Tracer Diffusion in a Brownian Fluid Permeating a Porous Medium

G. Viramontes-Gamboa, J. L. Arauz-Lara, and M. Medina-Noyola
Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí, Alvaro Obregón 64, 78000 San Luis Potosí, México
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Tracer diffusion in a colloidal suspension permeating a porous medium is modeled as a binary Brownian mixture in which the spatial configuration of one of the species (the porous matrix) is frozen. Brownian dynamics simulations are employed to assess the accuracy of two simple theoretical results borrowed from the theory of colloid dynamics. The theoretical predictions are found to be reasonably accurate for not too low porosities, i.e., when strong confinement or trapping of tracer particles is not the dominant feature.

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Recently there has been an increased interest in the study of porous structures [1–8]. Describing their structure and morphology [1,3], as well as the equilibrium [4,5] and transport [6–8] properties of fluids that permeate them, are a few of the issues involved in their study. In recent years, physical techniques, both experimental [1,6] and theoretical [3,5,7,8], have been applied, with the aim of developing a sound fundamental picture of the most basic and general properties of these systems. Unfortunately, due to the diversity of issues involved, no simple and universal model or approach exists to describe them in a unified fashion. Thus, whereas some models focus, for example, on the statistical mechanics or the transport properties of the permeating fluid in the interior of a single pore, other models incorporate at the outset the spatial randomness of the system [3,5,8]. One model of the latter class is that of a partially quenched fluid mixture, in which the kinetic energy of one species is totally quenched, thus freezing its structure to mimic the porous matrix. In this Letter we report the results of our work on a Brownian dynamics version of essentially this model, from the theoretical and computer simulation point of view. We focus on the Brownian motion of labeled particles, and on its dependence on the structure of the porous matrix, and on the interactions of the fluid particles among themselves and with the matrix. Initially, our model system corresponds to a typical model of a binary colloidal mixture without hydrodynamic interactions, i.e., it consists of $N = N_1 + N_2$ interacting Brownian particles, with N_1 particles of species 1 and N_2 particles of species 2, whose motion follow the Brownian dynamics laws [9,10] employed in the study of colloidal suspensions. These particles interact through a radial pair potential denoted by $u_{\alpha\beta}(r)$, where the indices α and β refer to species (1 or 2). Their free Brownian motion is determined by the free-diffusion coefficients D_1^0 and D_2^0, respectively. Such a model, with $u_{\alpha\beta}(r)$ given by the repulsive Yukawa potential, has been widely studied in the context of colloid dynamics [11,12]. There, a reasonable understanding has emerged, based on the results of Brownian dynamics simulations and on the development of corresponding theoretical approaches [11–14]. This understanding has led to a satisfactory interpretation of actual experimental measurements in suspensions of highly charged polystyrene spheres in water [15], where hydrodynamic interactions are indeed negligible, and even in hydrodynamically concentrated hard-sphere dispersions [16]. The connection with porous media could be conceived as an extremely asymmetric colloidal mixture, in which the particles of one species are extremely less mobile than the others, i.e., if $D_2^0 \ll D_1^0$. In this limit, the particles of species 1 will view the other species as a virtually frozen matrix of fixed obstacles. Although the experimental realization of this limit might involve a very highly size-asymmetric mixture, in a computer experiment we can set D_2^0/D_1^0 arbitrarily, without necessarily requiring any size asymmetry, or even any asymmetry at all in the pair interactions between particles of different species. Thus, in this work we consider the idealized limiting condition $D_2^0/D_1^0 \to 0$ without asymmetry in the pair potential. We then ask ourselves: What can we learn, on the basis of our understanding of tracer diffusion phenomena in model colloidal suspensions, about the Brownian motion of a labeled mobile particle, which interacts simultaneously with its fellow mobile particles of species 1, and with the rigid porous matrix of species 2? More specifically, we want to know how will such a tracer particle move, on the average, according to the Brownian dynamics simulations, and to what extent can this be understood in terms of theoretical concepts developed to describe tracer diffusion in binary colloidal mixtures, extrapolated to the limit $D_2^0/D_1^0 \to 0$.

To answer these questions, we start our Brownian dynamics experiments with the N particles moving with the same free-diffusion coefficient, $D_1^0 = D_2^0 = D^0$, and interacting with the hard-sphere plus Yukawa potential,

$$\beta u_{\alpha\gamma}(r) = \beta u(r) = K \frac{e^{-z[r/\sigma - 1]}}{r/\sigma}, \qquad r > \sigma, \quad (1)$$

where z and K are the dimensionless screening and coupling parameters, $\beta = (k_B T)^{-1}$, T being the temperature and k_B being Boltzmann's constant, and with σ the hard-sphere diameter. After equilibrium has been reached, we set $D_2^0 = 0$, thus freezing the positions of particles of

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species 2 in a certain spatial configuration, forming in this way a matrix of fixed obstacles, the porous medium, in which the other particles continue to diffuse with a free-diffusion coefficient $D_1^0 = D^0$, until the system equilibrates again. After this, averages are calculated. Results from this experiment are reported below.

From a theoretical point of view, one would like to understand the relevant results of this experiment in terms of the microscopic properties of the system. With this aim, we consider two independent theoretical approaches describing the Brownian motion in colloidal mixtures in the limit $D_2^0 \to 0$. We present results for the mean squared displacement $W(t) \equiv \langle[\Delta \mathbf{r}(t)]^2\rangle/6$ or, equivalently, the time-dependent self-diffusion coefficient $D(t) \equiv W(t)/t$, of labeled tracer mobile particles, and its asymptotic long-time value D^L.

The first theory derives from the generalized Langevin equation approach developed by Vizcarra-Rendón and Medina-Noyola [17–19]. This theory provides expressions for the time-dependent friction function $\Delta\zeta_\alpha(t)$ of a tracer particle of species α due to its direct interactions with the other Brownian particles in the equilibrium mixture, in terms only of the partial static structure factors $S_{\alpha\beta}(k)$ and of $\zeta_\alpha^0 \equiv k_B T/D_\alpha^0$. From $\Delta\zeta_\alpha(t)$, other tracer-diffusion properties, such as $W_\alpha(t)$, follow. Here we adopt about the simplest approximate version of this theory, referred to as the *Fick plus decoupling approximation* (FDA) [19]. In the corresponding results for a binary mixture, we set $D_2^0 = 0$, $D_1^0 = D^0$, and assume that the radial distribution functions (RDF) are such that $g_{\alpha\beta}(r) = g(r)$, with $g(r)$ being the RDF of a monodisperse system with particle concentration $n = n_1 + n_2$, with $n_\alpha = N_\alpha/V$. The resulting expression for $\Delta\zeta_1(t)$ is (dropping from now on the subscript 1)

$$\Delta\zeta(t) = \frac{k_B T}{(2\pi)^3}\int d^3k\, k_z^2 h^2(k) \exp[-k^2 D^0 t]\left\{\frac{n_1}{[1 + n_2 h(k)][1 + nh(k)]}\exp\left[-k^2 D^0 t\left(\frac{1 + n_2 h(k)}{1 + nh(k)}\right)\right] + \frac{n_2}{1 + n_2 h(k)}\right\}, \quad (2)$$

where $h(k)$ is the Fourier transform of $h(r) = g(r) - 1$. In the self-diffusion limit ($n_2 = 0$), this result coincides with Hess and Klein's mode-mode coupling expression [12].

The second theory is based on exact short-time conditions for the tracer-diffusion propagators provided by the many-particle Smoluchowski equation [20,21]. In the simplest version proposed by Arauz-Lara and collaborators [13,22], and referred to as the *single exponential approximation* (SEXP), we take the same particular cases and limits as above, with the following result:

$$W(t) = D_{\mathrm{SEXP}}^L t + \tau(D^0 - D_{\mathrm{SEXP}}^L)(1 - e^{-t/\tau}), \quad (3)$$

where $D_{\mathrm{SEXP}}^L = [1 - nA^2/B(2 - x_2)]D^0$ and $\tau = k_B T A/D^0 B(2 - x_2)$ with $A = \int d^3r\, g(r)(\hat{\mathbf{k}}\cdot\nabla)^2 u(r)$, $B = \int d^3r\, g(r)[(\hat{\mathbf{k}}\cdot\nabla)\nabla u(r)]^2$, and $x_2 = n_2/n$, the molar fraction of fixed particles.

Before going further, let us see how realistic the theoretical assumption that $g_{\alpha\beta}(r) = g(r)$ is, according to the computer simulation experiment. Before the position of the particles of species 2 are frozen, our system is just a monodisperse Brownian fluid in thermodynamic equilibrium, whose corresponding $g(r)$ is presented in Fig. 1 (open circles). After we freeze the position of the particles of species 2, we calculate the RDF of the mobile particles, $g_{11}(r)$, and of the fixed particles around a mobile particle, $g_{12}(r)$, for a given value of x_2. In Fig. 1 we also compare $g_{11}(r)$ and $g_{12}(r)$ with $g(r)$ for $x_2 = 0.5$ and 1.0. This figure indicates that the theoretical assumption is indeed consistent with the simulation results. Let us mention that the latter correspond to an average over different configurations of the matrix of fixed particles (around 10 for $x_2 \approx 0.5$ and around 200 for $x_2 \approx 1$), which is equivalent to sampling the configuration space of the fixed particles. A similar average will also be involved in calculating tracer-diffusion properties. In that case, however, there will be a strong dependence on x_2, and this dependence is precisely what we want to describe.

The previous results allow us to say that the assumption just discussed will not be an important source of error in the predictions of the two theories. Let us now describe some of the virtues and limitations of these theories that can be advanced even in the absence of simulation results. First, we expect them to perform better in the regime where the relative concentration of fixed particles is very small (i.e., for very high "porosities"), in which the friction on a tracer particle originates mostly from its collisions with other mobile particles. In the actual "self-diffusion" limit ($x_2 = 0$), these two theories have been studied, and

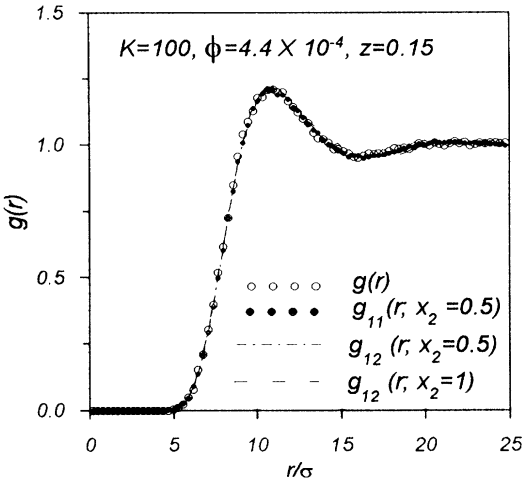

FIG. 1. Brownian dynamics results for the radial distribution function $g(r)$, $g_{11}(r)$, and $g_{12}(r)$.

moderate quantitative disagreement among themselves, and with computer simulations, has been observed [14]. Such quantitative disagreements become more severe for more strongly coupled systems, when the friction due to the direct interactions, $\Delta\zeta^L \equiv \int_0^\infty \Delta\zeta(t)\,dt$, becomes comparable to or larger than the "solvent" friction ζ^0, i.e., when $D^L/D^0 = (1 + \Delta\zeta^L/\zeta^0)^{-1}$ decreases below 0.5. A similar situation is expected for $x_2 \neq 0$, but with possibly still more severe quantitative difficulties for both theories since the friction on a tracer particle due to its interactions with a more rigid environment is expected to be larger than if all the particles around it can diffuse. To have a quantitative illustration of the above, let us look at Fig. 2, where we present the results of both theories for D^L. These, and all the results in this work, correspond to a fixed value $z = 0.15$ of the screening parameter, and to a fixed total concentration n, such that $\phi = \pi n\sigma^3/6 = 4.4 \times 10^{-4}$. These values, employed in previous applications of the theories [15], allow us to illustrate the main features of our results. Figure 2 describes the effect on D^L of increasing the fraction of fixed particles. Two cases are presented. A very weakly coupled system, $K = 5$, for which $D^L/D^0 \approx 0.9$ and $\Delta\zeta/\zeta^0 \approx 0.10$. In this regime, the two theories agree quite nicely with each other. The second case, $K = 100$, corresponds to a moderately high coupling regime, for which for self-diffusion ($x_2 = 0$) $\Delta\zeta^L/\zeta^0 \approx 0.6$. The increase in this effect due to the increase in x_2 is predicted by both theories to be very strong, although the quantitative agreement between their results deteriorates considerably in the regime $0.5 \lesssim x_2 \leq 1$.

The reason for this can be understood if we estimate, for $x_2 = 1$, the *effective* volume fraction of the matrix of fixed particles of diameter σ (the distance of closest approach between the tracer and any of these particles, which can be read from Fig. 1 to be about $\sigma_{ef} \approx 6\sigma$), which turns out to be $\phi_{ef} \approx 0.095$. For reference, a hard-sphere tracer of diameter σ_{ef} will be completely trapped in a matrix of hard spheres of the same diameter, arranged in a simple cubic lattice, when $\phi_{ef} \approx 0.185$. Thus, for $K = 100$, ϕ_{ef} is about half this reference value. In our system, an effective volume fraction of 0.19 is reached already for $K \approx 300$. Thus, for $K \gtrsim 300$, the motion of the tracer particle will be expected to be diffusive only in the interior of the pore in which it has been trapped. For the intermediate conditions illustrated by $K = 100$, this motion is expected to contain strong localization effects in the interior of the "pores" (local potential wells), with successive hopping from pore to pore. Such effects are outside the scope of the theories discussed here. Thus, they are expected to perform well in the low coupling regime, which correspond to a dilute Brownian fluid permeating a very porous matrix. In the high coupling regime, the theories are expected to be reasonably accurate only in the regime of high porosity, i.e., $x_2 \lesssim 0.5$.

Let us now turn to the opposite regime in terms of time scales. The short-time regime corresponds to times much smaller than the mean collision time $t_l \equiv l^2/D^0$, $l \equiv n^{-1/3}$. At the earliest times, the tracer's motion is thus essentially free diffusion, $W(t) \simeq D^0 t$. At slightly longer times, the effects of the interactions will produce the relaxation of $D(t)$ from its initial value D^0 towards its asymptotic value D^L. From the computer simulation experiments we can extract the behavior of $D(t)$ in the short and intermediate regimes, and they are illustrated in Figs. 3 and 4. In Fig. 3 we compare the theoretical results for $D(t)$ with the simulation results for a system under conditions where only a reasonable agreement was expected, namely, $K = 100$ and $x_2 = 0.5$ (half of the particles move in the presence of the other half that remain fixed). As we can see, the description of the initial and intermediate relaxation of $D(t)$ provided by both theories in the time interval indicated can be said to be quite good for this intermediate coupling. In contrast, for the higher cou-

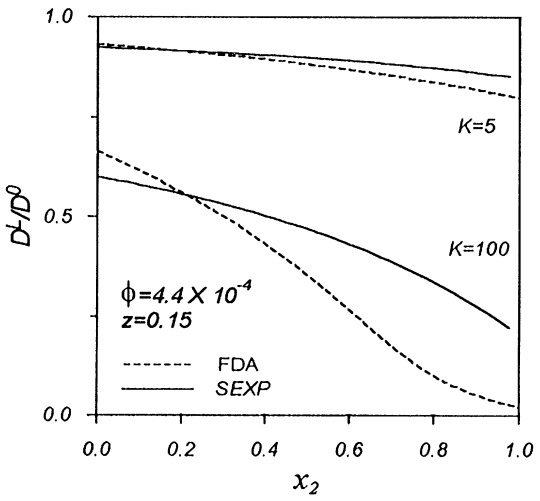

FIG. 2. Long-time tracer-diffusion coefficient D^L according to the FDA and SEXP approximations.

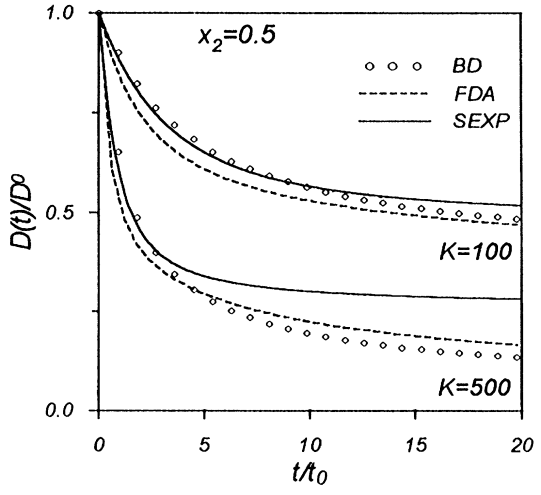

FIG. 3. $D(t)$ as a function of time (in units of $t_0 \equiv \sigma^2/D^0$). Simulations, FDA, and SEXP results, for fixed composition ($x_2 = 0.5$) and two values of K.

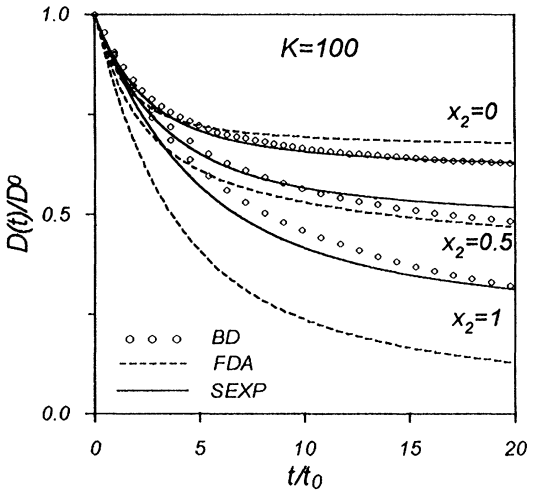

FIG. 4. As in Fig. 3, but varying the composition and fixed coupling, $K = 100$.

pling, $K = 500$, the two theories predict reasonably well the very initial drop of $D(t)$, but the inaccuracies expected at longer times for this strong coupling already manifest themselves, even at this intermediate porosity. The apparent better agreement of the FDA results, which indeed is observed in general at this value of x_2, is not a general feature of these comparisons, as we can see from Fig. 4, where we have $D(t)$ for fixed coupling, $K = 100$, and for $x_2 = 0$, 0.5, and 1. As expected, both theories yield accurate results for the first two cases (high and intermediate porosities), but exhibit the quantitative inconsistencies already expected from the previous discussion (see Fig. 2 for $K = 100$ and $x_2 \approx 1$). This time, the simulation data in the intermediate regime in Fig. 4 seems to favor the SEXP approximation over the FDA results.

The simulation results in Figs. 3 and 4 also exhibit another interesting feature, relating to the very initial decay of $D(t)$. Thus, from Fig. 4 we can see that the apparent initial slope of $D(t)$ is independent of x_2, whereas from Fig. 3 we see that it does depend on K. As for the theories, both of them predict this to occur. The physical reason is that in the very initial times at which the effects of the interaction of the tracer particle with its surrounding cage are first manifested, the tracer cannot yet distinguish if the particles around it are fixed or mobile. It moves as if in the bottom of the potential well produced by the repulsion of an average rigid cloud of particles with a local density around it given by $ng(r)$. These notions are built in the physical principles on which both theories are based. In fact, if we expand the SEXP result in Eq. (3) in powers of t, we find that the initial slope of $D(t)/D^0$ is given by $-n\beta D^0 A/2$, which does not depend on x_2, but depends strongly on K through the integral A involving $u(r)$. This is an exact result (at least for $x_2 = 0$), and it explains the close agreement of the SEXP short-time results with the Bode diagram (BD) data at all values of K and x_2. The FDA does not satisfy this exact short-time condition. Instead, it leads to the same result for the initial slope, but with $-c(r)$ replacing $u(r)$ in the expression for A [$c(r)$ being the direct correlation function]. This explains the early departure of the FDA results from the BD simulations. Still, the comparisons just presented allow us to conclude that, in spite of the complexity of the problem, and the apparent simplicity of the theoretical approaches, the qualitative and quantitative theoretical predictions are in reasonable general agreement with the experimental results, at least in the regime where strong trapping of the tracer particles by the pores of the matrix is not the dominant effect.

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