

Domain Coarsening of Binary Fluid Mixtures under Critical Quench

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Abstract

Understanding of the nonequilibrium evolution of domains in a phase separating system, both from theoretical and experimental point of view, is of much research interest and of fundamental importance. This article deals with the phase ordering kinetics of binary fluid mixtures with a comparative picture of its solid counterpart. The theoretical foundation has been presented in length in the introduction where I have precisely considered a system consisting of binary Lennard-Jones fluid undergoing liquid-liquid phase separation for which the results were obtained, mostly, from molecular dynamics simulation. Before getting into the detailed description of the phase ordering dynamics and quantification of domain coarsening process, the general concept of phase ordering kinetics in bulk systems has been discussed. Following an early time diffusive domain growth, known as LS growth, the system enters a faster growth regime when the hydrodynamic effects set in later. Similarly, the nonequilibrium domain coarsening of a geometrically constrained system follows the same trend as that of a bulk system with the only difference is the absence of linear growth regime. Unlike the bulk systems where complete phase separation occurs at a very late time, confinement compels the quasi-one-dimensional systems to settle in microscopic phase separated equilibrium state.

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Introduction

Over the last few decades, with the emergence of interdisciplinary science, much attention has been paid in discovering new avenues in soft condensed matter systems. Soft matter is a subfield of condensed matter that consists a variety of physical systems which can be structurally deformed by the application of external thermal or mechanical perturbations in the order of magnitude of thermal fluctuations. Typically, those include liquids, polymer gels, colloids, granular materials, liquid crystals, and, most importantly a huge number of biological materials. A number of pioneering studies, combining experimental observations with quantitative modelling, explained various degrees of macroscopic aspects of systems consisting of passive and active particles. Passive systems, in order to undergo dynamical evolution, need external stimuli. To cite an example, the vapor-liquid phase transition requires quench in temperature from a high temperature to a low temperature that must lie below the transition temperature ^[1]. Since the systems consume energies, they intrinsically remain out of

thermal equilibrium and special treatments are needed to describe their dynamic evolution. The general framework of such disordered-to-ordered transition and the current understanding of the kinetic aspects of the transition of two-component binary liquids and related bio-mechanical processes thus possess an immense importance in the branch of Statistical Mechanics in Physics. At a higher temperature, the system is in a homogeneous state. Following the sudden quench below the transition temperature, the system falls out of equilibrium and evolves towards the new equilibrium state which is nothing but the phase separated ordered state ^[1-2]. This transformation takes time and occurs via simultaneous formation, growth and merging of domains of different phases which is defined as the phase ordering dynamics or domain coarsening process ^[1-4]. In case of a ferromagnetic substance, at $T > T_c$, the system is in disordered state with zero net magnetization. However, the system exhibits magnetization below T_c which is known as spontaneous magnetization. Now, during this temperature quench, the system evolves via the formation and growth of regions of like spins. Similarly,

when a binary mixture ($A+B$) is quenched from a homogeneous phase at high temperature to a temperature below the critical temperature (T_c), the equilibrium ceases to exist and the system approaches the phase-separated state via domain coarsening dynamics. The dynamic evolution of these systems come up with a very interesting mechanisms in which the domains grow in a power law fashion; $l'(t) \sim t^\alpha$ [3-4]. Here $l'(t)$ is the time dependent average size of the domains at a time t and α is termed as growth exponent which depends on many system-specific parameters among which *order-parameter* is the most crucial one. In the context of an order-disorder transition, the density difference between the liquid and vapor phase ($\rho_l - \rho_g$) is defined as a relevant order parameter. It takes nonzero value below T_c and with the increase of T , the order parameter vanishes as T approaches T_c . In case of a binary liquid mixture ($A+B$), the density is replaced by the respective concentration of one of the components (say $\rho_A = N_A/N$, where N_A and N are the number of A particles and total number of particles, respectively). The system remains in a homogeneous mixture of A and B particles at above T_c and it separates into A - and B -rich phases as we go below T_c . Following a quench from homogeneous disordered state, the evolution of a system to a new equilibrium (ordered) state can be classified into different classes depending on the growth mechanism involved. The growth laws alter significantly depending on the conservation laws related to the order parameter. When the algebraic sum of all the components of the order parameter remains unchanged during the course of evolution, we call it a conserved order parameter dynamics. Domain coarsening in a binary fluid mixture ($A+B$), in case of a liquid-liquid transition, is a classic example of conserved order-parameter dynamics. Moreover, inclusion of hydrodynamic effects can significantly change the growth mechanism in case of conserved order parameter dynamics. In the following, different scenarios are briefly presented to address coarsening phenomena in corresponding situations.

Domain Coarsening & Growth Mechanism in Different Systems

Bulk Systems: In this section I discuss about different growth laws for bulk phase ordering in $d = 3$, for scalar order parameters. The kinetics of phase separation in a solid binary mixture is studied via Monte Carlo simulation of the Ising model. In this case one needs to incorporate the condition of conservation of order parameter which is taken care by the order parameter continuity equation $\frac{d\psi(\vec{r},t)}{dt} = -\nabla \cdot \vec{j}$. Here \vec{j} , the current density, is defined as $\vec{j} = -\nabla \mu$ where μ is the chemical potential. For the case of solid binary mixtures, the predominant growth mechanism involved is the diffusive transport of materials and one can relate the rate of the growth of average domain size $l(t)$ with the interfacial tension, γ , as $dl(t)/dt \sim \gamma/l(t)^2$. This immediately leads to $l(t) \sim t^{1/3}$ which is known as *Lifshitz-Slyozov* diffusive growth law [4-7]. However, the situation considerably changes in case of fluids and polymers in which hydrodynamics plays a pivotal role and the growth of domains becomes much faster. In this purpose, instead of Monte Carlo simulation, a straight forward method is deterministic Molecular Dynamics (MD) simulation of a continuous potential model in which hydrodynamics is automatically taken into account. In case of fluids, as in solids, initially the growth occurs via diffusive mechanism.

But the system enters into the hydrodynamic regime when the size of the domains becomes considerably large. In $d=3$, for a critical quench, one usually apprehends interconnected domain structures and the interfacial surface energy density is balanced by the viscous stress. This produces $v_i = \frac{dl(t)}{dt} = \gamma/4\pi\eta$ (v_i is the interface growth velocity and η is the shear viscosity) and, from this, one can easily obtain $l(t) \sim t^{5/6}$; referred as the viscous hydrodynamic growth. The crossover from the early time diffusive regime to the linear growth regime occurs when $l(t) \gg (D\eta)^{1/2}$, D being the diffusivity of the system. At later time it is required to balance the surface energy density with the kinetic energy density (ρv_i^2) that produces $l(t) \sim t^{2/3}$. This is referred to as the inertial hydrodynamic growth regime. So, the growth of domains in bulk fluids with conserved order parameter can be classified in the following manner [5-8]:

$$l(t) \sim \begin{cases} t^{1/3}; & \text{initial diffusive growth} \\ t; & \text{viscous hydrodynamic growth} \\ t^{2/3}; & \text{inertial hydrodynamic growth} \end{cases}$$

Systems under Geometrical Confinement

Considering the multiscale industrial applications like the extraction of oil and natural gases from rocks, designing technological devices etc., understanding the behaviour of fluids under geometrical confinement is of immense importance. Given that the system prefers to phase separate, one can observe the dynamic evolution is of anisotropic by nature. It is mostly due to the fact that only a few particles can be accommodated along the confinement. Moreover, the effects of finite system-size and presence of surfaces lead to a phase behaviour which cannot be observed in its bulk counterpart. Much attention has been invested in the past few decades to understand quasi two-dimensional systems, e.g. in a thin-film geometry [7-8]. The phase behaviour (including wetting) as well as the kinetic evolution more or less bears similarity with that of the bulk systems. However, in quasi one-dimensional systems, existing literatures merely elucidates the coarsening dynamics. Conclusions from therein, whatsoever, may be found inappropriate for low-porosity mediums. Subsequently, both the experimental and theoretical attention shifted to the “single pore model” that predicts a “plug-tube-capsule” phase diagram [9]. Particularly in those cases where the surfaces have biasness in attraction towards one of the components in the mixture. A general observation for weak surface (or in absence of attraction) field, in quasi one-dimensional confinement, is quite interesting. The confinement in narrow pores drives the systems to “freeze” into structures of partially phase-separated microscopic domains [10], instead of a macroscopic phase separated state, these domains settle in microscopically phase separated metastable states are kinetically barred from further condensation. The typical growth laws in this case are as follows:

$$l(t) \sim \begin{cases} t^{1/3}; & \text{initial diffusive growth} \\ t^{2/3}; & \text{inertial hydrodynamic growth} \end{cases}$$

One cannot observe the linear growth regime which is an attribute of geometrical confinement [10].

Conclusions

In this article I have briefly presented the basic growth mechanism and temporal evolution of domains during nonequilibrium dynamics of binary fluid mixtures under a quench below transition temperature. Analysing the evolving domain sizes, for bulk systems, one can identify two distinct power-law regimes. Following an early-stage diffusive domains growth having an exponent $1/3$, the system enters a relatively faster growth as hydrodynamics becomes predominant. Surprisingly, for quasi one-dimensional systems with geometrical confinement, linear viscous regime doesn't show up at a late time and it remains in the inertial hydrodynamic regime (with exponent $2/3$) before 'freezing' in the equilibrium state. In this context, it would be worth extending the present state of understanding by altering the surface potential for the phase separated binary liquids under confinement. Additionally, in future it would be interesting to study the kinetics of vapor-liquid transition for a single component fluid under confinement. The current framework can be implicated to investigate morphologies and domain growth kinetics of binary mixtures in much more complex real systems.

Conflict of Interest

The author declares no conflict of interest.

References

1. Bray AJ, Adv. Phys. 2002; 51:481.
2. Binder K, in Phase transformation of Materials RW, Cahn P, Haasen EJ. Kramer (Eds.), (VCH, Weinheim). 1991 5:405.
3. Puri S, Wadhawan V. (Eds.), Kinetics of Phase Transitions (CRC Press, Boca Raton, 2009).
4. Das SK, Puri S, Horbach J, Binder K. Phys. Rev. E 72, 061603, 2005.
5. Das SK, Puri S, Horbach J, Binder K. Phys. Rev. Lett. 96, 016107, 2006.
6. Das SK, Puri S, Horbach J, Binder K. Phys. Rev. E 73, 031604, 2006.
7. Mitchell SJ, Landau DP. Phys. Rev. Lett. 97, 025701, 2006.
8. Bucior K, Yelash L, Binder K. Phys. Rev. E 77, 051602, 2008.
9. Majumder S, Das SK. Phys. Rev. E 81, 050102, 2010.
10. Basu S, Majumder S, Sutradhar S, Das SK, Paul R. EPL 116, 56003, 2016.