Brownian dynamics simulations of self-diffusion and shear viscosity of near-hard-sphere colloids

D. M. Heyes
Department of Chemistry, University of Surrey, Guildford, GU2 5XH, United Kingdom

A. C. Brańka
Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179, Poland

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We use Brownian dynamics simulations to calculate the long-time self-diffusion coefficients and Newtonian viscosities of model near-hard-sphere colloidal liquids without hydrodynamic interactions using a continuous potential: (a) an r^{-n} interaction between the model colloidal particles, with exponents n varying between 6 and 72, and (b) a Yukawa potential. We show that the diffusion coefficients increase and the viscosity decreases as the interaction potential becomes softer. The time-dependent self-diffusion coefficients and shear-stress correlation functions can be represented by a fractional exponential form at all volume fractions up to 0.5.

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The Brownian dynamics (BD) computer simulation method evolves N interacting model colloidal particles with index i mass m_i, and position $\mathbf{r}_i$ through phase space. A popular BD algorithm is based on the Langevin equations of motion [1,2]

$$m_i\dot{\mathbf{r}}_i=\mathbf{F}_i+\mathbf{R}_i-\xi\dot{\mathbf{r}}_i \ , \tag{1}$$

where $\mathbf{F}$ is a body force on the particle $\mathbf{R}$ is the Brownian force, and ξ is the friction coefficient. If derived from pairwise additive direct interactions $V(r)$ between the particles, then

$$\mathbf{F}_i=-\nabla\sum_{j\neq i}^{N}V(|\mathbf{r}_i-\mathbf{r}_j|) \ . \tag{2}$$

The position update algorithm for the particles is

$$\mathbf{r}(t+h)=\mathbf{r}(t)+[\mathbf{F}(t)+\mathbf{R}(t,h)]h/\xi \ , \tag{3}$$

where h is the time step and $\mathbf{R}(t,h)$ is a normally distributed random force with zero mean and $\langle\mathbf{R}^2(t,h)\rangle=6k_BT\xi/h$. Although in any real colloidal liquid, solvent-mediated many-body hydrodynamical forces on the colloidal particles will be an essential component of the dynamics and physical properties, it is interesting to discover the properties of the above model colloidal system which may be considered in some sense as a "reference" state, in not including these. Many simulation studies have been performed using this algorithm, incorporating different analytic forms for the interaction potential. One potential form used by this group for model sterically stabilized colloids is the inverse-power potential [3]

$$V(r)=\epsilon(\sigma/r)^n \ , \tag{4}$$

with $n=36$. While Löwen and Szamel [4] have used the Yukawa potential,

$$V(r)=\epsilon\sigma\frac{\exp[-\lambda(r-\sigma)/\sigma]}{r} \ , \tag{5}$$

where again ϵ and σ set the energy and length scales. This analytic form is more appropriate for charge stabilized systems. The hard-sphere potential has been considered independently (but with similar algorithms) by Cichoki and Hinsen [5,6] for self-diffusion and by Heyes and Melrose [3] for rheology.

Despite many BD studies, there is still a lack of data on the influence of the potential form on the transport properties of model colloidal systems obeying these equations of motion, which we address here. In this work we explore the effect of the interaction potential on the long-time self-diffusion coefficients D and Newtonian shear viscosity using the Green-Kubo method and test a generalized Stokes-Einstein relationship for finite volume fraction colloidal liquids. We consider the mean square displacement $W(t)$ of a tagged particle in a suspension,

$$W(t)=\tfrac{1}{6}\langle[r(t)-r(0)]^2\rangle \ . \tag{6}$$

The rate of change of $W(t)$ gives the long-time self-diffusion coefficient

$$D=\frac{d\langle W(t)\rangle}{dt}, \quad t\to\infty \ . \tag{7}$$

We find, as did Cichocki and Hinsen [5,6] that Eq. (7) converges more rapidly to the asymptotic limit than another expression $W(t)/t$. At infinite dilution in a liquid of viscosity η_s, a Brownian particle of diameter σ has a self-diffusion coefficient $D_0=k_BT/\xi$, where $\xi=3\pi\eta_s\sigma$ is the friction coefficient. At finite concentration the diffusion process is slowed down by the interaction of the tagged particle with the other particles. The time scale of the velocity fluctuation of a single large mass m, called the Brownian relaxation time, is $\tau_B=m/\xi$. For times $t\gg\tau_B$ but $t\ll\tau_I$, the time it takes a particle to move a distance of order its diameter, the self-diffusion coefficient is D_S, the so-called short-time self-diffusion coefficient. The hydrodynamic interactions occur on the time scale as τ_B so these contribute to D_S. For $t\gg\tau_I$ the tagged particle experiences a substantial change in the interaction force from the other particles and distorts the surrounding cage of colloidal particles as it moves through the liquid. This leads to a further decrease in the self-diffusion below that of D_S. The mean

square displacement of the particle in this time domain is termed the "long-time" diffusion coefficient D. The natural time scale for structural evolution of colloidal systems is a^2/D_0, where $a=\sigma/2$.

We have carried out BD simulations using the model above to calculate D for a range of interaction potential forms and particle volume fractions. The time step in the simulations, h, was chosen with $h=\delta_m^2/2D_0$, where δ_m is the standard deviation of the random displacement. The value of δ_m is chosen as large as possible within the bounds of algorithm stability and accuracy (determined empirically from a trial series of simulations). We typically chose the value

$$\tau_B=0.316\times10^{-3}\sigma(m/\epsilon)^{1/2}$$

and $\delta_m=0.009\sigma$. Smaller time steps have to be adopted for steeper potentials. For the steepest potential ($n=72$) we chose $\delta_m=0.004\sigma$. The value of $h\tau_B<10^{-4}$ in these potential-based reduced units is comparable to the values chosen by other workers (e.g.,[7,4]). The simulations were typically for 10^6 time steps. For $\phi>0.4$ simulations were carried out for $N\equiv108$, 256, 500, and 864 particles and the transport coefficients in the thermodynamic limit obtained by N^{-1} extrapolation. In the $V(r)$ we set $\epsilon=k_BT$. The calculations were performed in the volume fraction range $0.1<\phi<0.5$.

The components of the stress tensor, σ, are

$$\sigma_{\alpha\beta}=\frac{\rho}{N}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}(\mathbf{r}_{\alpha ij}r_{\beta ij}/r_{ij})\frac{dV_{ij}}{dr_{ij}}\ , \tag{8}$$

where $\rho=N/V$, V is the volume of the N particles, and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. The unimportant kinetic component to the stress cannot be computed from the current algorithm.

In Fig. 1 the potentials $V(r)$ used for these computations are compared. The inverse-power potential tends to the hard-sphere interaction as $n\to\infty$. The Yukawa potential with $\lambda=8$ used by Löwen and Szamel [4] for $r>\sigma$ falls between the inverse-power potential choosing values $n=6$ and 12. In Fig. 2 we show the volume fraction ϕ ($=\pi N\sigma^3/6V$) dependence of D. We note that the values

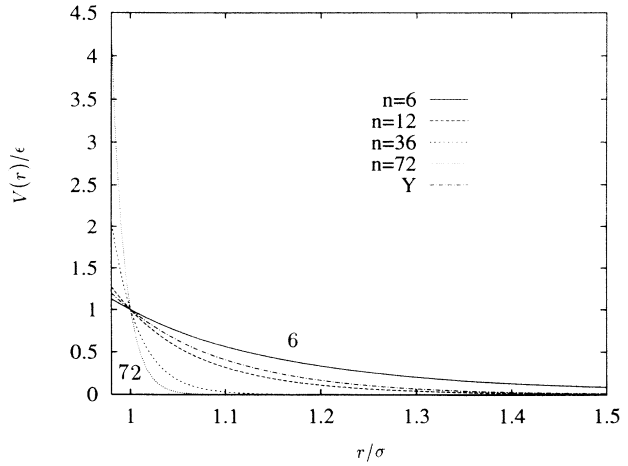

FIG. 1. The potential forms used in the simulations. The key is on the figure and Y denotes the Yukawa potential with $\lambda=8$.

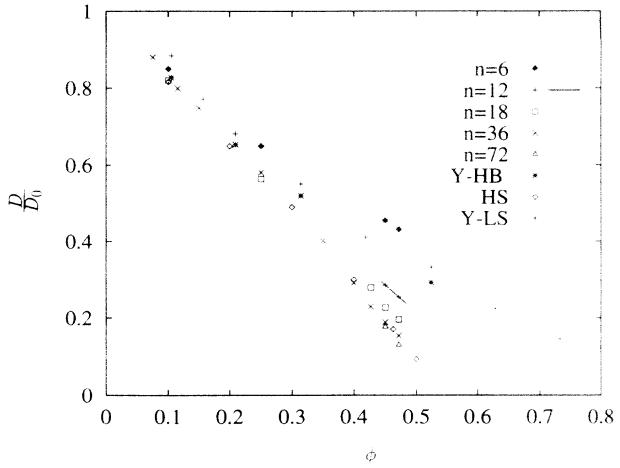

FIG. 2. The diffusion coefficients for the BD model systems as a function of particle volume fraction using the potential forms in Fig. 1. Y-HB denotes Yukawa simulations from this work and Y-LS denotes corresponding data from [4].

of D for $n=36$ and 72 are statistically indistinguishable from the hard-sphere data computed by Cichocki and Hinsen [5,6]. This suggests that the inverse-power potential for $n>36$ is a reasonable representation for the hard-sphere interaction, at least in this context. As the interaction becomes softer, then the value of D increases at fixed ϕ. We have computed D using the same Yukawa potential as Löwen and Szamel [4]. Our data follow closely but are consistently a little lower than those of [4]. For example, D/D_0 are 0.77 from [4] and 0.73 ± 0.02 from this work at $\phi=0.157$. The corresponding values at $\phi=0.314$ are 0.55 and 0.52 ± 0.01 respectively. The simulations of [4] were of duration $\sim10a^2/D_0$ and short compared with those in this work which were for typically $>100a^2/D_0$. We noticed that for simulation times

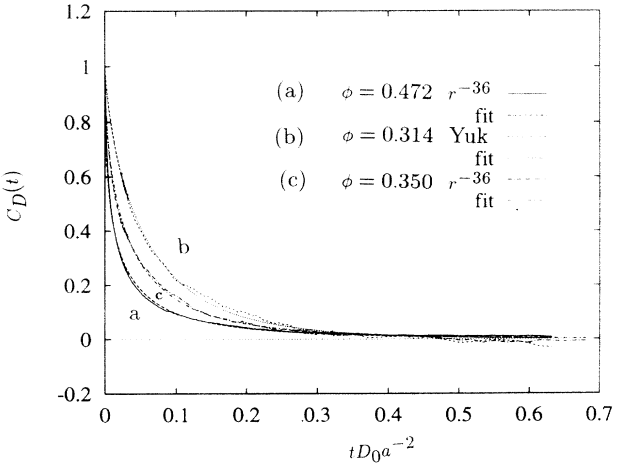

FIG. 3. The diffusion coefficient relaxation function $C_D(t)$ defined in Eq. (10) and fitted using Eq. (11) for the states (a) $n=36$, $\phi=0.472$, with a fit $\beta=0.4643$ and $\tau'=0.0162$; (b) the Yukawa potential from Eq. (5) with $\phi=0.314$, $\lambda=8$, and with a fit $\beta=0.7555$ and $\tau'=0.0588$; and (c) $n=36$, $\phi=0.350$ with $\beta=0.5895$ and $\tau'=0.0335$.

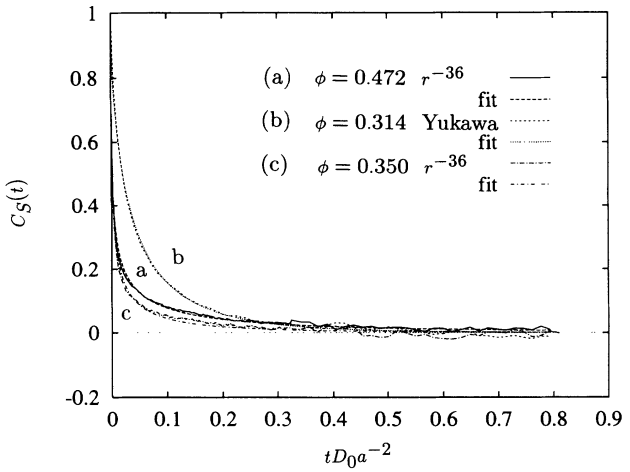

FIG. 4. As for Fig. 3 but for $C_s(t)$: (a) $n=36$, $\phi=0.472$, with a fit $\beta=0.3094$ and $\tau'=0.00475$; (b) the Yukawa potential from Eq. (5) with $\phi=0.314$ and $\lambda=8$, with a fit $\beta=0.6192$ and $\tau'=0.0369$; and (c) $n=36$, $\phi=0.350$, with $\beta=0.3549$ and $\tau'=0.0040$.

$\approx 10a^2/D_0$ we still observed significant changes in D. As for the potentials themselves, the Yukawa D fall in between those of the $n=6$ and 12 inverse-power potentials. The data follow the reasonable trend that the softer the interaction, the higher D is for the same particle volume fraction.

We define a time-dependent diffusion coefficient

$$D(t)=\frac{dW}{dt} . \tag{9}$$

The short-time diffusion coefficient in this model is D_0; then the relaxation function $C_D(t)$,

$$C_D(t)=\frac{D(t)-D}{D_0-D} , \tag{10}$$

has been defined [5,6]. We have found that our continuous potential data for $C_D(t)$ fit well to a stretched exponential form,

$$C_D(t)=\exp[-(t/\tau')^{\beta}] , \tag{11}$$

where τ' and β are adjustable parameters. Cichocki and Hinsen also observed this for their hard-sphere systems (they chose $\beta=0.5$). We find that β increases with the potential softness and decreasing density. Three examples of computed normalized $C_D(t)$ and their least squares fitted stretched exponentials are given in Fig. 3.

The shear-stress time autocorrelation function $C_s(t)$ is defined as

$$C_s(t)=\frac{N}{\rho k_B T}\langle \sigma_{xy}(0)\sigma_{xy}(t)\rangle . \tag{12}$$

where $\langle\ \rangle$ indicates that an average over time origins in Eq. (12) has been used from Levesque, Verlet, and Kurkijarvi [8] to calculate the shear viscosity of molecular liquids via a Green-Kubo relationship.

This formulation can be used in the Brownian dynam-

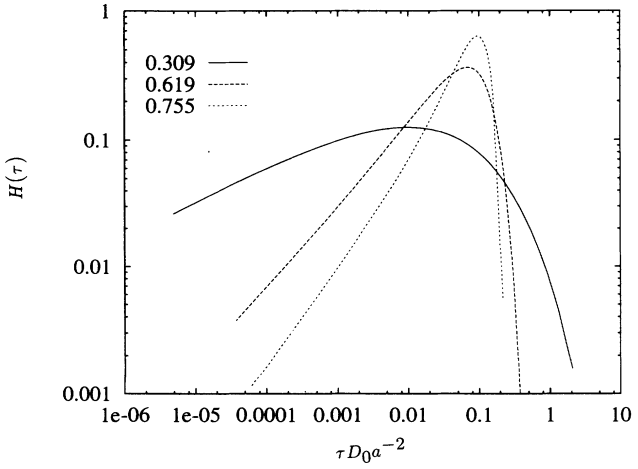

FIG. 5. Plot of the stretched exponential relaxation time spectrum distribution function for (a) $\beta=0.3094$ and $\tau'=0.00475$, (b) $\beta=0.6192$ and $\tau'=0.0369$, and (c) $\beta=0.7555$ and $\tau'=0.0588$.

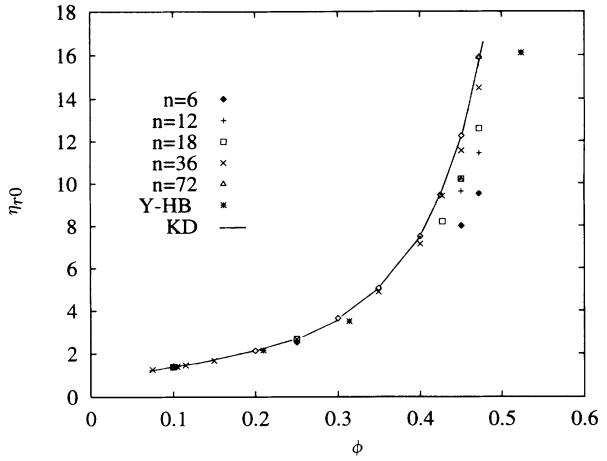

FIG. 6. The BD relative Newtonian viscosities as a function of volume fraction, ϕ, for the model systems. KD is the Krieger-Dougherty representation of the experimental data.

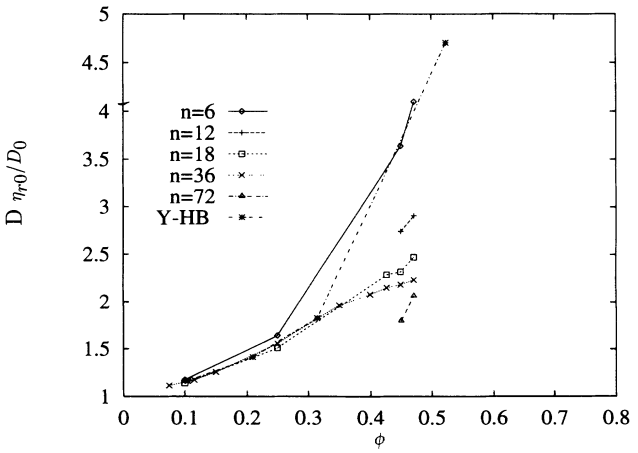

FIG. 7. The Stokes-Einstein ratio as a function of volume fraction for the model systems.

ics in the modified form

$$\eta_0=\eta_\infty+\int_0^\infty C_s(t)dt \ , \tag{13}$$

where η_0 is the Newtonian viscosity (the zero-shear limiting viscosity) and η_∞ is the so-called infinite-shear-rate viscosity. The BD algorithm and the computed stresses and viscosities omit many-body hydrodynamics, which are clearly an important factor in determining the behavior of real colloidal liquids. As in a previous study [3] we approximate the hydrodynamic contribution to the viscosity by adding on the experimental value for the infinite-shear-rate viscosity, η_∞. (The Ermak algorithm gives a value of $\eta_\infty=0$.) η_∞ is obtained using the Krieger-Dougherty (KD) formula

$$\eta_\infty/\eta_s=(1-\phi/0.71)^{-2} \ ,$$

which is a good fit to a range of experimental colloid viscosity data [9]. In Fig. 4 we show the $C_s(t)$ for some of the states used. We note again that for the $C_s(t)$ also, the stretched exponential represents these data well. Both $C_D(t)$ and $C_s(t)$ can be rewritten as a superposition of exponential relaxation functions, e.g.,

$$C_s(t)=G_\infty\int_0^\infty P_S(\tau)e^{-t/\tau}d\tau \ . \tag{14}$$

with the normalization condition $\int_0^\infty P_S(\tau)=1$. If we define $H(\tau)=\tau P_S(\tau)$, then the spectrum of relaxation times for three of the stretched exponentials computed for Figs. 3 and 4 are given in Fig. 5 using the numerical procedure developed in Ref. [10] specifically for the stretched exponential. The figure shows that as $\beta\rightarrow 1$, the distribution of relaxation times becomes more sharply peaked.

In Fig. 6 it is interesting to compare the computed η_0 using Eq. (13) with the predictions of the KD formula

$$\eta_{r0}=\eta_0/\eta_s=1/(1-\phi/0.63)^2 \ .$$

We note that as the potential becomes steeper, the relative Newtonian viscosity increases for fixed ϕ. The value of $n=36$ gives the best overall agreement with KD, which in some sense validates Eq. (13). The Stokes-Einstein relationship valid for $\phi\rightarrow 0$ is $D\eta_{r0}/D_0=1$. Although experimental D_0/D and η_{r0} show a similar volume fraction dependence, the evidence for the Stokes-Einstein relationship being valid at finite ϕ is inconclusive at present. From experiment Imhof *et al.* [11] concluded that a generalized Stokes-Einstein relationship does not hold. Adopting the experimental data for D from [12] and the KD formula for η_{r0}, we obtain a more reasonable result of $D\eta_{r0}/D_0=0.7\pm0.1$ for the experimental $0.1<\phi<0.5$ data. These BD computations give $D\eta_{r0}/D_0$ values which increase with volume fraction (see Fig. 7). The difference is caused by the experimental D being significantly lower than the BD values, presumably because of the lack of many-body hydrodynamics in the model. In some sense it is inconsistent to include hydrodynamics in the computed η_0 in Eq. (13) and yet not include it in D also. Therefore, with the present simple BD model it is expected that there should be differences with experimental trends.

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