On the other hand, for quenches close to the coexistence density (we considered only the vapor branch of the coexistence curve), formation and growth of disconnected liquid droplets are observed. Depending upon the proximity to the co-existence curve the nucleation of such droplets can be significantly delayed.

At late times, the motion and growth of these droplets are consistent with the prediction of Brownian diffusion and collision mechanics by Binder and Stauffer. Growth in the same system via Lifshitz-Slyozov (LS) mechanism has also been studied. The amplitude ratio for the BS and LS mechanism is obtained and compared with the theoretical predictions. Also, possible reasons for extraordinary fast growth, observed before the asymptotic $t^{1/3}$ regime is reached, have been pointed out. It will now be interesting to study, among other things, the growth dynamics as one continuously changes the overall density towards the critical value.

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