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Theoretical studies of phase-separation kinetics in a Brinkman porous medium

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Online at stacks.iop.org/JPhysA/43/202001**Abstract**

Although the coarsening of binary fluid mixtures in porous media has been of great interest for some time, there are still no complete theories for describing the relevant mechanisms, and more theoretical work needs to be carried out. In this work, we have proposed a simple model for phase separation of binary fluids in a porous medium, where the Brinkman-extended-Darcy equation and Cahn–Hilliard equation are the dynamical constitutions. Using the dimensional analysis approach, our findings lead to the prediction of domain coarsening in a porous medium for several regimes, including the conventional power laws. In addition, we have found that slowed-down coarsening dynamics are caused by the hydrodynamic screening effect, which is governed by the logarithmic law for this regime. Our theoretical results are at least qualitatively consistent with previous reports using simulations or experiments.

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1. Introduction

Phase separation of binary fluid mixtures in porous media has attracted much attention from both theorists and experimentalists [1, 2]. Many researchers have focused on domain coarsening in a confined mixture, finding several mechanisms which are different from the bulk mixture [3–8]. After being quenched below the critical temperature, the mixture separates into two phases that the domains form, coarsen and grow to a larger size. For the bulk mixture, the characteristic domain size $L(t)$ obeys the scaling law $L(t) \sim t^\alpha$, where α is the growth exponent. When the coarsening is driven by viscous hydrodynamics, the growth exponent

is $\alpha = 1$, as predicted by Siggia [9, 10]. But when the coarsening is driven by interface diffusion, the growth exponent is $\alpha = 1/3$, as per the Lifshitz–Slyozov law [10]. The latter coarsening is slower than the first one.

Studies on phase separation of binary fluid mixtures in porous media have reported that coarsening in a porous medium is dramatically slowed due to the confinement effect and unexpected growth law [1, 2]. This is typically observed when the characteristic domain size becomes comparable to the average pore size. The previous theoretical descriptions of the kinetics that were based on the ‘single-pore model’ [3] and ‘random-field approach’ [11] left unrevealed the exact formulation of this slow-down coarsening regime. Hence it was the main goal of our work to enhance the theoretical knowledge of the domain coarsening mechanism in porous media.

In our research we proposed a new model for the description of binary fluid phase separation in porous media and theoretically investigated the domain coarsening mechanisms of this model. Our model extends beyond the ‘random-field approach’ to take into account hydrodynamic interactions. In addition, randomness is omitted, thus resulting in the removal of the stochastic feature and leaving us with the mean-field prediction. Due to this exclusion of fluctuation effects, our model is limited to deep quench only. Since the Brinkman-extended-Darcy law formulation has lent validity to single phase flows in porous media [12], we extend this model to the binary fluids. Furthermore, the Brinkman-extended-Darcy hydrodynamic equation is coupled with the advective Cahn–Hilliard equation [13, 14] as the governing equations for binary fluid in a porous medium.

Regarding the Brinkman-extended-Darcy hydrodynamic equation, the linear damping force appeared in addition to the usual binary fluid model (as we will see later). This force represents the confinement effect in a porous medium. The interplay between the linear damping force and the viscous force introduces the hydrodynamic screening effect to the flow field. To investigate the growth law of fluid domains in porous media, we first calculate solutions for the velocity field using Green’s function technique and then apply dimensional analysis to our results [10] to investigate the domain coarsening. With these heuristic works, we are able to predict the domain coarsening in a porous medium for several regimes. And our results can recover the conventional power law when the screening effect becomes irrelevant. The screening effect was found to slow the domain coarsening, when the characteristic domain size is comparable to the average pore size. The coarsening for this regime is suggested to follow the logarithmic law. Comparisons with published evidence are also discussed in this paper, resulting in the conclusion that previously reported results, of both simulation and experiments, appear to support the validity of our model at least qualitatively.

This paper is organized as follows. In section 2, we describe the proposed model for phase separation of binary fluids in porous media and the special solutions are solved. In section 3, the establishment of domain coarsening is discussed.

2. Model and analysis

We consider an incompressible binary fluid mixture in a porous medium as demonstrated in figure 1. The distinguished phases are labeled by the ‘phase field,’ which is defined by the ‘order parameter’: $\phi(\vec{r}, t)$. The local velocity is defined by $\vec{v}(\vec{r}, t)$. The dynamics is governed by the Brinkman-extended-Darcy equation [12] coupled with the advective Cahn–Hilliard equation [13, 14]. The hydrodynamic equations for binary fluids in a porous medium can be written as

$$0 = \eta_e \nabla^2 \vec{v} - \vec{\nabla} p - \frac{\eta}{K} \vec{v} + \mu \vec{\nabla} \phi, \quad (1)$$

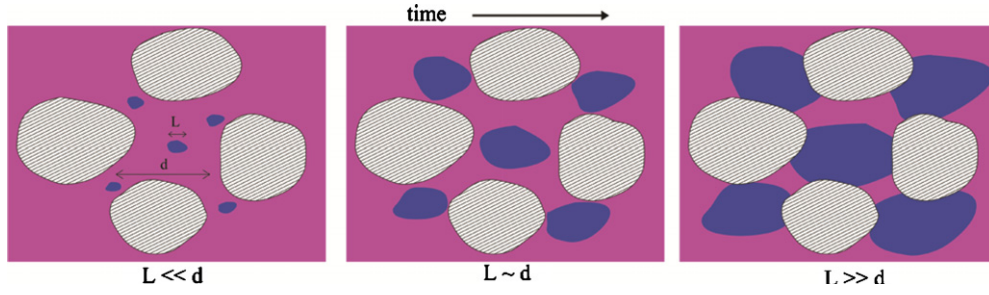


Figure 1. The illustration demonstrates the dynamic phase separation of binary fluids confined in a porous medium. The porous solids are represented by the swarm of solid-lined grains, where the average pore size is d . The two phases of fluids are labeled by blue for one phase and magenta for the other phase, where L is the characteristic domain size. At the early stage, the domains of the minority phase form and grow with $L \ll d$, where the effect of the confinement effect is irrelevant. Then the domain size becomes as large as the pore size $L \sim d$, so that the effect of confinement becomes important. At the very late stage, the domain size becomes much larger than the pore size $L \gg d$; the dynamics is dominated by the confinement effect.

$$\vec{\nabla} \cdot \vec{v} = 0, \tag{2}$$

$$\frac{\partial \phi}{\partial t} + (\vec{v} \cdot \vec{\nabla})\phi = M\nabla^2\mu, \tag{3}$$

where η is the viscosity; η_e is the effective viscosity (we can choose $\eta = \eta_e$ typically); K is the permeability of a porous medium; M is the mobility; $\mu = \mu(\phi)$ is the chemical potential; and $p = p(\vec{r}, t)$ is the fluid pressure. The permeability has the relation to average (or effective) pore size d , given by $K = Cd^2$, where C is a dimensionless constant [15]. The third term on the right-hand side of (1) is the linear damping force due to the confinement effect in a porous medium. The last term on the right-hand side of (1) represents the interfacial driving force; this force is discussed in [13]. Equation (2) is the incompressible constrain. The chemical potential can be calculated from the functional derivative of the Landau free energy $\mu = \mu(\phi) = \delta F/\delta\phi$, where the Landau free energy functional is given by [16]

$$F = \int d^3r \left[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa}{2}(\vec{\nabla}\phi)^2 \right], \tag{4}$$

where a and b are the constant parameters related to temperature, and κ is the interfacial energy constant related to the surface tension σ . The author of [10] has shown the solution for the chemical potential, given by $\mu = -\sigma/r$, for a spherical drop for a bulk mixture. Without the linear damping force, equations (3)–(5) are the well-known model H [17].

In equation (1), we can solve analytically the velocity field using Green’s function technique. Before proceeding any further, for simplicity, we replace the damping term in (1), according to $-(\eta/K)\vec{v} \rightarrow -(\eta_e/\xi^2)\vec{v}$, where $\xi \equiv (\eta_e K/\eta)^{1/2} = (\eta_e C/\eta)^{1/2}d$ is the constant proportional to the average pore size d (its physical meaning is discussed later). By applying the Fourier transform to (1) and (2), we obtain equations in Fourier space:

$$-\eta_e k^2 \vec{v}(\vec{k}) - i\vec{k}p(\vec{k}) + \vec{F}(\vec{k}) - \frac{\eta_e}{\xi^2} \vec{v}(\vec{k}) = 0, \tag{5}$$

$$i\vec{k} \cdot \vec{v}(\vec{k}) = 0, \tag{6}$$

where $\vec{F} = \mu \vec{\nabla} \phi$ and $k = \sqrt{\vec{k} \cdot \vec{k}}$. Then applying the incompressible constrain (6) to (5), we obtain the pressure in Fourier space:

$$p(\vec{k}) = -\frac{i\vec{k} \cdot \vec{F}(\vec{k})}{k^2}. \quad (7)$$

Substituting (7) into (5), we obtain the velocity field in Fourier space:

$$\vec{v}(\vec{k}) = T(\vec{k}) \cdot \vec{F}(\vec{k}), \quad (8)$$

with the tensor

$$T(\vec{k}) = \frac{1}{\eta_e(k^2 + \lambda^2)} \left(I - \frac{\vec{k}\vec{k}}{k^2} \right), \quad (9)$$

where $\lambda \equiv 1/\xi$ and I is an identity matrix tensor. We can find the solutions in real space by applying the inverse Fourier transforms to equations (7)–(9). By doing so, we first obtain the pressure in real space given by

$$p(\vec{r}) = \int d^3r' \frac{1}{4\pi|\vec{r} - \vec{r}'|} \vec{\nabla} \cdot \vec{F}(\vec{r}'). \quad (10)$$

And then, we obtain the velocity field in real space given by

$$\vec{v}(\vec{r}) = \int d^3r' T(\vec{r} - \vec{r}') \cdot \vec{F}(\vec{r}'), \quad (11)$$

with the tensor

$$T(\vec{r}) = \frac{e^{-\lambda r}}{8\pi\eta_e r} \left(I + \frac{\vec{r}\vec{r}}{r^2} \right), \quad (12)$$

where $r = \sqrt{\vec{r} \cdot \vec{r}}$. The tensor $T(\vec{r})$ is the Green function for (1) and is known as the screened Oseen tensor [18, 19]. By replacing $\lambda = 1/\xi$ in (12), we see that ξ is the screening length [15], which is proportional to the average pore size d as defined previously. From (11) and (12), we see that the screening effect ‘slows down’ the velocity field exponentially depending on the relative spatial position r/ξ . We note that if $r/\xi \ll 1$, the screening effect becomes irrelevant and the tensor $T(\vec{r})$ recovers the usual Oseen tensor [10].

There is another case that should be considered when the length scale is much larger than the average pore size or is equivalent to $k \ll \lambda$ in Fourier space. Equation (9) suggests that the viscous term can be neglected. Equation (1) is thus reduced to $\vec{v}(\vec{r}) = K(\vec{F}(\vec{r}) - \vec{\nabla} p)/\eta$, which is known as the Darcy law. This equation can be solved directly by using the resulting pressure in (10). Then, with $\xi = (\eta_e K/\eta)^{1/2}$, we obtain

$$\vec{v}(\vec{r}) = \frac{\xi^2}{\eta_e} \vec{F}(\vec{r}) - \frac{\xi^2}{\eta_e} \int d^3r' \vec{\nabla} \frac{\vec{\nabla} \cdot \vec{F}(\vec{r}')}{4\pi|\vec{r} - \vec{r}'|}. \quad (13)$$

Now we have the solutions for various regimes. In the next section, we will use these results in combination with dimensional analysis to predict the domain coarsening of binary fluids in a porous medium governed by this model.

3. Domain coarsening in a porous medium

To investigate the coarsening mechanisms of this system, we follow the dimensional analysis as presented in [10]. First, we denote the length scale and time scale by L and t , respectively. Therefore the rate of coarsening is proportional to the velocity and is defined by $dL/dt \sim v$. From dimensional arguments, we found $\mu \sim \sigma/L$, $\nabla\phi \sim 1/L$, $F \sim \sigma/L^2$ and $\partial\phi/\partial t \sim 1/t$.

Because the behavior of the system depends on the ratio of L/ξ , we classify the dynamic coarsening into three regimes as $L/\xi \ll 1$, $L/\xi \sim 1$ and $L/\xi \gg 1$, as depicted in figure 1. Recalling that $\xi \equiv (\eta_e K/\eta)^{1/2} = (\eta_e C/\eta)^{1/2} d$, we interpret the screening length as the (effective) average pore size equivalently.

3.1. Coarsening without the screening effect $L/\xi \ll 1$

We now consider the first regime when the characteristic length scale is very small compared to the average pore size (or equivalent to $L/\xi \ll 1$), and the screening effect thus becomes irrelevant. Since the exponential decay is omitted, we then obtain the usual Oseen tensor as

$$T(\vec{r}) = \frac{1}{8\pi\eta_e r} \left(I + \frac{\vec{r}\vec{r}}{r^2} \right), \quad (14)$$

with the dimensional argument of $T \sim 1/\eta_e L$. Applying these dimensional arguments to (11), we found that $dL/dt \sim \sigma/\eta_e$, which leads to

$$L \sim \frac{\sigma}{\eta_e} t, \quad (15)$$

which is the well-known viscous hydrodynamic coarsening [9, 10]. This coarsening competes with the diffusion as indicated by (3). If the hydrodynamic effect is not important, we drop the advective term from (3). Applying the dimensional argument to this equation, we obtain $1/t \sim (M\sigma)/L^3$, which leads to

$$L \sim (M\sigma)^{1/3} t^{1/3}, \quad (16)$$

which is the conventional diffusive coarsening [10]. The hydrodynamics become important if the hydrodynamic time scale $t_h \sim (\eta_e/\sigma)L$ is proportional to the diffusive time scale $t_d \sim L^3/M\sigma$. By comparing the two time scales, we obtain the diffusion-viscous cross-over length scale $L_d \sim (M\eta_e)^{1/2}$. Note that these coarsening regimes have been investigated in a bulk medium [10].

3.2. Coarsening with the screening effect $L/\xi \sim 1$

When the characteristic length scale is comparable to the average pore size (or equivalent to $L \sim \xi$), the screening effect becomes important. The screened Oseen tensor in (12) plays the crucial role in the system now. The screened Oseen tensor agrees in the dimension $T \sim (e^{-L/\xi})/\eta_e L$. Because the exponential term is already dimensionless, we leave it as a rescaling factor. Then, from (11), we obtain the coarsening rate equation $dL/dt \sim (\sigma/\eta_e) e^{-L/\xi}$. It is interpreted that the coarsening rate exponentially decays as the domain size increases. Therefore, the screening effect acts as a growth barrier of fluid domain in a porous medium. To our knowledge, this is still not a well-understood coarsening phenomenon, and it is found here for the first time for this particular system. This equation's solution is given by $\xi e^{L/\xi} \sim (\sigma/\eta_e)t + \text{const}$. With the initial condition $L(t=0) = 0$, we found the final form to be

$$L \sim \xi \ln \left[\frac{(t + \tau)}{\tau} \right], \quad (17)$$

where $\tau = \eta_e \xi/\sigma$ is defined as the screening time scale. We also noted that if $t \ll \tau$, equation (17) can be expanded to $L \sim \frac{\sigma}{\eta_e} t + O(t^2/\tau^2)$, which recovers the linear growth law in (15). Equation (17) is the logarithmic form where the coarsening is slower. This is in agreement with the numerical studies of [7, 20], and the slowed-down coarsening investigated in the previous studies [1, 2]. But for the first time, we now have shown analytically the exact formulation of the logarithmic law.

3.3. Coarsening with the Darcy law $L/\xi \gg 1$

When the length scale becomes much larger than the average pore size (or equivalent to $L/\xi \gg 1$), the flow field seems to be suppressed, consequently changing the behavior of (13), according to the Darcy law. From the dimensional analysis arguments, it is found that $dL/dt \sim [(\xi^2\sigma)/\eta_e]/L^2$, where the solution is

$$L \sim \left(\frac{\xi^2\sigma}{\eta_e}\right)^{1/3} t^{1/3} = \left(\frac{K\sigma}{\eta}\right)^{1/3} t^{1/3}. \quad (18)$$

Interestingly, the coarsening is similar to the diffusive mechanism as found so far [10]. This is consistent with the experiments and theory presented in [21]. The Brinkman screening regime crosses the Darcy diffusion regime. Comparing the time scale of the two regimes $\tau(e^{L/\xi} - 1) \sim (\eta_e/\xi^2\sigma)L^3$, we found the Brinkman–Darcy cross-over length scale L_D to be given by the relation $L_D \sim \xi(e^{L_D/\xi} - 1)^{1/3}$. This nonlinear equation can be solved numerically, where we obtain $L_D \sim 4.567\xi$ by a random search algorithm. Alternatively, by the approximation expansion, we have

$$L_D \sim \xi[(L_D/\xi)^3/3! + (L_D/\xi)^4/4! + (L_D/\xi)^5/5! + (L_D/\xi)^6/6! + (L_D/\xi)^7/7! + \text{remainders}]^{1/3}.$$

After rearranging, we obtain $0 \sim -5/3! + x/4! + x^2/5! + x^3/6! + x^4/7! + \text{remainders}$ where $x \equiv L_D/\xi$. Then, on solving this quartic equation, we find $L_D \sim 5.341\xi + \text{correction terms}$. Regarding this result, if the screening length ξ is much smaller than the diffusion-viscous cross-over length scale L_a , the hydrodynamic effect is completely suppressed from the system. Comparing these two length scales we have $(K\eta_e/\eta)^{1/2} \sim (M\eta)^{1/2}$. This means that for $K \ll (\eta/\eta_e)M\eta$, the two diffusion regimes are connected and the system is sole diffusion. We summarize the domain coarsening in a porous medium for all regimes as follows:

$$L \sim \begin{cases} (M\sigma)^{1/3}t^{1/3}, & L \ll (M\eta_e)^{1/2}, & \text{Lifshitz–Slyozov,} \\ (\sigma/\eta_e)t, & (M\eta_e)^{1/2} \ll L \ll \xi, & \text{Siggia,} \\ \xi \ln[(\sigma/\eta_e\xi)(t + \tau)], & \xi \ll L \ll L_D, & \text{Brinkman,} \\ [(K\sigma)/\eta]^{1/3}t^{1/3}, & L \gg L_D & \text{Darcy.} \end{cases} \quad (19)$$

From our theoretical findings, it will be interesting to see if they are consistent with those from computer simulations or even experimental results. However, that is not the aim of this communication.

4. Conclusion

We have theoretically investigated the coarsening of binary fluid mixtures in a porous medium, which has been the subject of much investigation but resulting in no complete theories for describing the mechanisms involved. We have proposed a model where the dynamical constitutions are the Brinkman-extended-Darcy equation coupled with the Cahn–Hilliard equation. Combined with the dimensional analysis approach, predictions of domain coarsening in porous media for several regimes, including the conventional power laws, have been made. Specifically, we have analyzed the solutions for the velocity that leads to the prediction of domain coarsening for several regimes. Our highlighted finding is that the logarithmic coarsening feature which describes the slowing coarsening dynamics is due to the effect of confinement in the porous medium. Our findings seem to be supported by the previous studies involving simulations and experiments, at least qualitatively.

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