Gravitational Effects on Structure Development in Quenched Complex Fluids

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Abstract

When binary liquid mixtures are cooled rapidly from a homogeneous phase into a two-phase system, domains of the two equilibrium phases form and grow ('coarsen') with time. In the absence of an external forcing due to gravity or an imposed shear flow, a dynamical-scaling regime emerges in which the domain morphology is statistically self-similar at different times with a length-scale that grows with time. In the presence of gravity, however, multiple length scales develop with the system coarsening more rapidly in the direction of the force. The late-time behavior of such a system is characterized in this study by the calculation of anisotropic growth laws. Gravitational effects significantly affect scaling laws even with small density mismatch and the growth mechanism has some similarities to the sedimentation process. However very few numerical studies have been made of such effects and this is one of the first.

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1 Introduction

Phase separation during quenching of binary-mixture melts occurs in a variety of practically important systems e.g. during the fabrication of multiphase materials. Physicists have characterized the phase transition of a binary mixture by a universal length scale that has a growth law dependent on the regime of the separation. Using scaling arguments it is possible to find three regimes: diffusive, viscous and inertial. Siggia [1] added a cut-off length above which gravitational forces have an important effect. However, very little work, either experimental or numerical has been done to elucidate phase separation phenomena with density mismatch between the domains - a circumstance that often occurs. Here we investigate numerically this problem using a phase field approach for small density mismatch.

Phase field models offer a systematic physical approach for investigating complex multiphase system behavior, such as near-critical interfacial phenomena. However, because interfaces are replaced by thin transition regions (diffuse interfaces), phase field simulations demand robust numerical methods that can efficiently achieve high resolution and accuracy. We use an accurate and efficient numerical method, developed by the authors in [2], to solve the coupled Cahn-Hilliard/Navier-Stokes system of equations for binary, known as Model H, with small density mismatch between the phases in the Boussinesq approximation. The numerical method is a time-split scheme that combines a novel semi-implicit discretization for the convective Cahn-Hilliard equation with a stiffly stable time-discretization of the projection method for the Navier-Stokes equations. We employ high-resolution spatial discretizations to be able to accurately resolve thin interfaces. The Cahn-Hilliard equation is discretized in space (pseudo) spectrally (via FFT for periodic boundary conditions). We solve the Navier-Stokes modified creeping flow equations with a pseudo-spectral method [3]. The numerical method is robust and with low computational cost.

We find that gravitational effects may significantly affect scaling laws even with small density

mismatch. Also, we present a simulation of the effect of gravity during the diffusive and viscous regime, which to our knowledge is the first reported, and characterize the break down of the usual Siggia-type universal scaling.

This work underlines the importance of gravitational forces in determining phase microstructure characteristics, and explains the experimental difficulties in validating theoretical growth laws on earth even with fluids that have small density mismatch [19]. Therefore, in testing theories for scaling of coarsening processes, particularly in the late stages, experiments in microgravity environments are very desirable as small density mismatches are nearly unavoidable in practical phase separating systems.

2 Phase separation and coarsening

We consider isothermal spinodal decomposition of symmetric binary mixtures under deep quenches. In this case, the fluid motion arise from moving interfaces which create a characteristic 'bicontinuous' pattern and thermal fluctuations can be disregarded at long times. The state of the system at any given time can be described by an order parameter ϕ which is the relative concentration of the two components. A free energy of a bulk system can be defined for times when the system is not in equilibrium [4] and if the effective interactions between the mixture components are short ranged, this free energy can be written as a functional of ϕ

$$F[\phi] = \int_{\Omega} \left\{ f(\phi(\mathbf{x})) + \frac{1}{2} k |\nabla \phi(\mathbf{x})|^2 \right\} d\mathbf{x}, \tag{1}$$

where Ω is the region of space occupied by the system. The term $f(\phi(\mathbf{x}))$ is the bulk energy density, which depends only on the local concentration and the temperature T. We use the Landau expression which has two minima corresponding to the two stable phases of the fluid

$$f(\phi) = \frac{\alpha}{4} \left(\phi - \sqrt{\frac{\beta}{\alpha}} \right)^2 \left(\phi + \sqrt{\frac{\beta}{\alpha}} \right)^2, \tag{2}$$

for the bulk free energy density, where $\alpha > 0$ and $\beta = \beta(T)$ with $\beta(T) < 0$ for $T > T_c$ and $\beta(T) > 0$ for $T < T_c$.

Thus $f(\phi)$ has two nontrivial minima $\phi_\pm = \pm\sqrt{\frac{\beta}{\alpha}}$ corresponding to local equilibrium solutions for $T < T_c$. For $T > T_c$ the equilibrium solution is simply $\phi_0 = 0$. The term $\frac{1}{2}k|\nabla\phi(\mathbf{x})|^2$ with k positive constant quantifies the additional free energy contributions arising from local concentration fluctuations, which, in the demixing process, appear in the interfacial regions between the emerging domains of the two stable phases with concentrations $\phi_\pm$.The chemical potential μ is defined as

$$\mu(\phi) = \frac{\delta F[\phi]}{\delta\phi(\mathbf{x})} = f'(\phi(\mathbf{x})) - k\nabla^2\phi(\mathbf{x}). \tag{3}$$

The equilibrium interface profile can be found by minimizing the functional $F[\phi]$ with respect to variations of the function ϕ, i.e. solving the equation $\mu(\phi) = \delta F[\phi]/\delta\phi = \alpha\phi^3 - \beta\phi - k\nabla^2\phi = 0$. Besides the two stable uniform solutions $\phi_\pm = \pm\sqrt{\frac{\beta}{\alpha}}$ representing the coexisting bulk phases, there is a one-dimensional (say along the z-direction) non-uniform solution $\phi_0(z) = \phi_+ \tanh(z/\sqrt{2}\xi)$ that satisfies the boundary conditions $\phi_0(z \to \pm\infty) = \pm\phi$ (see [5, 6]). This solution was first found by Van der Waals [7] to describe the equilibrium profile for a plane interface normal to the z direction, of thickness proportional to $\xi = \sqrt{k/\beta}$, that separates the two bulk phases. Cahn and Hilliard [8, 9] generalized the problem to time-dependent situations by approximating interfacial diffusion fluxes as being proportional to chemical potential gradients, enforcing conservation of the field. The convective Cahn-Hilliard equation can be written as

$$\frac{\partial\phi}{\partial t} + \mathbf{u}\cdot\nabla\phi = M\nabla^2\mu, \tag{4}$$

where $\mathbf{u}$ is the velocity field and $M > 0$ is the mobility or Onsager coefficient. Equation (4) models the creation, evolution, and dissolution of diffusively controlled phase-field interfaces [10] (for a review of the Cahn-Hilliard model see for example [11]). We define the interface thickness to be the distance from $0.9\phi_-$ to $0.9\phi_+$ so that the equilibrium interface thickness is $2\sqrt{2}\xi\tanh^{-1}(0.9) =$

4.164ξ. This width contains 98.5% of the surface tension stress [12]. In equilibrium the surface tension σ of an interface is equal to the integral of the free energy density along the interface. For a plane interface σ is given by [5]

$$\sigma = k \int_{-\infty}^{+\infty} \left(\frac{d\phi_0}{dz} \right)^2 dz = \frac{\sqrt{2}}{3} \frac{k^{1/2} \beta^{3/2}}{\alpha}. \tag{5}$$

It is evident that we can control the surface tension and interface width through the parameters k, α, and β.

We model the fluid dynamics by the Navier-Stokes equations with a phase field-dependent surface force [13] and simplified with the creeping flow approximation:

$$-\nabla p + \eta \nabla^2 \mathbf{u} + \mu \nabla \phi + (\rho - \rho_0)\mathbf{a} = 0, \tag{6}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{7}$$

where $\mathbf{u}$ is the velocity field, p is a scalar related to the pressure that enforces the incompressibility constraint (7), η is the viscosity and $\mathbf{a}$ is the acceleration (gravitational) field (Boussinesq approximation). The coupled Cahn-Hilliard/Navier-Stokes system $(4) - (7)$ is referred to as "Model H" according to the nomenclature of Hohenberg and Halperin [14].

2.1 Nondimensionalization

To nondimensionalize the governing equations (4)-(7) we choose as a convenient characteristic length, L_c, for our simulations the mean field thickness ξ of the interface, i.e $L_c = \xi$ while U_c is a characteristic fluid velocity. The characteristic time T_c is the time required for the fluid to be convected a distance of the order of the interface thickness (in the absence of capillarity), $T_c = \xi / U_c$. Local interfacial curvature generates stress which drives fluid motion. It is natural then to scale the pseudo-pressure with surface tension times a term of the same order as the local curvature i.e. the $1/\xi$. The order parameter ϕ is scaled with its mean-field equilibrium value $\phi_+ = \sqrt{\beta/\alpha}$. With

this scaling, $-1 \leq \phi \leq 1$ and the interface dividing the two fluids is between $\phi = -0.9$ and $\phi = 0.9$. Summarizing we have

$$\mathbf{u}' = \mathbf{u}/U_c, t' = t/T_c, \mathbf{x}' = \mathbf{x}/L_c, p' = p/(\sigma/L_c). \tag{8}$$

The equations (4)-(7) become

$$\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = \frac{1}{Pe} \nabla^2 \mu, \tag{9}$$

$$-\nabla p + Ca \nabla^2 \mathbf{u} + \mu \nabla \phi + Bo \mathbf{e}_z = 0, \tag{10}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{11}$$

where $\mu = \phi^3 - \phi - \nabla^2 \phi$ is the dimensionless chemical potential. The dimensionless groups used above are the Peclet number Pe, the capillary number Ca and the Bond number Bo given by

$$Pe = \frac{U_c \xi^2}{M\sigma}, \quad Ca = \frac{\eta U_c}{\sigma}, \quad Bo = \frac{(\rho - \rho_0) a \xi^2}{\sigma} \tag{12}$$

respectively. Physically, the Pe number is the ratio between the diffusive time scale $\xi^3/(M\sigma)$ and the convective time scale ξ/U_c, the capillary number Ca provides a measure of the relative magnitude of viscous and capillary (or interfacial tension) forces at the interface and the Bond number Bo is the ratio of the acceleration (gravitational) forces and surface tension forces. Note that with this nondimensionalization the length of the fluid domain is interpreted in units of interface thickness ξ.

2.2 Dynamical scaling and domain growth

The physics of spinodal decomposition involves diffusion, capillary forces, viscous forces and fluid inertia. In the case of a deep quench and no external drive we assume that the interface can be characterized by a single length scale that is smooth with radii of curvature that scales as the domain size itself, which is much larger than the interfacial thickness. This length gives a measure

of how fast the domains grow. The domain patterns grow with a time-dependent characteristic length-scale

$$L(t) \sim t^n \tag{13}$$

with a growth exponent n, where n depends on the mechanism controlling growth e.g. diffusion, viscous or inertial. Model H describes a system order parameter coupled to hydrodynamic flow and in the absence of an external drive gives rise to three different growth regimes. For the diffusive regime $L \ll \sqrt{M\eta}$ and $n = 1/3$, for the viscous regime $\sqrt{M\eta} \ll L \ll \eta^2/(\rho\sigma)$ and $n = 1$, for the inertial regime $L \gg \eta^2/(\rho\sigma)$ and $n = 2/3$.

Finally, we consider the presence of an external drive i.e. gravity. We can think of a transition to gravity dominated flow arising when heavy domains resting on top of light ones become unstable i.e. when the gravitational force on the more dense phase overcomes the interfacial tension which keeps them suspended. In our model gravity becomes important when [1]

$$L(t) \gg \frac{\sigma}{(\rho - \rho_0)g}. \tag{14}$$

This process can be considered analogous to sedimentation. In fact it is possible to derive similar criteria via the balance of the Stokes friction coefficient and the diffusion time [15] to get (14) (called also the "Laplace length"). Once the instability occurs we have additional length scales since we have a faster growth in the gravity direction and a method to measure the anisotropic growth laws needs to be defined. From the knowledge of the structure factor one computes the average size of domains in the different directions L_x, L_y and L_z, for example

$$L_x(t) = \pi \frac{\int d\mathbf{k} S(\mathbf{k}, t)}{\int d\mathbf{k} |k_x| S(\mathbf{k}, t)}, \tag{15}$$

and analogously for the other directions. In Figure 1 we give a qualitative (graphical) interpretation of the various coarsening regimes.

3 Numerical method

The numerical method we employ is based on that introduced in [2] with one main modification: because of the periodic boundary conditions and the Stokes flow approximation we can use a fully spectral discretization. The time discretization is based on a semi-implicit scheme combined with a time-split strategy. This discretization effectively decouples Cahn-Hilliard and Navier-Stokes solvers and yields an efficient and robust modular scheme.

The outline of the method is as follows. Given ϕ^n and $\mathbf{u}^n$ the objective is to solve for ϕ^{n+1} and $\mathbf{u}^{n+1}$ with the steps:

1. Solve the Cahn-Hilliard equation with a semi-implicit method and spectral spatial discretization to obtain ϕ^{n+1}.

2. Using ϕ^{n+1} compute the surface force and solve the Navier-Stokes modified creeping flow equations with a Fourier-Fourier-Fourier (spectral) method [3].

The C-H step consist of second order semi-implicit SBDF (Semi-backward difference formula) time advancement [2]. The accuracy and stability of the method are documented in [2]. The overall scheme for the convective Cahn-Hilliard equation and the creeping flow equation has only a CFL stability condition:

$$\Delta t_{cfl} \leq \left(\frac{|u|_{\max}}{\Delta x} + \frac{|v|_{\max}}{\Delta y} + \frac{|w|_{\max}}{\Delta z} \right)^{-1}, \tag{16}$$

where (u, v, w) are the components of the velocity field.

4 Numerical study of gravitational effects on spinodal decomposition

Our method has allowed us to numerically simulate gravitational effects on spinodal decomposition of a binary mixture with phases of equal viscosity and mobility, in three dimensions. The grid size is $192 \times 192 \times 192$, the domain size is $L = 266$ which corresponds to a 3 mesh-point thick interface [2] and the boundary conditions are periodic. The initial conditions consist of uniformly distributed random fluctuations of amplitude 0.05 around a zero background, i.e. critical quench. We implement adaptive time stepping based on the CFL condition (16).

Figure 1 shows the evolution of the interfaces during the coarsening process. Regions rich in the lighter component ($\phi = 1$) are rendered in grey and regions rich in the heavier component ($\phi = -1$) comprise the surrounding (transparent) phase. The two domains become anisotropic in time and elongated in the direction of gravity.

We can characterize how the gravitational field interferes with spinodal decomposition by computing the characteristic length scale (growth rate) $L(t)$ as a function of time for diffusive or viscous regimes and for different Bond numbers i.e. different gravitational field strengths. Because of the anisotropy of the system, we calculate growth rates in both the z gravity direction (vertical in Fig. 1) and the x direction (horizontal, normal to gravity in Figure 1) using definition (15). The growth rate in the y direction is similar to that in the x direction due to the symmetry of the system. Figures 2(a) and 2(c) (log-log scale) show the domain growth in the z direction as a function of time starting from a diffusive regime condition ($Pe = 0.5$, $Ca = 70.0$) and as a function of the Bo number. The growth law for $Bo = 0.0$ obeys the classic Lifshitz-Slyozov [17] growth law $L(t) \sim t^{1/3}$ thus validating our computational procedures. At a late stage and $Bo > 0.0$, the data exhibit an approximately linear growth $L_z \sim t$, typical of the viscous regime and independent of gravity (Bo),

giving a strong indication that a universal scaling exists in the gravity direction. Further, we find that the growth rate in the gravity (z) direction of $L_z(t)$ is considerably faster than that of the no-gravity case. This occurs even with small gravity values, with Bo values as low as 0.003. Moreover, $L_z(t) \gg L_x(t)$ (where $L_x(t)$ is the length scale in the x direction, see Fig. 2(b) and 2(d)). This is not surprising since experimental results show similar sensitivity to gravity [19, 15] but no measure of the growth law has been reported due to experimental difficulties.

The effect of gravity demonstrated by our numerical results is in accordance with the analytical result in (14). Figure 2(b) and 2(d) (log-log scale) show the characteristic domain size in the x direction $L_x(t)$ as a function of time t. In this regime a trend is not evident: the length scale in the x direction with gravity ($Bo > 0$) resembles the Lifshitz-Slyozov growth law [17] at the initial stage but it deviates at later times becoming slower. To understand more clearly the asymptotic fate of the regime in this direction we need higher resolution simulations to be able to explore a wider range of length scales.

In Figure 3 we show results corresponding to the viscous regime parameters ($Pe = 96.0$, $Ca = 20.0$). For $Bo = 0.0$ (no gravity) we find a linear growth $L(t) \sim t$ as predicted by [1]. Again the growth of the length scale, $L_z(t) \sim t^{1.5}$ i.e. is considerably faster than that for the no-gravity case, and in the other direction characterized by lengths scale L_x, even with small gravity values (Figure 3(a)). There is evidence of collapse to the same universal slope (independent of Bo) at later stages (Figure(3(c)). The conditions of deviation from the no-gravity case were characterized using (15). In the x direction (Figure 3(b) and 3(d)) the slowing down of the growth rate due to gravity is more evident than in the diffusive case (Figures 2(b) and 2(d)).

5 Concluding Remarks

We used an accurate and efficient numerical method to compute phase ordering kinetics coupled with fluid dynamics to study the effect of gravity on critical spinodal decomposition of a binary mixture. Our results demonstrate that there is reasonable dynamical scaling in the direction of gravity in the diffusive and viscous regime, but a breakdown appears in the dynamical scaling in the transverse directions. Furthermore, the growth in the direction of gravity is much faster than that in the transverse directions, and those in the no-gravity case. Our results are in broad agreement and extend numerical results from previous studies of different but related models [18], leading us to believe that all these models share similar asymptotic scaling. Finally, we should remark that gravitational effects are very important in the context of the segregation of binary fluids, even when density mismatches are small.

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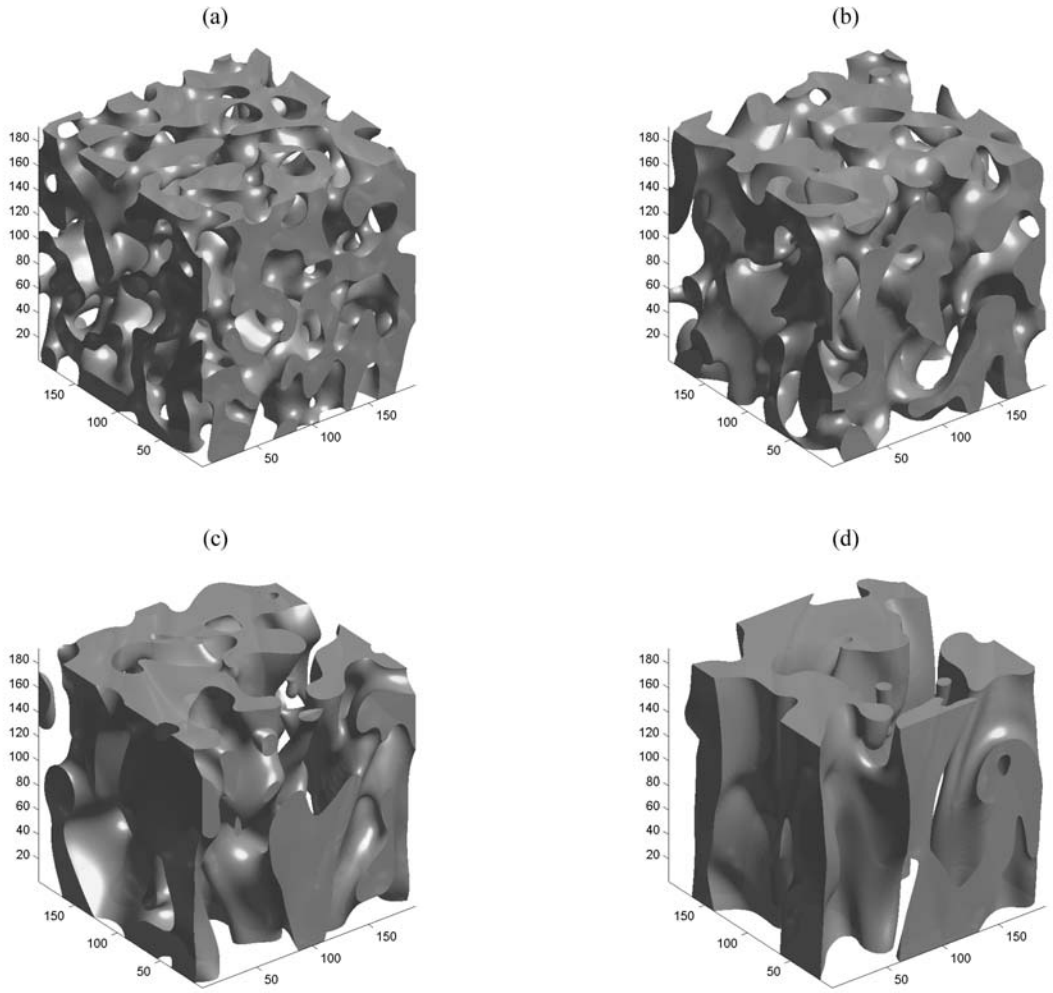

Figure 1: Evolution of ϕ represented by iso-surfaces of separation of the two fluids at $\phi = 0.0$, at different times. (a) $t = 3105.0$, (b) $t = 4741.0$, (c) $t = 7601.7$, (d) $t = 10686.5$. $Pe = 0.5$, $Ca = 70.0$, $Bo = 0.03$, $N = 192$, $L = 266$.

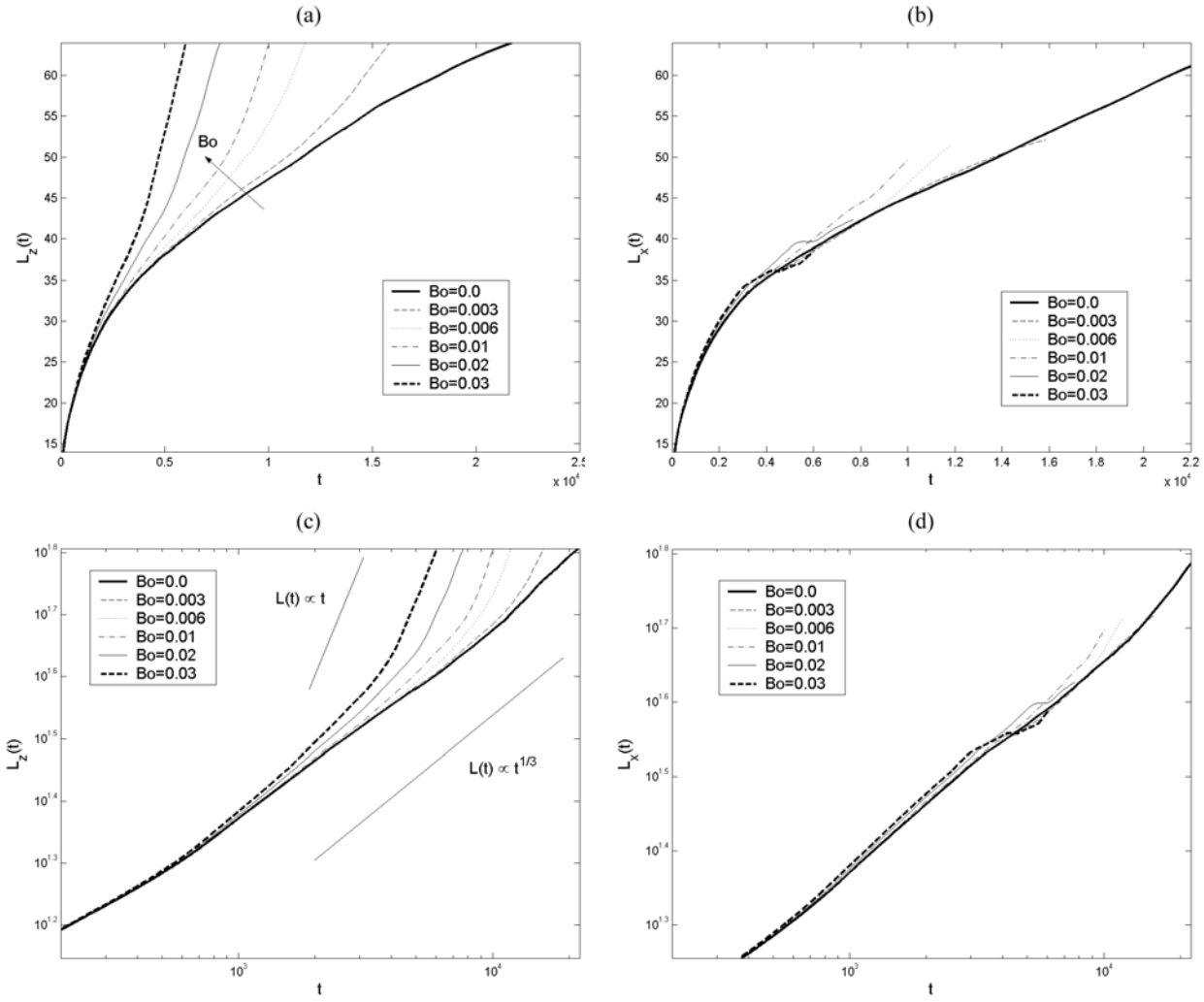

Figure 2: Length scales in the gravitational direction, L_z, and the transverse directions, L_x, vs time. $Pe = 0.5$, $Ca = 70.0$, Bo as a parameter. (a) $L_z(t)$, (b) $L_x(t)$, (c) $L_z(t)$ (loglog plot), (d) $L_x(t)$ (loglog plot).

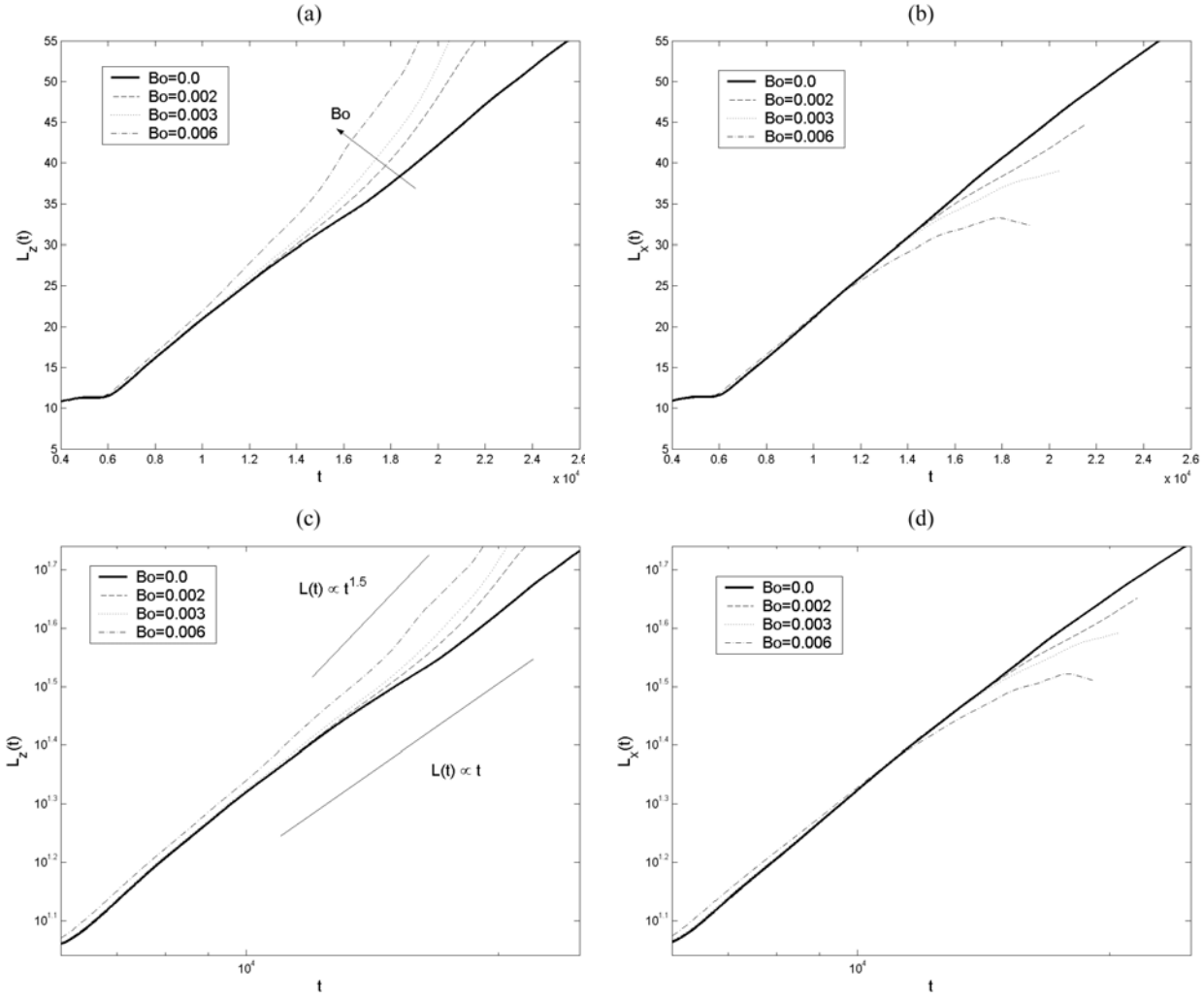

Figure 3: Domain size vs time. $Pe = 96.0$, $Ca = 20.0$, Bo as a parameter. (a) $L_z(t)$, (b) $L_x(t)$, (c) $L_z(t)$ (loglog plot), (d) $L_x(t)$ (loglog plot).