

Structure factors of binary fluids in a dilute gel

J. C. Lee*

University of Southern Mississippi, Hattiesburg, Mississippi 39406-5046
(Received 17 January 1995; revised manuscript received 21 June 1995)

The static and dynamic structure factors of binary fluids in a dilute gel are computed using a two-dimensional kinetic Ising model. The wetting effect of the gel strands is modeled with "gel atoms" which are distributed randomly among the spins and impose a field on their neighboring spins, all in the same direction. The result for the static structure factor shows the presence of adsorption clusters which mask the gel atoms. The result for the dynamic structure factor shows an extremely slow relaxation at late times which cannot be fitted in the form of the activated dynamic scaling known for random-field systems.

PACS number(s): 82.70.Gg, 05.50.+q, 64.60.Cn, 64.60.Qb

The behavior of binary fluids in porous media, such as Vycor glasses and gels, has been studied experimentally [1–7] and theoretically [8–14], but the disordering effects of the media on the static and dynamic behavior of the binary fluids are not well understood. That is particularly the case for the equilibrium dynamics which is the main subject of interest in this report. Dierker and Wiltzius [2] used lutidine-water mixtures embedded in Vycor glass of pore size 30 Å for a dynamic light scattering experiment. Here the pore size is much smaller than the correlation length and therefore the system may be regarded as being in a random-field regime. The results for the time autocorrelation function do indeed agree remarkably well with the activated dynamic scaling theory [13] developed for the random-field Ising models with a conserved order parameter. The trouble is that such slow nonexponential relaxations are also observable under conditions where the effects of media should be negligible. In a recent experiment, Aliev, Goldberg, and Wu [5] used samples of carbon disulfate–nitromethane mixtures embedded in a macroporous glass of pore size 1000 Å. Here the correlation length should be much smaller than the pore size, but the dynamics remains slower than in the bulk. Liu *et al.* [9] suggested treating the glass walls differently, shifting the emphasis from the randomness to the wetting and confining effects.

The equilibrium dynamics of binary fluids in gels has been studied recently by Frisken and Cannell [4] using Isobuteric acid–water mixtures and very dilute silica gel networks. Here again, the dynamics begins to slow down in the one-phase region where the liquid mixture should still have ample space reasonably free of the gel strands. Moreover, when the system is brought very close to the two-phase boundary, an even slower relaxation mode develops which cannot be explained as random-field behavior.

To the best of our knowledge, there have been no computational efforts to compute wave-vector-dependent time autocorrelation functions for binary fluids in porous

media. We wish to carry out such a computation here with a simple model designed to mimic binary fluids in a dilute gel network. Binary fluids ($A+B$) are modeled with ferromagnetic Ising spins and the gel strands with frozen centers of impurity, henceforth to be called gel atoms. On an $L \times L$ square lattice of size $L=256$, a total number of $0.03L^2$ gel atoms are distributed randomly and remain frozen; the spins occupy the rest of the sites. In order to mimic the wetting effect of the gel strands, the gel atoms impose a field (chemical potential) on their nearest-neighbor spins so as to favor one component of the spins over the other in their vicinity. The Hamiltonian is given by

$$H = -J \sum_{\langle i,j \rangle} S_i S_j + \sum_i h_i S_i, \quad (1)$$

where $S_i = +1$ (species A), $S_i = -1$ (species B), and $S_i = 0$ (gel atoms), and the symbol $\langle i,j \rangle$ limits the sum to nearest-neighbor pairs of spins only. The field in the second term is given by $h_i = hn_i$, where h is a constant and n_i is the number of nearest-neighbor gel atoms of the i th spin. The time evolution is governed by the Kawasaki spin exchange dynamics which only allows exchanges of nearest-neighbor pairs of opposite spins, thus conserving the order parameter. The exchange occurs in the Monte Carlo simulation with probability $\min\{1, \exp(-\Delta H/k_B T)\}$, where ΔH is the change in energy of the proposed exchange.

The present model allows much larger clusters of aligned fields than the random-field Ising models do. To see this, consider a pair of gel atoms which sit next to each other. This pair of gel atoms alone affects the surrounding cluster of six spins, all of which receive the same field in the same direction. The fields are correlated to a considerable extent and can create far more formidable energy barriers than random fields can. In our two-dimensional model, however, most of the gel atoms are isolated. In order for them to have an appreciable wetting effect on the spins, h has to be large. Thus, we choose $h=2$ (with J and k_B set to unity). The minus spins will be called wetting spins and the plus spins nonwetting spins.

*Electronic address: lee@whale.st.usm.edu

The temperature is set at $T=1.5T_c$, $T=1.2T_c$, $T=1.1T_c$, $T=1.05T_c$, and $T=1.01T_c$, where T_c is the transition temperature of the pure two-dimensional Ising model. At each temperature, equal numbers of plus and minus spins are randomly mixed and then thermalized for a long time until the equal-time structure factor shows no persistent pattern of change which we take as a sign of an equilibrium or quasiequilibrium state. Then we measure the spin fluctuation

$$\rho(q,t) = \sum_i \exp(iqr_i) S_i, \quad (2)$$

and compute the equal-time structure factor defined by

$$S(q) = \langle [\rho(q,t)\rho(-q,t)] \rangle, \quad (3)$$

where the inner vertical signs represent the ensemble averages while the outer angular signs represent the disorder averages over different realizations of the gel-atom distribution. The dynamic structure factor is defined by

$$C(q,t) = \langle [\rho(q,t+t_0)\rho(-q,t_0)] \rangle, \quad (4)$$

but it is more convenient to normalize it and compute the autocorrelation function defined by

$$g(q,t) = \langle [\rho(q,t+t_0)\rho(-q,t_0)/S(q)] \rangle, \quad (5)$$

where the ensemble average now includes the average over the initial time t_0 . For the delay time t , we choose: $t_1=4$, $t_2=2t_1$, $t_3=2t_2$, ..., $t_{10}=2048$, where time is given in units of the number of sweeps through the lattice. The wave vector q will be given from now on in units of $2\pi/L$.

We first measure the structure factor of the gel atoms without any spin. In Fig. 1, the result has been magnified by a factor of 100 so that it can be compared with the spin structure factors in the same figure. For this result,

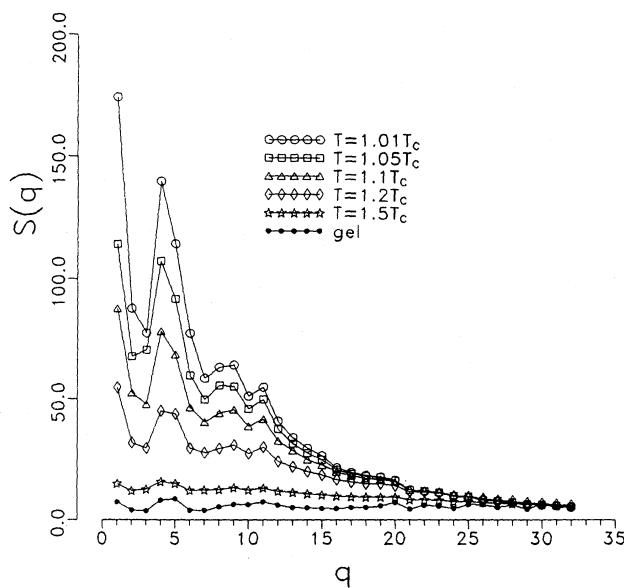


FIG. 1. The gel structure factor (closed circles) and the spin structure factors (open symbols) in arbitrary units.

only two different realizations of gel-atom distribution have been used, which is the reason for the noiselike peaks at $q=4, 5, 11, 20, 28$, and 30 . The peaks represent several length scales which happen to be prominent in those two realizations and as such will be smoothed out when the number of realizations is large enough. But the noiselike pattern is a useful signature of the gel structure which we may look for in other quantities. For this reason, we chose not to increase the number of realizations and instead devoted the computer CPU time saved to compute more accurate time averages.

Notice in the same figure that the spin structure factors increase as T approaches T_c and carry the characteristic noiselike gel signature. The signature can be seen even when T is very close to T_c and the overall pattern of the structure factor bears no resemblance to that of the gel structure factor. This shows that adsorption clusters are formed around the gel atoms and grow as the temperature approaches the two-phase boundary. The same behavior was observed by Frisken, Ferri, and Cannell [3] using a static light scattering experiment.

Figure 2 shows the autocorrelation function as a function of q at $t=t_{10}=2048$. Here we also see, rather surprisingly, the noiselike signature of the gel-atom distribution. The relaxation is impeded in those length scales characteristic of the gel structure, which means that the adsorption clusters are semifrozen. In Fig. 3 the autocorrelation function is plotted as a function of time for several values of q . We attempt to fit the data in the form of

$$g(q,t) = A_D \exp(-t/\tau_D) + A_A \exp\{-[\ln(t)/\ln(\tau_A)]^2\}, \quad (6)$$

where the first term represents the exponential diffusive relaxation and the second term the nonexponential ac-

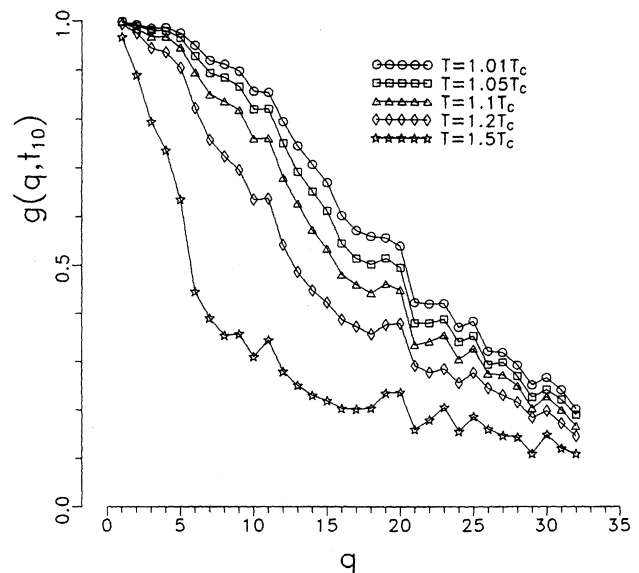


FIG. 2. The autocorrelation function as a function of q at $t=t_{10}$. The wave vector q is given in units of $2\pi/L$, where $L=256$ lattice spacings.

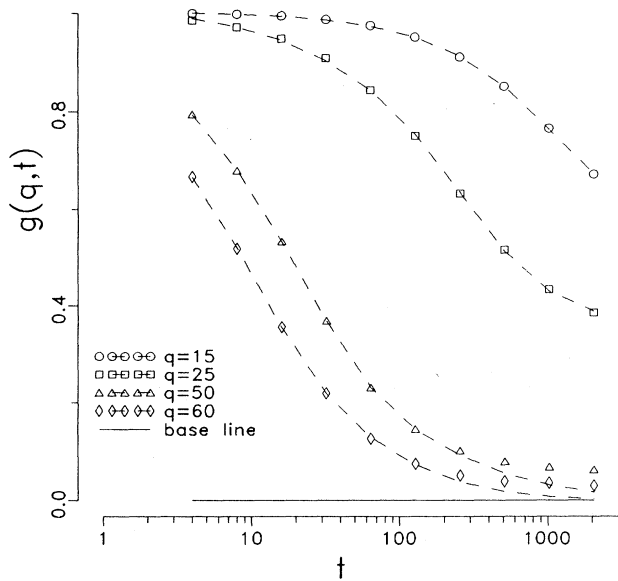


FIG. 3. The autocorrelation function as a function of time at $T = 1.01T_c$. The delay time t is given in units of the number of sweeps through the lattice. The symbols represent the computed data. The dashed lines connect the fitted data points (not shown in the figure). The horizontal base line shows where $g(q, t) = 0$ is.

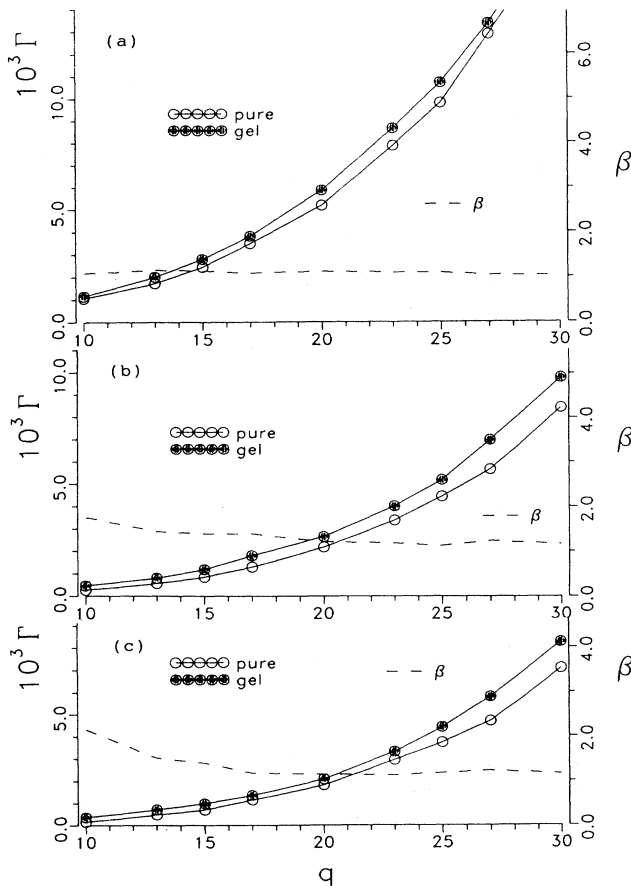


FIG. 4. The relaxation rates due to diffusion and the ratio β at: (a) $T = 1.35T_c$, (b) $T = 1.1T_c$, and (c) $T = 1.05T_c$.

tivated relaxation [13]. For $q = 15$ and 25 , the data can be fitted in this form quite well. For $q = 50$ and 60 , the early-time part of the data may be fitted in the same form, but the late-time part cannot. The slowly decaying tail suggests that the relaxation is slower at late times than assumed by Eq. (6) and may be related to the extremely slow relaxation that Frisken and Cannell [4] observed.

In order to find out how the gel atoms affect the diffusion process of spins, we have repeated the above computation without gel atoms. The results for the decay rate $\Gamma_q = 1/\tau_D$ are shown in Fig. 4. For comparison the figure also shows β , the ratio of the decay rate with gel atoms to that without gel atoms. At $T = 1.35T_c$, the gel atoms do not seem to have a significant effect on the diffusion of the free spins. But examine the behavior of β in the regime of small q . As the temperature approaches T_c , the relaxation is notably faster with the gel atoms than without. At $T = 1.05T_c$, this is mainly due to the critical slowing down of the pure system. But since the trend is observable at temperatures as high as $T = 1.1T_c$, it may be a sign of an anomalous diffusion process caused by the frozen adsorption clusters.

Figure 5 shows one of the two realizations of the gel-atom distribution and a typical spin morphology favored by that realization, at $T = 1.01T_c$. First, examine the gel-poor regions. There are isolated gel atoms, either single or in small clusters. The energy barriers posed by the fields around these gel atoms are basically the same in magnitude as those in random-field systems and are responsible for the activated relaxation. Monte Carlo snapshots show that wetting spins evaporate from, and condense into, these gel clusters. Next, examine the gel-rich regions and look for a much larger "supercluster" which is a large cluster of gel atoms or one consisting of several small nearby clusters of gel atoms. In this case,

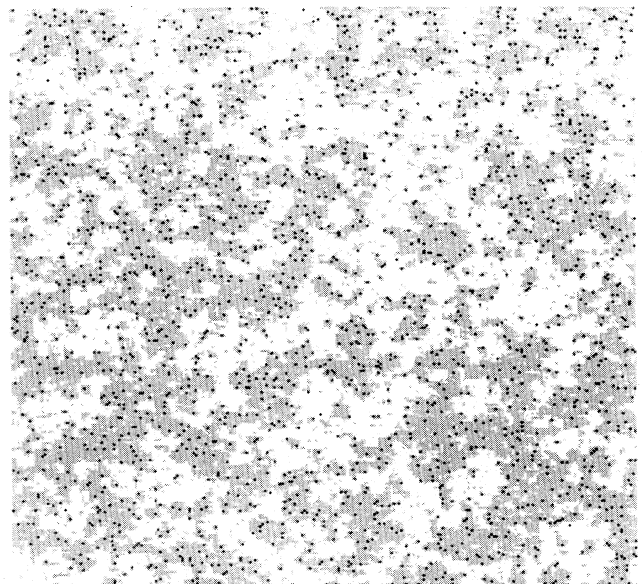


FIG. 5. A typical spin morphology at $T = 1.01T_c$. The large black dots represent the gel atoms, the gray shade the wetting spins, and the blanks the nonwetting spins.

since adsorption clusters grow from different parts of the gel cluster, they tend to trap nonwetting spins between them as the temperature approaches the two-phase boundary. The trapped spins look like long winding channels or closed lakes. Once such a spin configuration has formed, it remains for a long time. In order to break up such a large and structured adsorption cluster, the spins have to overcome a formidable energy barrier since large scale transport of spins through the channels is required. We believe that this is the reason for the long-lasting tail in the autocorrelation function.

In summary, we have computed both static and dynamic structure factors for binary fluids in a dilute gel. The results show that adsorption clusters dominate the static and dynamic behavior, as found earlier by Frisken, Ferri, and Cannell [3,4]. It is difficult to speak of the thickness of the adsorption clusters as they are not firmly and uniformly frozen. If the thickness can be computed as an effective quantity in some sense, a renormalization with the thickness may lead to the ultimate theory. The results for the dynamic structure factor exhibit a long-lasting tail in short length scales. The gel atoms occupy

only 3 % of the lattice sites, but by forming adsorption clusters, they effectively occupy far more than 3 % of the lattice sites, which is the reason for what appears to be a premature onset of the nonexponential relaxation. Moreover, statistical fluctuations leave large gel-rich regions here and there. The aligned fields in these regions result in very large adsorption clusters and ultimately the long-lasting tail. It is utterly unlikely that one would find such large clusters of aligned fields in random-field Ising models of the same system size. But randomness does play an important role; if the same number of gel atoms were distributed uniformly rather than randomly, this slow mode would be absent.

The author wishes to thank W. I. Goldberg, X.-l. Wu, and F. Family for very helpful discussions, and D. Cannell and B. Frisken for kind explanations of their experiments on this topic. The computation was performed on a Cray YMP computer at the Mississippi Center for Supercomputing Research. This research was supported by Donors of the Petroleum Research Funds administered by the American Chemical Society.

-
- [1] J. V. Maher, W. I. Goldberg, and D. W. Pohl, and M. Lanz, *Phys. Rev. Lett.* **53**, 60 (1984); J. S. Huang, S. K. Sinha, W. I. Goldberg, J. V. Maher, and S. K. Sagita, *Physica B* **136**, 291 (1986); M. C. Goh, W. I. Goldberg, and C. M. Knobler, *Phys. Rev. Lett.* **58**, 1088 (1987); K.-Q. Xia and J. V. Maher, *Phys. Rev. A* **36**, 2432 (1987).
- [2] S. B. Dierker and P. Wiltzius, *Phys. Rev. Lett.* **58**, 1865 (1987); see also S. B. Dierker and P. Wiltzius, *ibid.* **66**, 1185 (1991).
- [3] B. J. Frisken, F. Ferri, and D. S. Cannell, *Phys. Rev. Lett.* **66**, 2754 (1991).
- [4] B. J. Frisken and D. S. Cannell, *Phys. Rev. Lett.* **69**, 632 (1992).
- [5] F. Aliev, W. I. Goldberg, and X.-l. Wu, *Phys. Rev. E* **47**, R3834 (1993).
- [6] M. Y. Lin, S. K. Sinha, J. M. Drake, X.-l. Wu, P. Thiyagarajan, and H. B. Stanley, *Phys. Rev. Lett.* **72**, 2207 (1994).
- [7] A. P. Wong and M. H. W. Chan, *Phys. Rev. Lett.* **65**, 2567 (1990); A. P. Wong, S. B. Kim, J. Ma, W. I. Goldberg, and M. H. W. Chan, *ibid.* **70**, 954 (1993).
- [8] P. G. de Gennes, *J. Phys. Chem.* **88**, 6469 (1985).
- [9] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, *Phys. Rev. Lett.* **65**, 1897 (1990); see also, A. J. Liu and G. Grest, *Phys. Rev. A* **44**, R7879 (1992); L. Monette, A. J. Liu, and G. S. Grest, *ibid.* **46**, 7664 (1992).
- [10] D. Stauffer and R. B. Pandey, *J. Phys. A* **25**, L1079 (1992).
- [11] A. Chakrabarti, *Phys. Rev. Lett.* **46**, 8648 (1993).
- [12] J. C. Lee, *Phys. Rev. Lett.* **70**, 3599 (1993); J. C. Lee, *Phys. Rev. B* **46**, R8648 (1993); W.-h. Li and J. C. Lee, *Physica A* **210** (1994); J. C. Lee, *ibid.* **210**, 127 (1994).
- [13] D. A. Huse, *Phys. Rev. B* **36**, 5383 (1987); see also, A. T. Ogielski and D. Huse, *Phys. Rev. Lett.* **56**, 1298 (1986).
- [14] A. Falicov and A. N. Berker, *Phys. Rev. Lett.* **74**, 426 (1995).

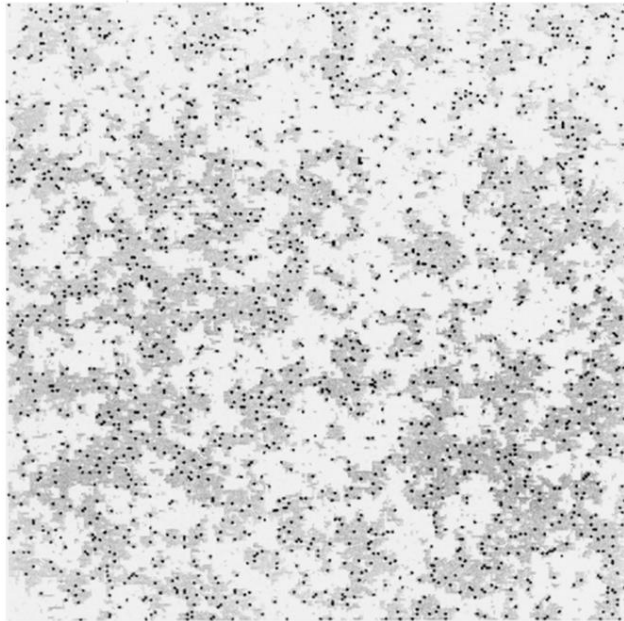


FIG. 5. A typical spin morphology at $T = 1.01T_c$. The large black dots represent the gel atoms, the gray shade the wetting spins, and the blanks the nonwetting spins.