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Short-Time Motion of Colloidal Particles: Numerical Simulation via a Fluctuating Lattice-Boltzmann Equation

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A new and general technique for simulating solid-fluid suspensions, which combines molecular dynamics for the solid particles with a lattice-Boltzmann model for the fluid, is described. The many-body hydrodynamic interactions are fully accounted for, both for small particle velocities and at higher Reynolds numbers. Brownian motion of the solid particles is included by adding a fluctuating component to the fluid stress tensor. Simulations of the dynamics of colloidal particles at short times compare favorably with recent diffusing-wave spectroscopy experiments.

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In this paper a new simulation technique for particulate suspensions is described. It can efficiently track the motion of large numbers of suspended solid particles over a wide range of flow conditions. In particular, we can simulate colloidal suspensions of submicron sized particles, suspensions of macroscopic particles, and flows at small but nonzero Reynolds number. The technique combines Newtonian dynamics of the solid particles with a lattice-Boltzmann model [1,2] for the fluid. It is closely related to earlier suspension modeling using lattice-gas cellular automata [3,4], but has the advantage that unnecessary statistical fluctuations are avoided, reducing the need for computationally expensive ensemble averaging. Instead, the fluctuations leading to Brownian motion are incorporated through random stress fluctuations in the fluid [5]. The simulations can easily track the motion of solid particles at very short times, even prior to the onset of Brownian motion. Until recently, there has been little interest in this regime as it could not be probed experimentally; however, with the advent of diffusing-wave spectroscopy [6] the short-time motion of colloidal particles can be measured accurately. Numerical simulations can complement these experiments by providing detailed information on the spatial and temporal development of the hydrodynamic interactions. Our first investigation of this kind of problem is reported in this paper; here we have studied the short-time dynamics of spherical particles in dilute to dense suspensions. The experimentally observed scaling of the mean-square displacement [7,8] has been reproduced by the simulations, over the combined time regime probed by both sets of experiments. A possible explanation for the continuation of this scaling to very short times is suggested.

The classical description of colloidal particle dynamics is the Einstein-Smoluchowski equation, in which the details of the short-time dynamics are ignored. The hydrodynamic interactions are assumed to be fully developed, so that there is a complete separation of time scales between the dynamics of the fluid and the (diffusive) motion of the particles. However, because of the assumed time-scale separation these interactions are global, that is, every part of the system affects every other part; thus large-scale matrix inversion is required to determine the $6N \times 6N$ diffusion tensor, which characterizes the hydrodynamic interactions in this approximation. Therefore, early simulations of Brownian motion either ignored the hydrodynamic interactions altogether or used oversimplified pairwise-additive approximations [9]; in either case quantitative results could only be obtained at very low volume fractions. More recently, improved methods of computing these hydrodynamic interactions have been developed [10,11], but their computational cost is high, increasing as the *cube* of the number of particles. The motivation underlying the lattice-gas/lattice-Boltzmann approach is that, by allowing for the natural time evolution of the hydrodynamic forces and torques, the interactions remain purely local; thus the computational cost scales *linearly* with the system size.

The major drawback of the lattice-gas approach to fluid dynamics has been that it requires extensive ensemble averaging or time averaging to produce statistically significant results. However, by ensemble averaging over the microstates of the lattice gas with the molecular chaos approximation, we can obtain a coarse-grained description of the time evolution of the lattice gas, analogous to the Boltzmann equation for a dilute gas, but discretized in velocity, space, and time [12]. Thus, in the lattice-Boltzmann method, we simulate the macroscopic motion of a fluid by following the time evolution of the one-particle velocity distribution function $f_i(\mathbf{r},t)$ [2], which describes the number of particles at a particular node of the lattice $\mathbf{r}$, at a time t, with a velocity $\mathbf{c}_i$; $\mathbf{r}$, t, and $\mathbf{c}_i$ are discrete, whereas f_i is continuous. The hydrodynamic fields, mass density ρ, momentum density $\rho\mathbf{u}$, and stress σ are moments of this velocity distribution:

$$\rho = \sum_{i=1}^{18} f_i, \quad \rho\mathbf{u} = \sum_{i=1}^{18} f_i\mathbf{c}_i, \quad \sigma = \sum_{i=1}^{18} f_i\mathbf{c}_i\mathbf{c}_i. \qquad (1)$$

In our implementation there are 18 possible velocities, corresponding to the first and second neighbor directions of a simple cubic lattice. At each time step, the velocity distribution is advected from node to node of the lattice according to the evolution equation [2]

$$f_i(\mathbf{r}+\mathbf{c}_i t_0, t+t_0) = f_i(\mathbf{r},t) + \Delta f_i^{\mathrm{coll}}(\mathbf{r},t), \tag{2}$$

where t_0 is the time step. The collisional term, $\Delta f_i^{\mathrm{coll}}$, can be simplified by linearizing about the local equilibrium distribution $f_i^{\mathrm{eq}}(\mathbf{r},t)$ [2],

$$\Delta f_i^{\mathrm{coll}} = \sum_{j=1}^{18} \mathcal{L}_{ij}\left(f_j - f_j^{\mathrm{eq}}\right). \tag{3}$$

The eigenvectors of the linearized collision operator, $\mathcal{L}$, comprise the hydrodynamic modes of the fluid (mass, momentum, and stress), together with short-lived nonhydrodynamic modes of no physical significance. Thus the eigenvalues of $\mathcal{L}$ are chosen to conserve mass and momentum, and to attenuate the shear stress by an amount that depends on the assigned kinematic viscosity; higher order moments of the distribution function, which are irrelevant to simulations of incompressible fluid dynamics, are set to zero.

The collision operator given in Eq. (3) has the effect of driving any velocity distribution towards the preset local equilibrium. In colloidal suspensions the Reynolds number is very small; in this case the equilibrium distribution is of the form

$$f_i^{\mathrm{eq}} = \frac{\rho}{24}\left(\alpha_i + 4\frac{\mathbf{u}\cdot\mathbf{c}_i}{c_i^2}\right), \tag{4}$$

where the coefficient α_i is equal to 2 for [100] velocity directions and equal to 1 for [110] velocity directions. As in the kinetic theory of gases, the mass density, momentum density, and pressure ($p = \rho/2$) are moments of the equilibrium distribution, whereas the deviatoric stress tensor is derived from moments of the nonequilibrium distribution, $f_i - f_i^{\mathrm{eq}}$. Note that at nonzero Reynolds numbers, the equilibrium distribution must contain terms proportional to $(\mathbf{u}\cdot\mathbf{c}_i)^2$ in order to generate the proper nonlinear terms in the Navier-Stokes equations [13].

The solid-fluid boundary conditions are modeled in a similar way to the earlier lattice-gas based simulations [14,15]. The solid surface, a sphere of radius a in this case, is placed onto the lattice, thereby cutting some of the links between lattice nodes. The fluid particles moving along these links interact with the solid surface at boundary nodes placed halfway along the links. Thus we obtain a discrete representation of the solid surface, which becomes more and more precise as the particle gets larger. The lattice nodes inside and outside the particle are treated in an identical fashion, so that the fluid fills the whole volume of space, both inside and outside the particles. However, because of the relatively small volume inside each particle, the interior fluid relaxes quite quickly to rigid-body motion, characterized by the particle velocity and angular velocity. Thus, on physically important time scales, the interior fluid only contributes an additional inertia to the solid particle.

At each boundary node there are two incoming distributions f_i and $f_{i'}$, corresponding to velocities $\mathbf{c}_i$ and $\mathbf{c}_{i'}$ ($\mathbf{c}_{i'} = -\mathbf{c}_i$) parallel to the link direction. By exchanging population density between f_i and $f_{i'}$ we can modify the local momentum density to match the velocity of the solid particle surface, without affecting either the mass density or the stress [see Eq. (1)]. Because the stress tensor is not affected by the boundary-node collision rules (by symmetry), the hydrodynamic stick boundary condition applies right up to the solid surface, without any intervening boundary layer. This point is discussed in more detail in Ref. [4]. The change in fluid momentum at each boundary node is transferred into forces and torques acting on the solid particles, which in turn is converted into changes in particle velocity and angular velocity, according to the assigned mass and inertia.

In recent years, it has become increasingly obvious that the the lattice-Boltzmann equation is a much better simulation tool for hydrodynamics than lattice gases. However, in its normal state the lattice-Boltzmann equation cannot model the molecular fluctuations in the solvent that give rise to Brownian motion. The main contribution of this paper is to show that this difficulty can be overcome, within the framework of fluctuating hydrodynamics [5], by adding a random component to the fluid stress tensor. Thus, in the fluctuating lattice-Boltzmann equation, the updated velocity distribution contains a stochastic term $f_i'(\mathbf{r},t)$, representing thermal fluctuations,

$$f_i(\mathbf{r}+\mathbf{c}_i t_0, t+t_0) = f_i(\mathbf{r},t) + \Delta f_i^{\mathrm{coll}}(\mathbf{r},t) + f_i'(\mathbf{r},t), \tag{5}$$

where f' is chosen so that only its stress moment $\sigma' = \sum_{i=1}^{18} f_i'\mathbf{c}_i\mathbf{c}_i$ is nonzero. These random stress fluctuations are uncorrelated in space and time [5],

$$\begin{aligned}\langle \sigma'_{\alpha\beta}(\mathbf{r},t)\sigma'_{\gamma\delta}(\mathbf{r}',t')\rangle \\ = A\delta_{\mathbf{rr}'}\delta_{tt'}\left(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}\right);\end{aligned} \tag{6}$$

the choice of the variance A serves to define the effective temperature of the fluid, via the fluctuation-dissipation theorem. The details of the calculation will be given in future work; essentially one must solve a discrete Langevin equation for the fluid stress tensor. In the limit that the correlations in the total fluid stress (not just the random part) decay instantaneously, we recover the Landau-Lifshitz result $A = 2\eta_0 k_B T$ [5], where η_0 is the viscosity of the pure fluid. This approach is quite different from Brownian dynamics [9] or Stokesian dynamics [10], where random fluctuations are applied directly to the particles; these methods cannot account for the short-time particle motion that is examined in this paper.

As a preliminary test of the simulation method, a direct comparison has been made between numerical and theoretical results for the motion of an isolated sphere in suspension. In Fig. 1, the decay of an initially im-

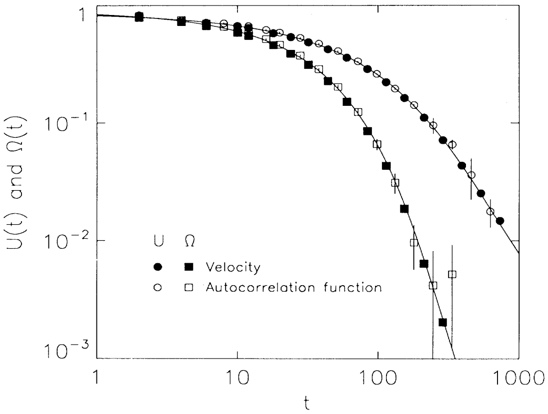

FIG. 1. Translational velocity $U(t)$ and rotational velocity $\Omega(t)$ of an isolated sphere. The time-dependent velocities of the sphere are shown as solid symbols; the relaxation of the corresponding velocity autocorrelation functions are shown as open symbols (with statistical error bars). A sufficiently large fluid volume was used so that the periodic boundary conditions had no effect on the numerical results for times up to $t = 1000$. The solid lines are theoretical results, obtained by an inverse Laplace transform of the frequency dependent friction coefficients [16] of a sphere of appropriate size ($a = 2.6$) and mass ($\rho_s/\rho = 12$); the kinematic viscosity of the pure fluid $\nu = 1/6$.

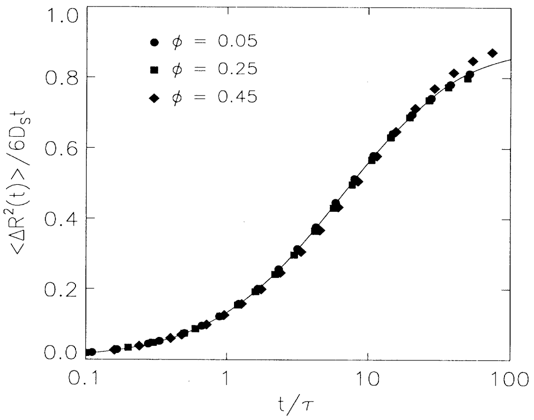

FIG. 2. Scaled mean-square displacement $\langle \Delta R^2(t)\rangle/6D_s t$ at short times, vs reduced time t/τ. Simulation results for 128 spheres (solid symbols) are shown at packing fractions ϕ of 5%, 25%, and 45%; the solid line is the isolated-sphere result. The simulation parameters were the same as in Fig. 1 except that a sphere of radius 4.5 was used at the highest volume fraction.

posed translational velocity $U(0)$ or rotational velocity $\Omega(0)$ is compared with the velocity autocorrelation function of an identical particle, set in motion by stress fluctuations in the fluid. Within the statistical error bars, the normalized velocity correlation functions are identical to the steady decay of the translational and rotational velocities of the sphere; thus our simulations satisfy the fluctuation-dissipation theorem. Moreover, the simulations agree almost perfectly with theoretical results derived from the frequency-dependent friction coefficients [16], even though there are no adjustable parameters in these comparisons; thus we see that the fluctuating lattice-Boltzmann equation can account for the hydrodynamic memory effects that lead to long-time tails [17].

Next we consider the motion of colloidal particles at very short times, prior to the onset of Brownian motion, where diffusing-wave spectroscopy has recently shown an unexpected scaling [7]. If the mean-square displacement, normalized by the self-diffusion coefficient times the time $\langle \Delta R^2(t)\rangle/6D_s(\phi)t$, is plotted versus a reduced time t/τ, then, for all solids volume fractions, there is a scaling time $\tau(\phi)$ which collapses the experimental data onto one master curve, indistinguishable from the isolated-sphere result. Moreover, τ seems related to the time it takes fluid vorticity to diffuse a particle radius; values of τ determined from the scaled mean-square displacements are in good agreement with independent estimates of the vortex diffusion time $\eta(\phi)/\rho a^2$, based on the suspension viscosity η. Simulation data for a number of Brownian particles ($N = 128$) under the same scaling is shown in Fig. 2. Results with different size systems ($N = 16$ and $N = 1024$) indicate that the periodic boundary conditions have a negligible effect on the 128-sphere results for times up to about 100τ. The scaled data at various volume fractions collapse onto the dilute (single-particle) result, in excellent agreement with experiment. Moreover, the self-diffusion coefficient and viscosity that are required to scale the mean-square displacement are in quantitative agreement with independent simulations and experimental data (see Ref. [18]). A comparison in shown in Fig. 3.

The simulation data plotted in Fig. 2 show that the scaling extends to very short times ($t/\tau < 1$), beyond the range of the experimental data from Ref. [7]; very recent experiments [8] independently confirm that scaling exists in this time regime as well. Although the existence of a diffusive time scale based on the suspension viscosity seems reasonable for times $t \gg \tau$, an explanation for the short-time scaling ($t < \tau$) is still called for, since the many-body hydrodynamic interactions which contribute to the suspension viscosity cannot develop at such short times. We have recently studied this problem through simulations of stress relaxation in colloidal suspensions. Our results show that substantial contributions to the suspension viscosity arise essentially instantaneously, from the interactions of the fluctuating fluid with the solid particles. The stress-stress correlation function of the suspension decays very rapidly, just like the force-force correlation function between the solid particles, with only a weak tail correction arising from the time-dependent hydrodynamic interactions. Changes in suspension viscosity as a function of time are only of the order of (10–30)%. Thus it is quite plausible that,

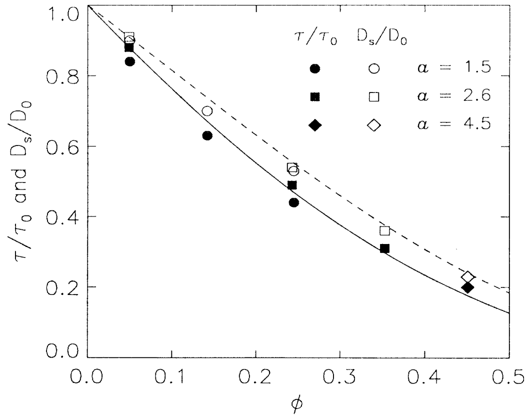

FIG. 3. Scaled relaxation time τ/τ_0 ($\tau_0 = a^2/\nu$) and self-diffusion coefficient D_s/D_0 vs packing fraction ϕ. The data points are determined from the scaling of the 128-sphere simulation data for various particle sizes. The uncertainty in fitting the data is about 5%. Independent results [18] for η_0/η (solid lines) and D_s/D_0 (dashed lines) are shown for comparison.

even at short times, the suspension behaves as an effective medium, so that the particle motions are essentially uncorrelated with one another. This is fruitful ground for further simulations, since it will be possible to probe the time and the space dependence of the hydrodynamic interactions directly.

In summary, the combination of molecular dynamics for the particulate phase and the lattice-Boltzmann equation for the fluid phase is a promising technique for quantitative simulations of hydrodynamically interacting particles. The method is also very flexible; the particle size and shape, the electrostatic interactions, the flow geometry, the Peclet number (i.e., the ratio of viscous forces to Brownian forces), and the Reynolds number can all be varied independently. Moreover, applications of the fluctuating lattice-Boltzmann equation are not limited to particulate suspensions. For instance, the techniques described here could be extended to study the dynamics of emulsions of immiscible liquids, or light scattering from thermally conducting liquids. Since lattice-Boltzmann simulations treat the fluxes of the hydrodynamic fields as dependent variables, rather than as spatial derivatives, solutions of fluctuating hydrodynamics problems are straightforward.

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