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LETTER TO THE EDITOR

Molecular dynamics simulations of phase separation in porous media

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Abstract. The phase separation of a binary fluid mixture in a two-dimensional porous medium was investigated with molecular dynamics simulations. A variety of wetting conditions were studied. After a transient period of relatively fast growth, a domain pattern consisting of alternating plugs (both species wet the pores) or a series of capsules (one species preferentially wets the pores) forms, which coarsens extremely slowly. Dynamical scaling is observed throughout the time period of the simulations.

The question of how a binary fluid mixture phase separates inside a porous medium has attracted considerable experimental [1–5] and theoretical [6–12] attention. Porous media typically consist of two interpenetrating and percolating phases, one of which is a solid with a large surface-to-volume ratio [6]. Fluid mixtures imbibed into the porous media display radically different phase behaviour from the bulk mixture. In bulk, binary liquids separate into macroscopically-sized domains after a quench through the critical temperature. By contrast, the kinetics of phase separation inside the porous medium is extremely slow. Growth of the ordered domains does not proceed to a macroscopic scale. Rather, a history-dependent domain structure consisting of a large number of microscopic domains forms.

Theoretically, phase separation inside porous media has been analysed in terms of a random-field [7] and a ‘single-pore’ model [8]. In the random-field description, it is the random convolutions of the pores that lead to the slow kinetics and the metastability of the clusters. However, the clusters can, in the context of the model, become significantly larger than the pore size. This model is believed to be most applicable to high porosity systems such as gels [4]. The ‘single-pore’ model, on the other hand, was developed to model low porosity systems such as Vycor glass [9]. For straight pores, it was shown that long-lived metastable structures such as ‘plugs’ and ‘capsules’ arise from an interplay between the wetting properties of the fluids and the temperature of the system [8].

There has been a number of simulations of phase separation inside porous media. These have mostly been based on conserved Ising models [10] or Langevin descriptions [11] that do not incorporate any hydrodynamic modes. However, experiments [12], theory [13] and molecular dynamics (MD) simulations [14, 15] show that these play an important role in the phase separation of bulk fluids, and are therefore likely to be important in porous media as well. One exception is provided by the interesting lattice-gas simulations of Grunau and coworkers [16], which incorporate both hydrodynamic and wetting effects. But, lattice-gas and MD simulations [15, 17] have yielded different growth exponents for phase separation between bulk fluids. This stresses the need for a further study, which incorporates the fluid effects on a more fundamental level. We have therefore carried out extensive MD simulations of phase separation in a two-dimensional model system similar to Vycor glass. An additional

advantage of such an approach is that the simulations allow for the direct visualization of the phase separation processes. Furthermore, by tuning the interaction between different atomic species, different wetting situations are easily investigated [18].

We now give details of our simulations. The binary fluid mixtures consisted of two fluid species, labelled A and B. The interaction potential between the two species was taken to be the extended and shifted (12-3) Lennard-Jones potential:

$$U(r_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \gamma_{i,j}(2\delta_{i,j} - 1) \left(\frac{\sigma}{r_{ij}} \right)^3 \right)$$

where $r_{ij} = r_i - r_j$ is the distance (truncated at 4.2σ), between the species i and j . The parameters $\gamma_{A,A} = \gamma_{A,B} = \gamma_{B,B} = 1$, so that forces are attractive between like species and repulsive between unlike species. This potential has previously been used to study phase separation in bulk fluid mixtures [14, 15]. Square systems with periodic boundary conditions were used. Simulations were carried out for ~ 17000 atoms with density $\rho\sigma^2 = 0.74$, using the standard Verlet algorithm [19]. Velocity rescaling was used to keep the system at a constant temperature of $k_B T/\epsilon = 2$, where k_B is the Boltzmann constant. A small timestep of 0.005τ was used, where the timescale is $\tau = (m\sigma^2/\epsilon)^{1/2}/2$. The data up to 15τ were averaged over at least ten runs; and three runs up to 165τ .

The porous medium was formed in analogy to Vycor glass. Initial configurations were prepared by scaling the atoms on a hexagonal lattice to their proper density, and then labelling each atom A or B at random. Phase separation was then allowed to proceed normally until a desired pore size, quantified by the average size of the interconnected domain structure, was reached. The process of phase separation was then stopped. Subsequently, one of the species was treated as a wall (labelled w) and kept frozen throughout the simulations. The atoms of the other species were then relabelled A or B at random and the simulation allowed to proceed. In order to model different wetting properties between the wall and fluid atoms, the parameters $\gamma_{i,j}$ were modified. Specific choices investigated were $(\gamma_{A,w}, \gamma_{B,w}) = (-1, -1)$ —both species are attractive to the wall; $(-1, 1)$ —one species is attractive to the wall, the other is repulsive; and $(1, 1)$ —both species are repulsive to the wall.

During the simulations, a number of quantities were monitored. Chief of these was the circularly-averaged structure factor $S(k, t)$ as a function of wavenumber k , and the pair-correlation function $g(r, t)$. The evaluation of these was standard, except that the contribution from the 'wall' atoms was set to zero. The first zero of the pair-correlation function was found to give a good measure of the average domain size $R(t)$ of the clusters. Other quantities measured were the species-species interface length, and the size and number distributions of the clusters.

Figure 1 shows typical sample configurations as a function of time for the different wetting situations. After the quench, the instability forms a complicated and interconnected network of ordered domains. Initially these domains are small and the structure is only weakly affected by the presence of the walls. Domains grow by the coalescence of the interfaces followed by a relatively rapid reshaping of the interfaces. These are important hydrodynamic effects. At time $\sim 12\tau$, the domain sizes become comparable to the width of the pores. Growth then slows down considerably. In the case of both fluid species being attractive or repulsive to the walls (figures 1(a) and (c)), the system forms a series of alternating plugs. While these plugs still diffuse inside the pore, the late time patterns are quite stable over the time scales of our simulations.

In the case of figure 1(b), one species preferentially wets the pores as is evidenced by a thin film at the walls. After a quench, the wetting species 'rushes' towards the walls

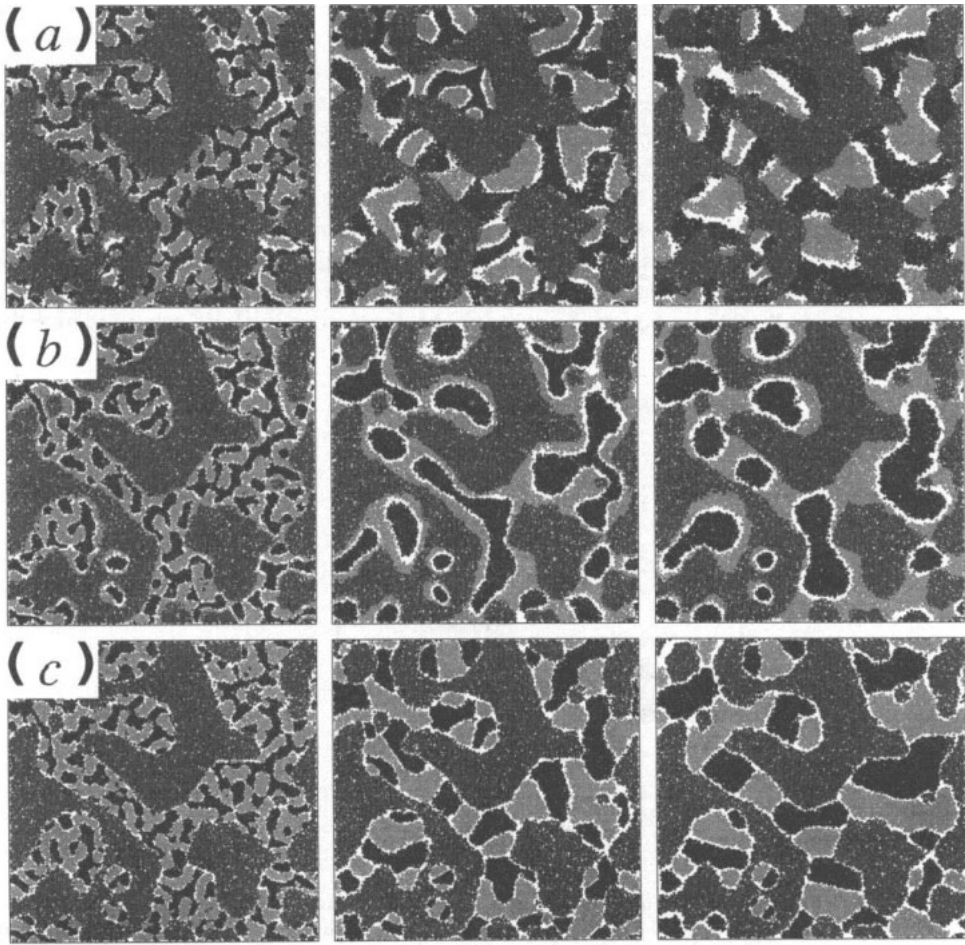


Figure 1. Sample configurations showing phase separation inside the porous medium (pore size 13.5σ): the dark and light grey represents the two components of the binary fluid mixture, while the intermediate shade of grey represents the walls. The panels are at times 2, 15 and 150 τ (left to right panel) for the different wetting situations. Here, $(\gamma_{A,w}, \gamma_{B,w}) =$: (a) $(-1, -1)$; (b) $(-1, 1)$; and (c) $(1, 1)$. Note the typical breakup of the tube into a series of capsules separated by plugs in (b).

pushing the non-wetting species towards the centre of the pore. This forms a series of capsules which then merge to form long tubes. The tubes later break up again into a series of capsules separated by plugs of the wetting species. This breakup is assisted by the random curvature of the pores. MD simulations of tubes inside straight pores (under similar conditions of density and temperature) show that these are long-lived, as compared to tubes in curved pores which breakup quite readily. This behaviour of the tubes in pores is different from the behaviour of domains in a two-dimensional bulk, where the domains are stable against breakup with respect to shape fluctuations [20]. During the late stages, the domains migrate from regions where the pores are narrow towards regions where the pores are relatively wider. Stable locations for the domains appear to be at the junctions between several pores, where the domains can optimize their surface-to-volume ratio.

The evolution of the average domain size, as measured through the first zero of the correlation function for two different pore sizes (8.5σ and 13.5σ), is shown in figure 2. Other measures of length such as those defined through the first and second moment of the structure factor give similar results. Two growth regimes are readily identified: an early and a late time regime. At early times, when the average domain size is smaller than the pore size, growth is relatively rapid. However, this regime is relatively short and after about $\sim 12\tau$, a crossover to a much slower growth regime takes place. Naturally, this crossover takes place at somewhat earlier times for systems with smaller pores. Effective growth exponents n , calculated by fits to $R \sim t^n$ for this time regime, range from 0.37 to 0.40. These values are somewhat less than $1/2$, which is the expected value for the coalescence of interfaces in bulk. Thus, even at the early stages, the porous medium acts to reduce the growth somewhat.

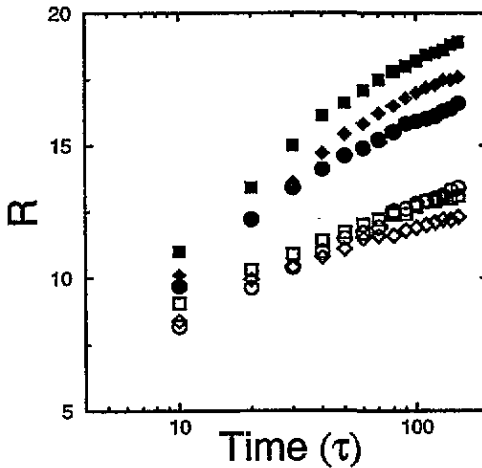


Figure 2. Average domain size, as measured by first zero of the pair-correlation function, as a function of time. The full symbols represent data for pore size 13.5; the open symbols, pore size 8.5. Here, circles represent data for $(\gamma_{A,w}, \gamma_{B,w}) = (-1, -1)$; squares, $(\gamma_{A,w}, \gamma_{B,w}) = (-1, 1)$; and diamonds for $(\gamma_{A,w}, \gamma_{B,w}) = (-1, -1)$. The broken line represents $R \sim t^{1/2}$.

At late times, growth of the domains inside the porous medium is very slow. Since the majority of domains consist of plugs with almost flat interfaces, the driving force for the coalescence of these plugs is small. Growth, however, which never quite ceases over the timescales of our simulation, takes place by the diffusive coalescence of the confined droplets. The data are well fit by $R(t) \sim \log(t)$, characteristic of growth induced by fluctuations[†].

From the average domain size against time data, it is difficult to distinguish between the different wetting conditions. We have therefore monitored the fractions of the various interface types as a function of time. These were evaluated by dividing the length of each type of interface by the total length of all interfaces. Note that the latter number decreases as a function of time because the amount of A:B interface decreases as the phase separation proceeds. The results are shown in figure 3. For all the different wetting situations, the fraction of A:B interfaces decreases from its initial value of ~ 0.70 to a final value of ~ 0.30 . For the case of both fluid species being attracted to the wall, the fractions of A:w

[†] The data are also well fit by a power law, with low growth exponents of $n \approx 0.11$ for all of the different wetting situations.

and B:w track each other fairly closely, as is expected. Their value rises from an initial value of ~ 0.20 to ~ 0.40 . Figure 3(b) shows the situation where A wets the wall, and B does not. In this case the A:w and B:w fractions are quite different, with the A:w fraction saturating near 0.60, when species A wets nearly all the pores. The results for the situation of both types of atoms 'disliking' the wall are quite similar to the case of both atoms being attracted to the wall (figure 3(a)). Note that there is little difference between the data for the two different pore sizes.

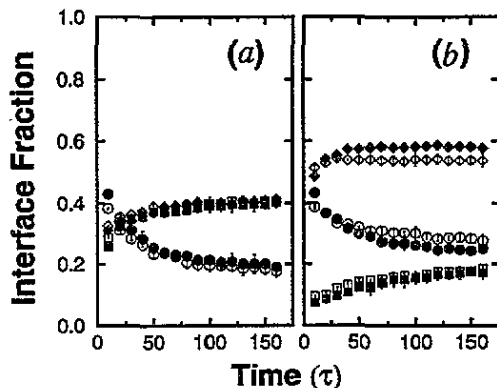


Figure 3. Time evolution of the fraction of various interface types for $(\gamma_{A,w}, \gamma_{B,w}) =$: (a) $(-1, -1)$; and (b) $(-1, 1)$. Here filled symbols represent data for pore size 13.5 open symbols, pore size 8.5. Circles represent fraction of A:B interfaces; squares, A:w interfaces; and diamonds, the B:w interfaces.

To study the question of scaling during phase separation in porous medium, we have examined the structure factor $S(k, t)$. If there is scaling, then $S(k, t) = R(t)^d F(x)$, where $F(x)$ is a scaling function and $x = kR(t)$. Figure 4 shows the scaling function for the case $(\gamma_{A,w}, \gamma_{B,w}) = (-1, -1)$. The other wetting situations give similar results. Thus, contrary to previously reported results [11], we find no evidence of the breakdown of scaling.

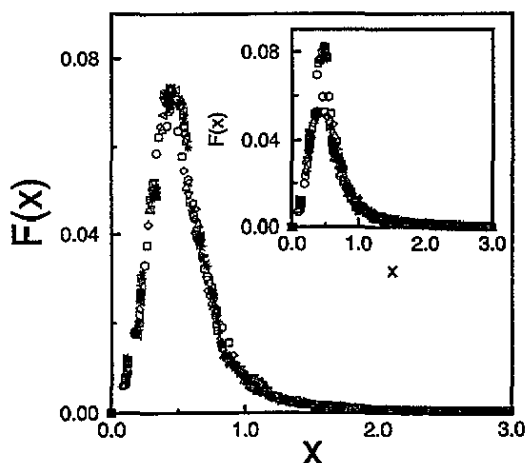


Figure 4. Scaling function $F(x)$ against x at times greater than 15τ for $(\gamma_{A,w}, \gamma_{B,w}) = (-1, -1)$. The inset shows the function for $(\gamma_{A,w}, \gamma_{B,w}) = (-1, 1)$. The data are for pore size 13.5.

In summary, we have carried out extensive MD simulations of phase separation in a porous medium, under a variety of wetting conditions. After an initial transient period, during which the interfaces coalesce and the domains become comparable to the pore size, the domains arrange themselves into a series of plugs or, in the case of one species preferentially wetting the pores, into a series of capsules broken up by plugs. Hydrodynamics plays an important part in the development of these domain structures. At late times, growth proceeds by the coalescence of droplets. However, because these are effectively confined by the pores, the kinetics are quite slow. We do not observe any evidence of the breakdown of scaling over the time scales of our simulations.

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References

- [1] See, for example, Dulliens F A 1976 *Porous Media: Fluid Transport and Pore Structure* (New York: Academic)
- [2] Maher J V, Goldburg W I, Pohl D W and Lang M 1984 *Phys. Rev. Lett.* **53** 60
Goh M C, Goldburg W I and Knobler C M 1987 *Phys. Rev. Lett.* **58** 1008
- [3] Dierker S B and Wiltzius P 1987 *Phys. Rev. Lett.* **58** 1865; 1991 *Phys. Rev. Lett.* **66** 1185
Wiltzius P, Dierker S B and Dennis B S 1987 *Phys. Rev. Lett.* **58** 1008
- [4] Frisken B J, Ferri F and Cannell D S 1991 *Phys. Rev. Lett.* **66** 2754
Frisken B J and Cannell D S 1992 *Phys. Rev. Lett.* **69** 632
- [5] Lin M Y, Sinha S K, Drake J M, Wu X I, Thiyagarajan P and Stanley H B 1994 *Phys. Rev. Lett.* **72** 2207
- [6] Monette L, Grest G S and Anderson M P 1994 *Phys. Rev. E* **50** 3361
- [7] de Gennes P G 1985 *J. Phys. Chem.* **88** 6446
Brochard F and de Gennes P G 1983 *J. Physique Lett.* **44** L785
- [8] Liu A J, Durian D J, Herbolzheimer E and Safran S A 1990 *Phys. Rev. Lett.* **65** 1897
Liu A J and Grest G S 1991 *Phys. Rev. A* **44** 7894
Monette L, Liu A J and Grest G S 1992 *Phys. Rev. A* **46** 7644
- [9] Wiltzius P, Bates F S, Dierker S B and Wignall G D 1987 *Phys. Rev. A* **36** 2991
- [10] Lee J C 1992 *Phys. Rev. B* **46** 8648; 1993 *Phys. Rev. Lett.* **70** 3599
- [11] Chakrabarti A 1992 *Phys. Rev. Lett.* **69** 1548
Bhattacharya A, Rao M and Chakrabarti A 1994 *Phys. Rev. E* **49** 524
- [12] Tanaka H 1993 *Phys. Rev. Lett.* **70** 53; 1994 *Phys. Rev. Lett.* **72** 3690; 1993 *Phys. Rev. Lett.* **70** 2770; 1995 *Phys. Rev. E* **51** 1313
- [13] Siggia E D 1979 *Phys. Rev. A* **20** 595
- [14] Leptoukh G, Strickland B and Roland C 1995 *Phys. Rev. Lett.* **74** 3636
- [15] Valesco E and Toxvaerd S 1993 *Phys. Rev. Lett.* **71** 388
Ossadnok P, Gyure M F, Stanley H E and Glotzer S 1994 *Phys. Rev. Lett.* **72** 2498
Ma W J, Maritan A, Banavar J and Koplik J 1992 *Phys. Rev. A* **45** 5347
- [16] Grunau D W, Lookman T, Chen S Y and Lapedes A S 1993 *Phys. Rev. Lett.* **71** 4198
- [17] Alexander F J, Chen S and Grunau D W 1993 *Phys. Rev. B* **48** 634
- [18] Previous MD simulations have focused on the formation of composition waves at the surfaces of pores:
Ma J, Keblinski P, Maritan A, Koplik J and Banavar J 1993 *Phys. Rev. E* **48** 2362
Zhang Z and Chakrabarti A 1994 *Phys. Rev. E* **50** 4290
- [19] See, for example, Hockney P W and Eastwood J W 1981 *Computer Simulations Using Particles* (New York: McGraw-Hill)
- [20] San Miguel M, Grant M and Gunton J D 1985 *Phys. Rev. A* **31** 1001