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LETTER TO THE EDITOR

Simulation of demixing transition for binary fluid within a gel

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Abstract. Monte Carlo simulations are used to study phase separation of binary fluid mixtures in the porous space within a solid gel. The fluid mixture is stimulated by a 3D Ising model, the gel by random percolation. Phase transition and phase separation are then studied for fixed spins and no spin on the percolating clusters and the surface fluid on the perimeter of the clusters with a bulk field on remaining spins. We find a non-symmetric miscibility gap and very slow motion towards equilibrium.

The behaviour of binary fluids in porous media was studied experimentally in many papers several years ago; the present letter tries to complement these experiments by computer simulations. It is well known that the phase separation of the binary fluids in the bulk can be simulated by the magnetic Ising model, where up spins correspond to constituents (i.e. molecules) of one fluid and down spins to the molecules of the other type. In this case, the miscibility gap is completely symmetric since spin up and spin down are equivalent for zero external field.

De Gennes [1] has suggested that binary fluids within a porous medium could be modelled by Ising magnets in a random field. The solid walls of the porous medium may attract one type of molecules; this wetting process corresponds to a preference for one spin orientation at the walls and could be modelled by a magnetic surface field there. Because of the random geometry of the porous medium, this magnetic field could then be taken as random.

Experiments have been undertaken in both vycor glass [2] and pores in gels [3]. Computer simulations for well-defined channel geometries have been carried out already for both the Ising model of binary fluids [4] and the more complicated Widom model for microemulsions [5]. These channels with flat walls might be identified with vycor glass. Therefore we concentrate here on the case where a binary fluid sits in the pores within a gel.

The critical behaviour of gelation of macromolecules [6] seems to be described by the random percolation theory [7], where every site of a large lattice is occupied randomly (by gelling macromolecule) with probability p and left empty (non-gelling fluid) with probability $1-p$. Neighbouring occupied sites form clusters which are identified with the branched macromolecules of a gel. For p above the percolation

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threshold ($p_c = 0.312$ on the simple cubic lattice) an infinite macromolecule is formed giving the gel some shear stability; for p lower than this threshold only a sol with finite clusters exists. The non-gelling binary fluid is modelled by the Ising spins by putting an Ising spin at each empty site. Above the threshold, finite clusters exist within the holes of the infinite network. We study two models: (i) Ising spins are fixed upon the gel sites, and a bulk field B is considered on the fluid sites, (ii) gel sites contain no spin, but a surface field H is considered on the perimeter sites of the gel clusters in addition to the bulk field B.

In our model (i) we took the macromolecules (gelling matter) as sites with fixed spins and in model (ii) as sites with no spins, whereas in the fluid space between the macromolecular sites the spins could be up and down, corresponding e.g. to isobutyric acid and water, respectively. In model (ii), the macromolecules exert a certain surface field H on those fluid sites which are nearest neighbours to macromolecular sites (i.e. on the perimeter of the gel clusters). (This model without fields would correspond to the standard dilute Ising model and is not studied here.)

We used Glauber kinetics for the nearest-neighbour Ising model on the simple cubic lattice. Our $L * L * L$ lattices usually had $L = 130$ and 150 for most production runs; however we have occasionally used lattices as large as 384^3, and 464^3. We used 20 to 5000 (in one case even 20 000) Monte Carlo steps per spin starting usually with all spins up or down. We used IBM RS/6000 workstations (models 320H, and 550), a Honeywell mainframe with vector facility, and an Intel iPSC/860 hypercube with 32 processors.

With model (i) and the more complicated model (ii) with fixed surface field H, one may simulate two different experimental situations: the infinite macromolecule may be extracted after the gelation experiment, and is then put into the binary fluid; or the infinite network coexists with the many finite clusters, and the binary fluid flows through the space occupied by neither the infinite nor the finite cluster. For both models (i) and (ii) we use two methods to generate clusters: (1) a random distribution of the gel sites at a fixed concentration p leads to clusters of various sizes along with one infinite cluster at $p > p_c$. (2) With the Leath algorithm in the vectorizable form of Evertz [8] on the other hand, we create one large percolating cluster; for p above the threshold, if we found no cluster spanning the lattice in our first attempt, we tried again and again until we got such a cluster. In both cases, the clusters were assumed fixed in space, without swelling, and represent the gelling macromolecule.

For the simple model (i) with all clusters and fixed up spins on a random fraction p of all sites we observed a spontaneous magnetization $M = \Sigma_i S_i / N$ for all temperatures simulated; here i runs over all N fluid sites and the temperature (T) was measured in terms of the bulk critical temperature T_c and varied between 0.2 and 10. No singularities were apparent at $p = 0.312$ or its complementary value $p = 0.688$. The reason for this behaviour is obvious: As long as p is neither zero nor unity, the up–down symmetry of the Ising model is broken due to the presence of sites with fixed up spins.

Figure 1 shows schematically this lack of up–down symmetry. In the usual Ising model as well as the random field model with phase separation, the critical point appears at zero magnetization (concentration 1/2) and zero (average) field. In a real fluid, and in our Ising model with fixed up spins on the gel, the system is no longer symmetric; the critical point may correspond to a positive magnetization (concentration below 1/2). Thus to search for criticality it is no longer sufficient to cool the system at zero field, and numerical studies thus are quite difficult due to free parameters. Instead we vary the magnetic field at a fixed temperature (horizontal lines in figure 1)

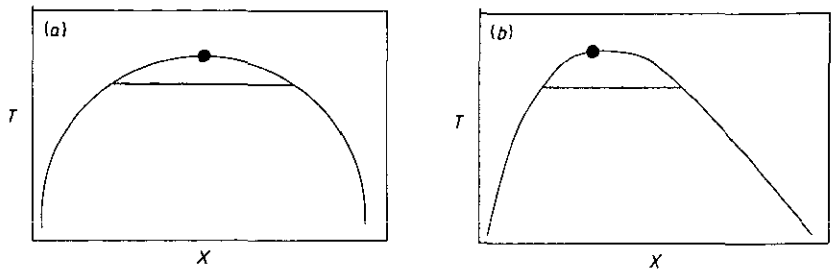

Figure 1. Sketch of the temperature (T) versus the composition ($X=(1-M)/2$) of a three-dimensional fluid. Part (a) represents a symmetric Ising model (also in a random field) and part (b) real fluids and our models.

and check for hysteresis: does starting with all fluid spins up result in the same long-time magnetization as starting with all fluid spins down? Experimentally this variation of a field corresponds to a variation of the composition of the fluid.

For the simple model (i) with only the infinite network (fixed up spins on a large Leath cluster) the results are more interesting than with all gel clusters: For p below the threshold the largest cluster is finite and in the thermodynamic limit its influence on the average system properties is negligible. Thus the spontaneous magnetization is the same as in the bulk Ising model: zero above the Curie temperature T_c, and non-zero below it. Even right at the percolation threshold this statement still holds since the largest cluster is fractal even if it spans the lattice. Thus in the thermodynamic limit the average density of sites with fixed up spins goes to zero, roughly as $1/\sqrt{L}$. For p above the threshold of 0.312, the infinite cluster with its fixed up spins fills a finite fraction of the whole lattice and thus creates a spontaneous magnetization at all finite temperatures, even above the Curie temperatures. Our data confirm this and show that for p appreciably above 0.312 the difference between the two methods of taking into account or ignoring the finite clusters becomes very small. Extensive simulations at $p=0.6884$ showed no significant difference in our results for the two methods. Inspection of configurations near $p=0.32$ shows formation of large domains, with the up domains usually centred about the macromolecule with its fixed up spins.

Clearly, this behaviour is different from that of a random field Ising model since the fixed up spins favour a positive magnetization, even at high temperatures. Therefore we do not find here a transition as a function of temperature (for the case of now finite clusters at concentration p above the threshold 0.312). In a random field Ising model, on the other hand, the field is equally often positive or negative, and the up-down symmetry is conserved.

Thus we now include in the simple model (i) with fixed up spins on the macromolecule (we ignore the finite clusters now) a magnetic field B acting on the field sites. This field corresponds to a chemical potential difference between the two components of the binary fluid and allows us to search for phase transitions away from the traditional case of zero magnetization. We measure this homogeneous field B in units of Ising interaction constant J divided by the magnetic moment of the spins. Thus the probabilities for flipping up spins contain an additional factor $\exp(-2BJ/kT)=\exp(-2B*9.221\,656/T)$.

Now the phase separation of the usual Ising model, which was lost due to the fixed up spins on the gel, is recovered, but in an asymmetric form: it no longer occurs at $B=0$ and between phases having the same absolute value of the magnetization M.

Instead, when two phases coexist with different M, the sum of their two M values is positive. Thus finding the transition is numerically quite difficult.

We restrict ourselves to the more interesting case of only the infinite gel. For large p, nearly all sites are either part of the gel or its neighbours, and no phase transition was found as a function of field B for the temperatures studied here. For p at and below the threshold 0.312, we recover (see above) the usual bulk behaviour as there is no effective field due to fixed spins on the gel clusters. Thus we selected $p = 0.32$. Already at $p = 0.33$ and $T = 0.8$ the area of the hysteresis loop for 300 iterations was about 4 times smaller than at $p = 0.32$. In other words, the presence of the large gel cluster reduces the critical demixing temperature from 1.0 to 0.8 if p is near 1/3.

Figure 2 shows our results at a temperature $T = 0.8$ (in units of the bulk Curie temperature) at $p = 0.32$. Varying the field B from zero to more negative values, the magnetization M first remained positive and was only slightly diminished. At about $B = -0.22$, the magnetization as a function of time first settled on a metastable level -0.38, and then decayed. This behaviour is typical for nucleation events at first-order phase transitions. A different behaviour was found when we started with all fluid spins down for the same field and temperature. We found no metastable plateau for short times and instead M grew slowly from $M = -1$ towards an equilibrium value. (Our interpretation as nucleation in a phase with most of the spins up is consistent with the observation that the nucleation field changes to about $B = -0.26$ when we decrease the system size from $L = 130$ to $L = 50$: the larger the system is and the longer we observe it, the more likely is nucleation to happen.)

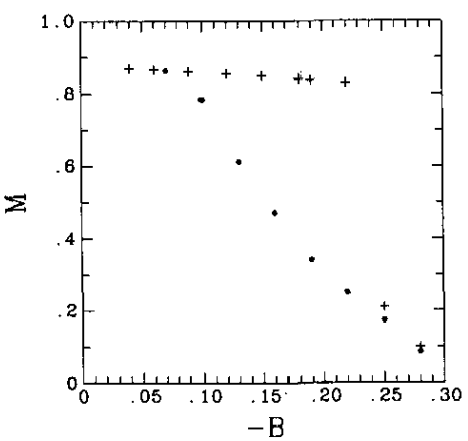

Figure 2. Magnetization versus the bulk field B at 80 per cent of the pure Ising critical temperature and $p = 0.32$. We started with all spins up (crosses) or with all spins down (dots) to see the hysteresis loop.

This qualitative difference between the two initial configurations may be due to the fixed up spins on the gel. When we start with all spins up, we need to nucleate a supercritical droplet of down spins [9] before we can leave the metastable starting state. This nucleation event can be rare and thus lead to long lifetimes for metastable states. In contrast, when the fluid spins are all down initially, the supercritical droplet would be oriented up. There are, however, numerous up spins in the system due to the gel which has all spins fixed up. Thus the gel serves as a nucleation centre, like small particles creating rain drops in the atmosphere. In this interpretation we have

homogeneous nucleation if the fluid spins are initially parallel to the gel spins, and heterogeneous nucleation if they are antiparallel. However, even when we start with all fluid spins down, the 'equilibrium' value for M near $B=-0.2$ at $T=0.8$ does not agree with the one obtained by starting with all spins up. Perhaps, if we had waited here much longer, we would have observed a homogeneous nucleation event even when starting with all fluid spins down, due to down regions far from any gel sites. In any case, very slow motion into equilibrium was found, related perhaps to the glassy state expected by de Gennes [1].

Due to the concentration $p=0.32$ being close to the percolation threshold 0.312 the fluctuations in the number of gel sites are strong, and only very large systems give reliable results. The simulation is much easier if we take into account not only the infinite network but all clusters. Then only at much lower p values does phase separation occur, i.e. in our simulations with $L=20$ and 200 iterations. For $T=0.8$ we found phase separation for p below about 0.1, and for $T=0.9$ that threshold concentration diminished to about 0.06. (Trivially, it must approach zero for T going to the Curie temperature.) While this decrease of the critical demixing temperature with increasing concentration p may fit experimental results, we do not regard it as realistic since for these low p values we have only small isolated clusters, which in reality would not stick to their sites. Thus no further computational effort was put into the case of taking into account all clusters.

All this work was done for the simple model (i) where the gel spins were fixed up, and the same field was applied to all fluid sites. In the more complicated model (ii), we set the gel spins to zero, applied a positive field H to all fluid sites adjacent to the gel, i.e. on the perimeter sites of the gel, and a negative bulk field B to all other fluid sites. B was varied and for some values of B the average field over all fluid sites was zero; in this way we hoped to be closest to the random field analogy with the complete up–down symmetry.

However, even now the symmetry between positive and negative magnetizations was not restored. At $p=1/3$, where roughly 20 per cent of the sites are gel, 40 per cent are fluid adjacent to the gel, and the remaining 40 per cent are fluid sites further away from the gel (thus B close to $-H$), we still found a significant non-zero magnetization, which even switched sign as B was varied. Apparently the requirement that the average field over all fluid sites must vanish did not restore up–down symmetry completely, since the H field near the gel surface (five or fewer fluid neighbours) is influencing the spins differently from the B field in the bulk (six fluid neighbours).

Taking $T=0.8$ and $p=0.32$ as for the simple model and varying the bulk field B independently of the surface field H, we found a phase transition somewhat similar to the simpler model: Starting with all spins up the magnetization jumped from about 0.74 to about -0.4 near $B=-0.25$, for fixed $T=0.8$, $p=0.32$, $H=0.5$, $L=130$, and 5000 iterations. Figure 3 shows the variation of the magnetization with the bulk field at various temperatures with fixed perimeter (surface) field. At a perimeter field $H=0.50$ and $p=0.32$, the hysteresis is well defined at the temperature $T=0.80$. The area under the hysteresis loop decreases upon increasing the temperature; at the high temperature $T=2.0$, the hysteresis has vanished altogether (see figure 3). At a lower surface field, $H=0.10$, the hysteresis becomes even more pronounced at $T=0.80$, and seems to decrease on increasing the temperature (see figure 4). This observation is consistent with a similar qualitative behaviour at higher surface field (i.e. $H=1.0$). One may interpret the variation in the bulk field as the variation in the composition of the fluid, and the change in the surface field to the change in the type of the molecules. Thus

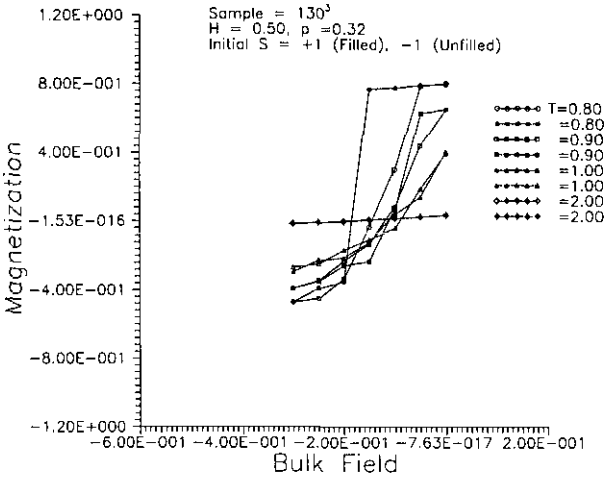

Figure 3. Magnetization versus the bulk field B at a fixed perimeter field $H = 0.50$.

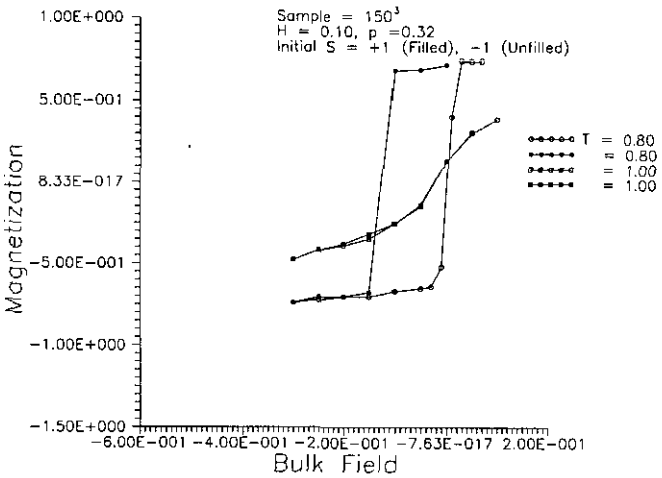

Figure 4. Magnetization versus the bulk field B at a fixed perimeter field $H = 0.10$.

our model suggests that one may observe a phase separation in a fixed gel matrix at certain temperatures by changing the bulk field (i.e. the composition of the fluid).

We have extended this study of model (ii) to a quenched (fixed) medium of various finite clusters, i.e. this is the case in which the gelling sites are randomly distributed with concentration $p(<p_c)$ and carry spin zero. As before the surface field H is applied on each perimeter sites of each clusters, and a bulk field B to the remaining spins (i.e. the bulk fluid). At the temperature $T = 0.80$, and $p = 0.08$, we observe a hysteresis in the magnetization at the surface field $H = 0.50$ (see table 1). For example, at $B = -0.246$ with initially all spins down, the magnetization was still negative after 5000 Monte Carlo steps per spin; after 20 000 such time steps it became positive and close to 0.8. In order to be closer to the random field Ising model one may assign up and down spins on each sites of the clusters randomly, i.e. a cluster has either all spins up or down; but we are little experimental significance in these models. In both cases, one may expect to have up and down spin symmetry.

Table 1. $L=130$, $T=0.80$, $p=0.08$, $H=0.50$, MCS = 5000, Nruns = 2. No stable magnetization was found at the blank spaces.

Initial spins up		Initial spins down	
B	*M*	*B*	*M*
−0.400	−0.722	−0.400	−0.722
−0.360	−0.710	−0.300	−0.684
−0.330	−0.698	−0.250	−0.595
−0.320		−0.246	
−0.310	−0.750	−0.243	
−0.250	+0.775	−0.240	+0.775
−0.150	+0.801	−0.220	+0.783
		−0.150	+0.801

In summary, we found phase separation for a binary fluid model within a gel, but no exact correspondence to the Ising model in a random field, because of the lack of symmetry. However, very slow kinetic behaviour was found.

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