

Diffusion of colloidal fluids in random porous media

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The diffusive relaxation of a colloidal fluid adsorbed in a porous medium depends on many factors, including the concentration and composition of the adsorbed colloidal fluid, the average structure of the porous matrix, and the nature of the colloid-colloid and colloid-substrate interactions. A simple manner to describe these effects is to model the porous medium as a set of spherical particles fixed in space at random positions with prescribed statistical structural properties. Within this model one may describe the relaxation of concentration fluctuations of the adsorbed fluid by simply setting to zero the short-time mobility of one species (the porous matrix) in a theory of the dynamics of equilibrium colloidal mixtures, or by extending such dynamic theory to explicitly consider the porous matrix as a random external field, as recently done in the framework of mode coupling theory [V. Krakoviack, *Phys. Rev. Lett.* **94**, 065703 (2005)]. Here we consider the first approach and employ the self-consistent generalized Langevin equation (SCGLE) theory of the dynamics of equilibrium colloidal mixtures, to describe the dynamics of the mobile component. We focus on the short- and intermediate-time regimes, which we compare with Brownian dynamics simulations involving a binary mixture with screened Coulomb interactions for two models of the average static structure of the matrix: a porous matrix constructed by quenching configurations of an equilibrium mixture in which both species were first equilibrated together, and a preexisting matrix with prescribed average structure, in which we later add the mobile species. We conclude that in both cases, if the correct static structure factors are provided as input, the SCGLE theory correctly predicts the main features of the dynamics of the permeating fluid.

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Many relevant systems and processes in industry and nature involve the diffusion of colloidal dispersions through porous media [1]. The most relevant issues involve either the equilibrium and phase behavior [2] or the transport and dynamic properties [3] of the permeating colloidal liquid. Thus, one would like to understand, from a fundamental perspective, how these properties depend on factors such as the porosity and morphology of the matrix, the nature of the interaction forces (among the particles and with the porous matrix), or the concentration of the colloidal dispersion. Some of these issues require the development or extension of the fundamental description of the dynamic behavior of bulk colloidal systems [4,5] to the case in which these systems permeate a porous matrix.

The fundamental study of the phenomena above rely on simplified models. Thus, a porous medium is sometimes modeled as a simple geometry (planar slit, cylindrical pore, etc.) to describe local phenomena, whereas random arrays of locally regular pores incorporate the intrinsic randomness of most natural or synthetic porous materials [1]. One may adopt, instead, a simplified model of a random porous medium, namely, a matrix of spherical particles with random but fixed positions. This matrix is permeated by a colloidal liquid, whose dynamics we wish to understand. Such model systems have been employed to describe mostly equilibrium structural properties [6], although simple model experimental realizations of this system have been prepared [7], in which one could also measure the dynamic properties of the mobile species. The interpretation of such measurements requires

sound theoretical schemes to describe the dynamics of the permeating dispersion. One possible approach uses available theories of the dynamic properties of bulk colloidal mixtures [8–10] in which the mobility of one of the species is artificially set equal to zero. Another possibility is to first reformulate these theories to explicitly consider the porous matrix as a random external field [11]. In this Rapid Communication we demonstrate that the first of these approaches suffices to correctly predict the main features of the dynamics of the permeating fluid, provided the correct average static structure of the matrix and of the adsorbed fluid is available.

This conclusion is based on the use of the multicomponent self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [9] to describe the relaxation of concentration fluctuations of the mobile component in the model porous matrix. By setting the free-diffusion coefficient of one species to zero, this theory is readily adapted to the description of the dynamics of the model system above, thus allowing the numerical calculation of the partial intermediate scattering function $F(k, t)$ of the mobile species. As a concrete and illustrative application, here we report the theoretical predictions for a binary colloidal mixture of particles interacting through screened Coulomb potentials in which one of the two species plays the role of the porous matrix. The theoretical results for this specific system are compared with the corresponding results of a Brownian dynamics (BD) simulation on a model system consisting of $N=N_1+N_2$ Brownian particles in a volume V , with $N_1(=n_1V)$ particles of species 1 and $N_2(=n_2V)$ particles of species 2 interacting

through direct forces, but not through hydrodynamic interactions. A more limited version of this exercise, referring only to tracer diffusion phenomena, was carried out by Viramontes-Gamboa *et al.* [12] in 1995.

We carry out two kinds of computer experiments that differ in the manner we generate the structure of the porous matrix. In the first kind, we let the N particles of both species undergo Brownian motion, according to the conventional Brownian dynamics algorithm [13] with the same free-diffusion coefficient $D_1^0 = D_2^0 = D^0$ until equilibrium is reached. At this point, we artificially arrest the motion of the particles of species 2 by setting $D_2^0 = 0$ at an arbitrary configuration. In the second kind of experiment, a preexisting matrix is formed in the absence of the mobile species, by choosing the arrested configurations according to a prescribed distribution, afterward “pouring” the mobile particles into this matrix of obstacles. The prescribed average structure of the matrix that we consider below corresponds to the structure of an equilibrium monocomponent fluid of species 2. In both cases, after choosing a particular configuration of the matrix, we let the mobile species equilibrate in the external field of the fixed particles at that particular frozen configuration, and then proceed to the calculation of the dynamic properties of interest. Since these properties depend on the specific configuration of the fixed particles, and in order to average out this dependence, the results presented here correspond to an average of over more than 50 different configurations of the porous matrix. In both cases we also record the radial distribution functions between the two species, to be employed as the static input required by the SCGLE theory. In our illustrative application, the direct interactions are described by a hard sphere plus a strong repulsive screened Coulomb interaction. For simplicity, we assume that both species have the same hard-sphere diameter σ , so that the potential (in units of the thermal energy $k_B T = \beta^{-1}$) is given by $\beta u_{\alpha\beta}(r) = +\infty$ for $r < \sigma$, and for $r > \sigma$ by

$$\beta u_{\alpha\beta}(r) = \frac{\sqrt{K_\alpha K_\beta} \exp[-z(r/\sigma - 1)]}{r/\sigma}. \quad (1)$$

One may think of the parameter $\sqrt{K_\alpha}$ as proportional to the electric charge Q_α of species α , and the parameter $z = \kappa\sigma$ as the dimensionless inverse Debye length κ [5].

The relevant dynamic information of an equilibrium ν -component colloidal suspension is contained in the $\nu \times \nu$ matrix $F(k, t)$ whose elements are the *partial intermediate scattering functions*

$$F_{\alpha\beta}(k, t) \equiv \langle [n_\alpha(\mathbf{k}, t) - \langle n_\alpha(\mathbf{k}, t) \rangle] [n_\beta(-\mathbf{k}, 0) - \langle n_\beta(-\mathbf{k}, 0) \rangle] \rangle,$$

where $n_\alpha(\mathbf{k}, t) \equiv \sum_{i=1}^{N_\alpha} \exp[i\mathbf{k} \cdot \mathbf{r}_i(t)] / \sqrt{N_\alpha}$, with $\mathbf{r}_i(t)$ being the position of particle i of species α at time t . The initial value $F_{\alpha\beta}(k, 0)$ is the partial static structure factor $S_{\alpha\beta}(k)$ [5]. In our simulation experiment, we are interested in the dynamic properties of the mobile species, represented by $F(k, t) \equiv F_{11}(k, t)$. This dynamic property will be theoretically calculated applying the multicomponent self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [9] with the particular condition $\nu=2$ and $D_2^0=0$.

The SCGLE theory, explained in more detail in Refs. [9,10], is summarized by a self-consistent system of equations for the $\nu \times \nu$ matrices $F(k, t)$ and $F^{(s)}(k, t)$ (the latter defined as $F_{\alpha\beta}^{(s)}(k, t) \equiv \delta_{\alpha\beta} \langle \exp[i\mathbf{k} \cdot \Delta \mathbf{R}^{(\alpha)}(t)] \rangle$, where $\Delta \mathbf{R}^{(\alpha)}(t)$ is the displacement of any of the N_α particles of species α over a time t , and $\delta_{\alpha\beta}$ is Kronecker's δ function. Written in matrix form and in Laplace space, and omitting the explicit k dependence, the self-consistent system of equations reads

$$F(z) = (z + \{I + [\Delta \zeta^*(z)] \lambda\}^{-1} k^2 D S^{-1})^{-1} S \quad (2)$$

and

$$F^{(s)}(z) = (z + \{I + [\Delta \zeta^*(z)] \lambda\}^{-1} k^2 D)^{-1}, \quad (3)$$

where S is the matrix of partial static structure factors, D and $\lambda(k)$ are diagonal matrices given by $D_{\alpha\beta} \equiv \delta_{\alpha\beta} D_\alpha^0$ and $\lambda_{\alpha\beta}(k) = \delta_{\alpha\beta} [1 + (k/k_c^{(\alpha)})^2]^{-1}$, where $k_c^{(\alpha)}$ is the location of the first minimum (following the main peak) of $S_{\alpha\alpha}(k)$. $\Delta \zeta^*(t)$ is a diagonal matrix with its diagonal element $\Delta \zeta_\alpha^*(t)$ given by

$$\Delta \zeta_\alpha^*(t) = \frac{D_\alpha^0}{24\pi^3} \int d^3k k^2 [F^{(s)}(t)]_{\alpha\alpha} [c \sqrt{n} F(t) S^{-1} \sqrt{nh}]_{\alpha\alpha}, \quad (4)$$

where the elements of the k -dependent matrices h and c are the Fourier transforms $h_{\alpha\beta}(k)$ and $c_{\alpha\beta}(k)$ of the Ornstein-Zernike total and direct correlation functions, respectively. Thus, h and c are related to S by $S = I + \sqrt{nh} \sqrt{n} = [I - \sqrt{nc} \sqrt{n}]^{-1}$, with the matrix \sqrt{n} defined as $[\sqrt{n}]_{\alpha\beta} \equiv \delta_{\alpha\beta} \sqrt{n_\alpha}$.

The control parameters of our system are the interaction parameters z , K_1 , and K_2 , and the volume fractions ϕ_1 and ϕ_2 (with $\phi_\alpha \equiv \pi n_\alpha \sigma^3 / 6$). Here we fix the value of the screening parameter to $z=0.15$, and start by considering an equimolar mixture with $\phi_1 = \phi_2 = 2.2 \times 10^{-4}$. In our first simulation experiment we start with the simplest case, namely, a monodisperse suspension of $N = N_1 + N_2$ identical particles interacting with the same pair potential ($K_1 = K_2 = 100$), which execute Brownian motion. After thermalization, we stop the motion of half of them, and let the other half constitute the mobile species. Two additional experiments of the same kind were performed for systems with the same parameters as above, but varying the coupling parameters K_1 and K_2 . Thus, the second experiment corresponds to a more interacting system, $K_1 = K_2 = 500$, and the third to an asymmetric mixture such that the matrix is formed by the more strongly interacting particles, $K_2 = 500$ and $K_1 = 100$. These three experiments belong to the first kind referred to above, i.e., they involve a matrix whose average static structure is identical to the partial static structure factor $S_{22}(k)$ of an equilibrium mixture of both species. In this kind of experiment, $S_{22}(k)$ and the other static structural properties may be determined during the initial equilibration stage, before arresting the motion of the matrix. As an example, in Fig. 1(a) we present the various radial distribution functions $g_{\alpha\beta}(r)$ simulated in this manner in the third of these experiments.

We also performed parallel experiments of the second kind, involving a preexisting matrix with prescribed average structure. The prescribed structure we chose corresponds to the equilibrium structure of a *monocomponent* system containing only species 2. Thus, we first let the N_2 particles

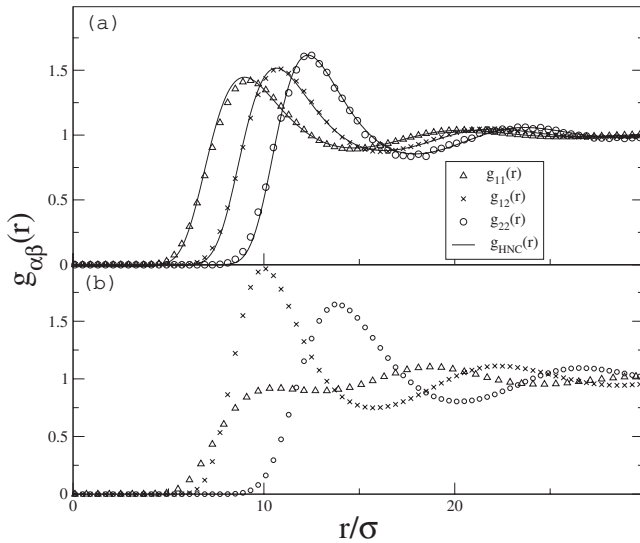


FIG. 1. Brownian dynamics simulated radial distribution functions $g_{\alpha\beta}(r)$ of a colloidal fluid (species 1) diffusing through a porous matrix formed by a second species of fixed particles, interacting with the repulsive Yukawa potential with fixed screening parameter $z=0.15$, volume fractions $\phi_1=\phi_2=2.2\times 10^{-4}$, and repulsion strength parameters $K_1=100$ and $K_2=500$ with the porous matrix generated in the presence (a), and in the absence (b), of the mobile species.

equilibrate, and then freeze an arbitrary configuration in which we then place the N_1 particles of the other species. The static and the dynamic properties involving the mobile species are then simulated after the fluid of species 1 equilibrates in the external field of the matrix in that particular configuration. The results are then averaged over a sufficient number (~ 50) of configurations of the matrix. In Fig. 1(b) we present the resulting $g_{\alpha\beta}(r)$ corresponding to the third experiment of this second kind, involving a system with the same parameters as in Fig. 1(a).

These simulated structural properties are now employed as the static input needed by the SCGLE theory, thus avoiding the use of liquid state approximations [5]. The predictions of the SCGLE theory for the dynamic properties of the Brownian fluid immersed in the porous matrix are presented in Fig. 2 for the three experiments of the first kind and for only the last experiment of the second kind, namely, that involving the asymmetric mixture with $K_2=500$ and $K_1=100$. These results are compared with the corresponding BD results for the normalized time-dependent diffusion coefficient $D^*(t)\equiv\langle(\Delta\mathbf{r}(t))^2\rangle/(6D^0t)$ and for the collective intermediate scattering function $F(k,t)=F_{11}(k,t)$ of the mobile species at fixed k and for the times $t=0$, t_0 , and $10t_0$, with $t_0\equiv\sigma^2/D^0$. Notice that for $t=10t_0$, $D^*(t)$ has relaxed from its initial value of 1 toward, and close to, its asymptotic value, characteristic of the long-time regime. Thus, the illustrative data in this figure covers the so-called short- and intermediate-time regimes, most easily accessible by Brownian dynamics simulations or video-microscopy experiments.

From information such as that summarized in Fig. 2, we may highlight the following. First, the description of the SCGLE theory for symmetric systems (illustrated by the first

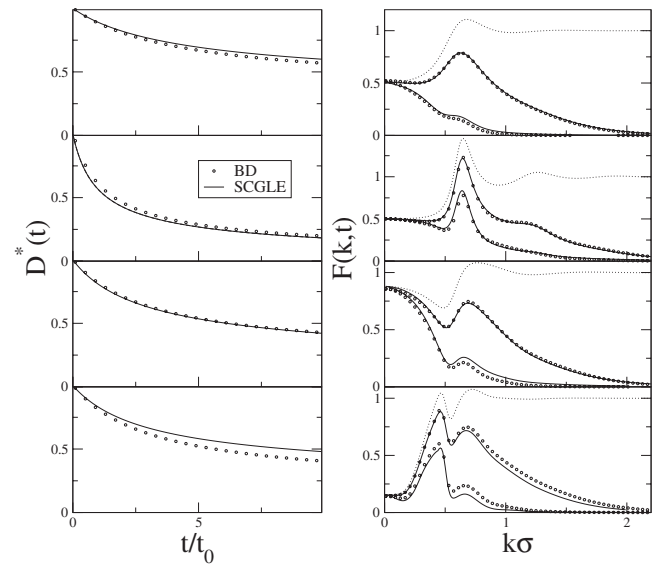


FIG. 2. Time-dependent self-diffusion coefficient $D^*(t)$ (left-hand column) and partial intermediate scattering function $F(k,t)$ for $t=0$, t_0 , and $10t_0$ (right-hand column) of the diffusive species permeating the porous matrix, interacting with the repulsive Yukawa potential with fixed screening parameter $z=0.15$ and volume fractions $\phi_1=\phi_2=2.2\times 10^{-4}$, but with parameters K_1 and K_2 given by $K_1=K_2=100$ (first row), $K_1=K_2=500$ (second row), and $K_1=100$ and $K_2=500$ (third and fourth rows, respectively). The symbols represent Brownian dynamics results and the solid lines are the SCGLE theoretical predictions.

two rows) is highly accurate in the time regimes illustrated in the figure. Second, the comparisons in Fig. 2 have essentially the same quality as the corresponding comparisons involving fully thermalized mixtures in which both species diffuse [9]. Third, the theoretical predictions for $F(k,t)$ in asymmetric systems for both kinds of experiments (last two rows) have similar levels of quantitative accuracy; the largest discrepancies with the simulation data are illustrated by the results of the fourth experiment, which are not particularly severe. Clearly, reducing the rather small differences between theory and simulation observed in Fig. 2 will require either reformulating the intrinsic approximations of the SCGLE theory or developing an extension similar to that carried out by Krakoviack [11] for the mode coupling theory (MCT) [14]. The comparisons above indicate, however, that the SCGLE theory, devised to describe the dynamics of equilibrium colloidal mixtures, provides quite a reasonable description of the dynamics of a monodisperse suspension permeating a porous medium formed by a random array of fixed particles.

This approach may now be applied to explore other interesting phenomena such as, for example, the dynamic properties of colloidal mixtures in porous media [2]. In fact, the present theory, complemented by adequate liquid state approximations for the static structure [6], may be used as a fully theoretical first-principles approach to qualitatively scan other regions of the state space to locate interesting dynamic phenomena for which simulations or experiments would be difficult to carry out, or are not yet available. In doing this we only lose quantitative precision, but no qualitative accuracy. In fact, one of the objectives of adapting the

SCGLE theory to the description of the dynamics of colloidal dispersions adsorbed in porous media is the description of dynamic arrest phenomena in these systems. The analysis of its accuracy in the short and intermediate times presented here is an important step in the process of assessing its overall reliability. The SCGLE theory, however, has already been successfully employed to describe dynamic arrest in bulk monodisperse [10,15,16] and multicomponent [17] colloidal systems.

Ordinary binary mixtures in which both species remain mobile are, however, fundamentally different in principle from the quenched-annealed mixtures considered here, in which one species serves as the porous matrix in which the other species diffuses. Thus, a relevant statistical mechanical question involves the comparison of the two alternative routes to describe the relaxation of the concentration fluctuations of the mobile species, namely, the present approach, and that developed by Krakoviack [11]. Although the latter

method might seem more systematic, spelling out the level of equivalence with the present approach is an issue that remains to be addressed. The results reported here indicate that even if our method involves additional approximations, it seems to provide a very satisfactory description of the dynamics of the adsorbed fluid, at least in the regimes considered here. It will also be quite interesting to see the performance of the present theory when applied to the description of the dynamics of the system close to the transition of dynamic arrest of the adsorbed fluid described by Krakoviack [11]. These issues are, of course, the subject of current work.

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