

Dynamic correlations in porous media

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When binary liquid mixtures are infused into various random porous media, past experiments have shown that different media affect the dynamic correlations of concentration fluctuations in different ways. Vycor glasses of relatively small pore size and dilute gels allow the exponential bulk mode to remain in the final ensemble average, but Vycor glasses of very large pore size do not. We take this to mean that the relaxation time of the bulk mode is spatially homogeneous in the two former media but heterogeneous in the latter media. Thus we search for a heterogeneous dynamic mode with an Ising model. We find one, but it is not the bulk diffusion mode. [S1063-651X(97)10002-2]

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The dynamic correlations are reasonably well understood for pure liquids [1], but not when the liquid molecules are subject to a random quenched disorder. The latter situation has been studied with binary liquid mixtures infused into various random porous media such as gels and Vycor glasses. Dierker and Wiltzius (DW) [2] used a critically mixed sample of lutidine and water in a Vycor glass of relatively small pores. The results for the time autocorrelation function of the concentration fluctuations of wave vector q may be fitted in the form

$$g(q, t) = A_D \exp(-t/\tau_D) + A_A \exp(-x^p), \quad (1)$$

where $x = \ln(t)/\ln(\tau_A)$ and $p = 3$. The presence of the slow activated term is in accord with the dynamic scaling theory of Huse for random field Ising models with a conserved order parameter [3].

Friskén and Cannell (FC) [4] used samples of isobutyric acid and water in a dilute but inert silica gel. In the one-phase region far away from the two-phase boundary, the relaxation pattern is the same as that found by DW. Very near the two-phase boundary, however, another very slow mode of relaxation develops which FC find transient and history dependent.

Aliev, Goldberg, and Wu (AGW) [5] used samples of carbon disulfate and nitromethane in a Vycor glass of much larger pores than that used by DW. Their results for the autocorrelation function are in the form

$$g(q, t) = 1/(1 + x^3), \quad (2)$$

where $x = \log_{10}(t)/\log_{10}(\tau)$. The relaxation rate $1/\tau$ does not follow the usual q^2 dependence, and τ is shorter than its bulk counterpart τ_D ; this difference becomes more and more pronounced as the scattering angle is reduced.

Equations (1) and (2) are the ensemble-averaged results taken over many different scattering volumes [6]. It is notable that the bulk mode is absent in Eq. (2). This is particularly puzzling because the glass walls of AGW provide the mixture with much larger free spaces than those of DW. To address this issue, we assume that the bulk mode actually exists for each scattering volume but is hidden in the ensemble average because its relaxation time is different for

each scattering volume [7]. Thus we ask: can the dynamics be spatially heterogeneous in random porous media?

With this in mind, compare gels and glasses. In gels, the structure factor or the density correlation function (the density of gel strands) increases as the wave vector q decreases and becomes saturated when q approaches zero [8]. In glasses, it reaches a peak at a finite value of q and decreases as q decreases toward zero [9]. These results indicate that the gel structure involves more widely distributed length scales than the glass structure, and therefore, if either of the two types of random media are to provide an environment favorable for a heterogeneous dynamics, gels are the better candidate. For this reason, we set out to search for a heterogeneous dynamics with a mixture-gel model.

To construct a two-dimensional model of binary liquids in a dilute gel, we place impurity atoms on a randomly chosen 3% of 256×256 square lattice sites and Ising spins on the rest. The impurity atoms remain frozen and impose a field on the neighboring spins. The Hamiltonian is given by

$$H = -J \sum_{\langle i, j \rangle} S_i S_j + \sum_i h_i S_i, \quad (3)$$

where $S_i = +1$ (α atoms), $S_i = -1$ (β atoms), and $S_i = 0$ (impurity atoms). The field in the second term is given by $h_i = h n_i$, where $h = 2.0$ (with J and k_B set to unity), and n_i is the number of impurity atoms neighboring the i th spin. Our Monte Carlo simulation is based on the Kawasaki spin exchange dynamics. The α - β composition ratio is 50:50.

Several comments concerning the model are in order. By choosing a two-dimensional model, we limit our interest to the general trend of the dynamic correlations and side-step all questions involving the exact time scales and related quantities of the real three-dimensional systems. With the impurity atoms occupying only 3% of the lattice sites, there are impurity-atom-rich regions as well as impurity-atom-poor regions. The purpose of the field term is to represent the preferential attraction of the media for one component of the mixture over the other, but this adsorption effect cannot be fully represented with the nearest-neighbor fields. Moreover, most of the impurity atoms are isolated which further under-represents the adsorption effect. The large value $h = 2$ compensates for these under-representations and help create ad-

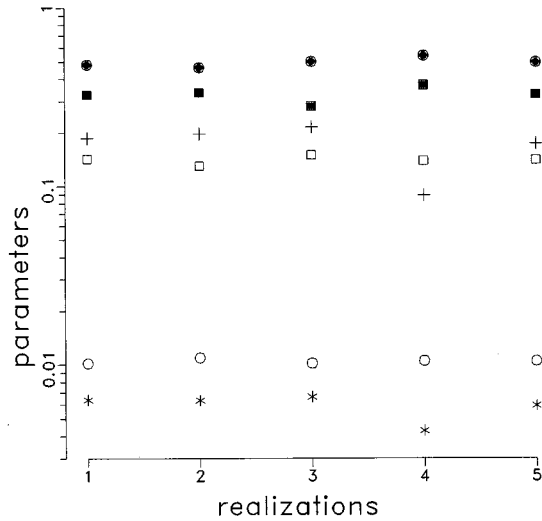


FIG. 1. The results for the fitting parameters for the 1st, 2nd, 3rd, and 4th realization at $T=1.2T_C$; the fifth refers to the results for the ensemble-averaged $g(q,t)$. The open circles represent $1/\tau_D$, the open squares $1/\ln(\tau_A)$, the filled circles A_D , and the filled squares A_A , the crosses C , and the asterisks $S_{\text{imp}}(q)$ (in arbitrary units). τ_A and τ_D are in units of MC steps.

sorption clusters at temperatures as high as $1.5T_C$. The high temperatures minimize the finite size effect.

We studied previously the same type of Ising models [10], but the computations were not adequate to address the present issue. Different scattering volumes may be represented with different realizations of the disorder. An adequate ensemble average requires a large number of realizations, but it was taken over only two realizations. We increase the number to four and attempt to find out whether or not the dynamics differs in each realization. The pertinent auto correlation function is

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

where $\rho(q,t) = \sum \exp(iq \cdot r_i) S_i$ and the outer average signs represent the average over different realizations. The delay times t are 1,2,4, ..., 1024 Monte Carlo (MC) steps. The time average is taken over 1500 samples.

Simply to find out how the dynamics differs in each realization, we first fit the results for each realization separately. Our data cannot be fitted with Eq. (2). The best choice for the fitting function is the sum of Eq. (1) with $p=2$ and a constant term C . This suggests that there exists an additional mode of relaxation which is so slow that it can be represented by its amplitude C without the detailed time dependence. Our data can support (reject) this idea if it shows small (large) $\delta = A_D + A_A + C - 1$. The results of fitting are as follows. (i) $q < 10$ (in units of $2\pi/256$ lattice spacings). If we set C to zero, the fitting appears good, but the minima are flat in all directions in the parameter space. Thus we have no reliable result for any of the parameters in this important region. (ii) $10 < q < 20$. Here the fitting works but the behavior of C as a function of q is erratic. The only reliable parameter is τ_D . This is because the exponential term now dominates and therefore even a small variation of τ_D has a dominating effect which the rest of the parameters cannot

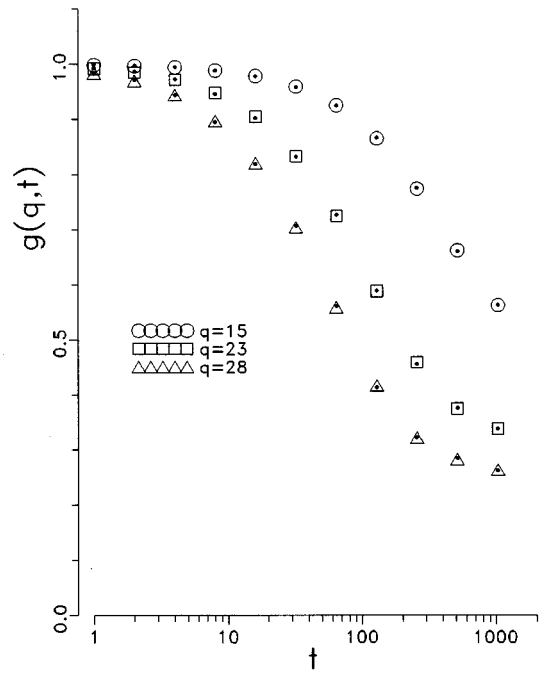


FIG. 2. The ensemble-averaged data points for $g(q,t)$ at $T=1.1T_C$ (the large open symbols) and the corresponding data points (small filled circles) taken from the best fitting function. The delay time t is in units of MC steps.

easily compensate for. (iii) For $20 < q < 30$, the fitting is reliable for all parameters. χ^2 remains reasonably small throughout, but δ gradually increases and reaches 2% approximately at $q=30$. (iv) For $q > 30$, χ^2 remains small and the minima remain steep, but δ is larger than 2%. In this regime τ_D is so short that our longest delay time is long enough to probe the asymptotic regime where the additional mode dominates. The unacceptably large value of δ indicates that the slow mode can no longer be represented with its amplitude alone.

Figure 1 shows the fitted parameters for $q=25$ and $T=1.2T_C$, where T_C is the transition temperature of the pure system. The results of fitting the final ensemble-average $g(q,t)$ are shown in the fifth column. It is notable that τ_D is about the same for all realizations. Therefore the ensemble-averaged $g(q,t)$ can be fitted with the *same* fitting function as that used for each realization, and we find no persistent signs which may be interpreted as calling for a different fitting function. Figure 2 compares the data with the fitting function.

What does each term of the fitting function represent? The preferred component β is rather rare in the free fluid away from the adsorption clusters. The exponential term represents the fast motions of the less prevalent β atoms in the free fluid. The two slow terms represent the slowly relaxing adsorption clusters which require an activation for relaxation. The random thermal energy is sufficient for relatively small adsorption clusters, which results in the logarithmic term. Large adsorption clusters require a much larger activation energy which the random thermal energy cannot often provide. The consequent slow mode of relaxation is represented by the third term C .

C is quite different in each realization. For $q=25$ (in the

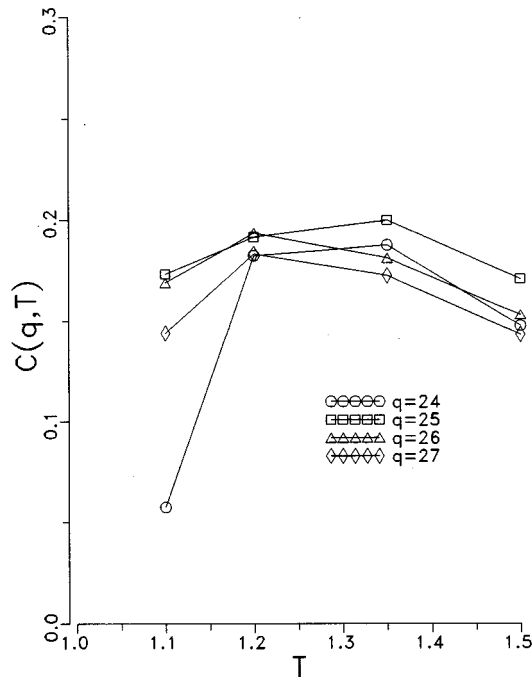


FIG. 3. The temperature dependence of C .

length scale $\lambda=256/25$), it is smallest in the fourth realization, meaning that the slowly relaxing adsorption clusters are distributed in this realization with the weakest Fourier component among the four. Since the adsorption clusters coat the impurity atoms, C should then change with the structure factor of the impurity atoms, $S_{\text{imp}}(q)$, and Fig. 2 shows that it does. Thus the heterogeneous distribution of the impurity atoms introduces a heterogeneous mode of relaxation but the bulk diffusion mode remains homogeneous.

Figure 3 shows how C changes with the temperature. When T is reduced from $1.5T_C$ to $1.35T_C$, C increases slightly, suggesting that the adsorption clusters become more frozen and fluctuate less. When T is reduced from $1.35T_C$ to $1.2T_C$, C does not change significantly. But when T is reduced further from $1.2T_C$ to $1.1T_C$, C now decreases. There is a competition between the adsorption clusters, which want to remain frozen maintaining the pattern dictated by the distribution of the impurity atoms, and the free atoms in the free fluid, which want to execute large-scale critical fluctuations of all patterns. The decrease in C suggests that the latter wins the competition and a global phase separation is forthcoming.

We now plot the results for τ_D in Figs. 4 and 5 in the scaling form [11], $\tau_D(q, T)\xi^{-z} = f(q\xi)$, $\tau_D(q, T)q^z = h(q\xi)$, where ξ is the correlation length and $z=4-\eta=3.75$ is the dynamic exponent of the pure system. The figures also show the results for the pure system which satisfies the scaling almost perfectly. At the two higher temperatures $T=1.5T_C$ and $1.35T_C$, the data approximately support the scaling. At the two lower temperatures and when q is small, however, the data deviate from the scaling. We observed the same anomalous behavior previously [10] and attributed it to the adsorption clusters. The small number of mobile β atoms can only diffuse in the confined space between the adsorption clusters. The confined space takes many different shapes including those which look similar to a long one-dimensional

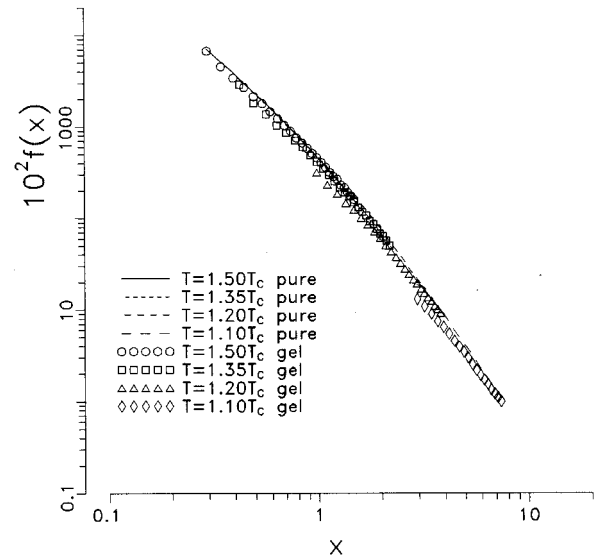


FIG. 4. Scaling plot for τ_D with the scaling function $f(x)$.

channel. The reduced effective dimensionality causes the diffusion to deviate from the usual q^2 behavior. In this way, the impurity atoms shorten τ_D .

The impurity atoms can be distributed so as to mimic the glass walls of Vycor, but the results of the present model leave no doubt that the diffusion cannot be heterogeneous in any Ising model of the form given by Eq. (3). The lattice gas Ising model is based on the assumption that the media damp out all hydrodynamic effects. Some hydrodynamic effects may remain in the large glass pores of AGW, and hydrodynamic effects are known to cause some unique dynamic correlations. In two-dimensional pure liquids, Alder and Wainwright [12] discovered a cagelike flow pattern (or backscattering) which results in a diverging diffusion coefficient. This divergence occurs only in two dimensions and therefore may be regarded as a confining effect of the two dimensions. In a similar fashion, the binary mixture confined in the large glass pores may exhibit a spectrum of mutual

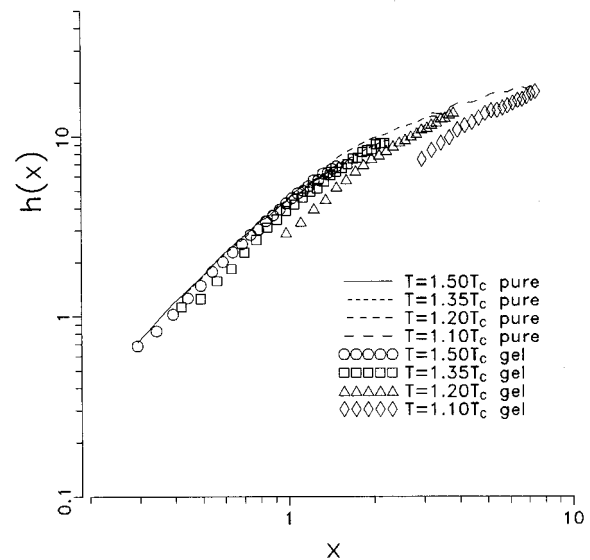


FIG. 5. Scaling plot for τ_D with the scaling function $h(x)$.

flow patterns due to the complex way the pores wind, split, and merge, etc., and due to the preferential attraction of the glass walls for one component over the other. If so, the flow patterns can result in a spectrum of anomalous mutual diffusion coefficients. Perhaps that is what AGW observed.

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