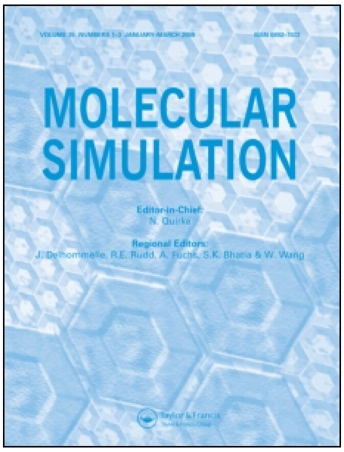

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Brownian Dynamics Simulations of Colloidal Liquids: Hydrodynamics and Stress Relaxation

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BROWNIAN DYNAMICS SIMULATIONS OF COLLOIDAL LIQUIDS: HYDRODYNAMICS AND STRESS RELAXATION

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We describe the statistical mechanics background and additional algorithmic features of a recently proposed simple mean-field Brownian Dynamics algorithm formulated to include many-body hydrodynamics, using a local density approximation for the friction coefficient. We show that the equations of motion satisfy the incompressibility of phase space. We make further developments to the model, computing the hydrodynamic effects on the shear stress relaxation function. We show that stress relaxation takes place over two well-defined regimes, in both cases with and without mean field hydrodynamics, MFH. At short times $ta^2/D_0 < 10^{-3}$, where a is the radius of the colloidal particle and D_0 is the self-diffusion coefficient at infinite dilution, decay of the stress autocorrelation function, $C_s(t)$ is essentially independent of volume fraction and does not fit to a simple analytic form. At longer times than $ta^2/D_0 < 10^{-2}$ the decay has the fractional exponential form $\sim \exp(-t^{\beta})$ with $\beta \ll 1$. The transition between these two regimes coincides with a rapid fall in the time-dependent diffusion coefficient from the so-called short-time to long-time values. We do not find any evidence for power law decay in the $C_s(t)$ as predicted by recent mode-coupling based analytical expansions.

KEY WORDS: Brownian dynamics, colloidal liquids, hydrodynamics, stress relaxation.

1 INTRODUCTION

There is considerable interest in providing a theoretical description for the dynamical behaviour of colloidal particles suspended in a liquid. A complete description is a formidable (as yet unachieved) task as these systems contain interactions between the colloidal particles that are both direct ('thermodynamic') in nature and also consist of a configuration-dependent hydrodynamic interactions that are highly coupled to the direct interactions. The latter are not well represented on a pair-wise additive basis, as the thermodynamic interactions can be in many cases. In recent years we have used a simple Brownian Dynamics algorithm, in fact the original version invented by Ermak in 1975, [1] to model colloidal dispersions. This algorithm ignores many body hydrodynamics, and while a useful reference model for colloidal liquids, can fail seriously in certain cases. Notably, it gives a value for the short-time time self-diffusion coefficient which is independent of solids volume

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fraction and is equal to that of the particle at infinite dilution [2]. In fact, the short-time self-diffusion coefficient depends strongly on volume fraction [3]. Also the algorithm exaggerates the appearance of long-range order at high shear rates down to low volume fractions (*e.g.*, 0.3 for spherical particles) [4], which in the light of recent neutron and light scattering experiments is probably unrealistic [5].

A more rigorous model for the colloidal liquid dynamics requires the incorporation of solvent-mediated many-body hydrodynamics, MBH, effects. There are a number of different methods currently being developed to introduce these effects. One approach has been to couple the forces and trajectories of N model colloidal particles through a pair-wise additive $3N \times 3N$ diffusion tensor, $\mathbf{D}$ [6]. At infinite dilution the analytic form of $\mathbf{D}$ is the Oseen tensor, which can be treated as pairwise additive. However, as colloidal particle number density increases the analytic form of $\mathbf{D}$ becomes more uncertain and the pair-wise additive approximation breaks down. Higher order terms must be considered. The close approach of the colloidal particles has to be treated in the so-called resistance formalism, in which the resistance tensor, $\mathbf{D}^{-1}$, is more closely pair-wise additive in the relative particle coordinates (see *e.g.*, [7]). A relevant adaption of this approach (especially in the context of this work) was the proposal of van Megen and Snook to use an effective volume fraction dependent two-body diffusion tensor in MBH [8].

There are other methods for treating the hydrodynamics, for example, by representing the host liquid on a lattice or a mesh using a lattice gas model or a continuum mechanics solution of the creeping flow equations [9]. Each of these methods has potential advantages for different applications, and eventually a range of different methods will probably be in wide spread use. At this stage, it should be noted that none of these are currently *ab-initio* methods, and they all require analytical and numerical approximations to provide working algorithms, the consequences of which are not yet fully established.

Although admittedly simple, Ermak's original hydrodynamics free or 'Rouse-level' algorithm has the advantage that there is an unambiguous relationship between the properties of the constituent particles and the observed macroscopic behaviour emerging from the simulation. In the MBH developments of this algorithm, described above, this 1:1 correspondence is lost. Clearly the introduction of explicit hydrodynamics couples all of the particle trajectories in a non-trivial manner. While this is formally correct, the question we pose is: is it possible to model these systems at a single particle mean-field level in a way that does not have this $N \times N$ coupling and yet still is relevant for colloid macroscopic behaviour on a certain time scale? In a recent article [10] we proposed an extension of the Ermak algorithm which attempts to achieve this. By emphasising the so-called 'long time' behaviour, and semi-empirically including the effects of the short time dynamics (through the known short-time self-diffusion coefficients of the particles at arbitrary volume fraction) we attempted to bypass the necessity to couple the Brownian forces to the diffusion/resistance tensors, which is perhaps the most time consuming step in current methods. In this manner, we have proposed a mean-field treatment of MBH cast in essentially the same form as Ermak's original algorithm. This new method has increased the range of distance and time scale over the current MBH methods. It should be noted that the proposed technique makes no attempt to follow the coupled trajectories on the time scale of a simulation timestep, as is the case for the above described MBH schemes, but instead focusses on longer time behaviour, and in this respect we consider that it is better referred to as a mean-field hydrodynamics, MFH, method. We consider that, as well as being significantly more economical to implement, that the 'scale of scrutiny' is more appropriate for many colloidal phenomenon of interest *e.g.*, rheology and aggregation which are of most industrial interest. (The short-time regime is of comparitively little interest in commercial applications.)

In this report we provide a further analysis of the statistical mechanics underpinning the new algorithm, and some issues concerning computational implementation. Also we compare the time dependent diffusion behaviour of the particles and stress time correlation functions for simulation cases in which the Rouse and MFH dynamics schemes are used. We discuss these results in the light of recent analytic predictions based on mode-coupling theory.

2 THEORY

We begin our analysis from the single particle distribution function for particle i, $P_i(\underline{r}^N)$, where $\underline{r}^N \equiv \underline{r}_1, \ldots \underline{r}_N$ and $\underline{r}_k$ is the coordinate of particle k. Initially we follow the same derivation procedure of Ermak [1] except that we allow for the possibility of a configuration dependent local self-diffusion coefficient. In the original treatment this was a constant, and equal to the infinite dilution value, D_o. Given an instantaneous force on particle i, $\underline{F}_i$ at time t and local self-diffusion coefficient, $D_i(\underline{r}^N)$, the requirement of conservation of colloid mass leads to,

$$\frac{\partial P_i}{\partial t} = \underline{\nabla}_i D_i(\underline{r}^N).\ \underline{\nabla}_i P_i - \underline{\nabla}.\left(\frac{D_i(\underline{r}^N)}{k_B T}\underline{F}_i P_i\right), \tag{1}$$

where $D_i(\underline{r}^N) = k_B T/\zeta(\underline{r}^N)$ and $\zeta_i(\underline{r}^N)$ is the local friction coefficient.

$$\frac{\partial P_i}{\partial t} = \frac{k_B T}{\zeta_i}\underline{\nabla}_i^2 P_i - \frac{1}{\zeta_i}\left(\frac{k_B T \underline{\nabla}_i \zeta_i}{\zeta_i}\right).\underline{\nabla}_i P_i - \underline{\nabla}_i.\left(\frac{1}{\zeta_i}\underline{F}_i P_i\right). \tag{2}$$

The second term in equation (2) was not present in Ermak's original work and has been termed the "spurious flow" component by van Kampen [11]. It occurs because the self-diffusion coefficient is local in space. On retaining only terms in gradients of P_i we have

$$\frac{\partial P_i}{\partial t} = \frac{k_B T}{\zeta_i}\underline{\nabla}_i^2 P_i - \frac{1}{\zeta_i}\left(\frac{k_B T \underline{\nabla}_i \zeta_i}{\zeta_i} + \underline{F}_i\right).\underline{\nabla}_i P_i. \tag{3}$$

In the above equation and below we assume $\underline{\nabla}_i \zeta_i = \underline{0}$ and $\underline{\nabla}_i . \underline{F}_i = \underline{0}$ only when involved in terms resulting in $\underline{\nabla}_i P_i$. This is an approximation and is justified on the grounds that the terms in $\underline{\nabla}_i P_i$ and $\underline{\nabla}_i^2 P_i$ dominate the diffusion equation. The Smoluchowski equation is in fact only valid with a "sufficiently" soft interaction law [12]. The effect of these two omitted terms appears in practice to be quite insignificant, as our simulation results show. The term in brackets in equation (3) is a force which can be considered as being partly thermodynamic and partly 'hydrodynamic' in origin. If we let,

$$\underline{F}_{0i} = \underline{F}_i + k_B T \zeta_i^{-1} \underline{\nabla}_i \zeta_i, \tag{4}$$

and assume that both terms in equation (4) are solely configuration dependent (not depending on the velocities) then we can think of the force field $\underline{F}_{0i}$ as being derived from an 'effective' position dependent interaction field U_0. As both the terms on the righthandside of equation (4) can be constrained to depend only on position, then we can replace them by a single term, $\underline{F}_{0i}$ derived from an interaction field, U_0. The statistical mechanical properties of this effective system are essentially those of the Rouse-level Ermak system (albeit modified by a local friction coefficient). Substitution of Eqn. (4) in Eqn. (3) gives,

$$\frac{\partial P_i}{\partial t} = \left(\frac{k_B T}{\zeta_i}\underline{\nabla}_i^2 - \frac{\underline{F}_{0i}}{\zeta_i}.\underline{\nabla}_i\right)P_i. \tag{5}$$

This is in the form,

$$\frac{\partial P_i}{\partial t} = \hat{L}P_i, \tag{6}$$

where,

$$\hat{L} = \frac{k_B T}{\zeta_i}\underline{\nabla}_i^2 - \frac{\underline{F}_{0i}}{\zeta_i}.\underline{\nabla}_i, \tag{7}$$

is the Smoluchowski operator $\hat{L}$, which has the stationary distribution function, $P_e = A\exp(-U_0/k_B T)$ and associated Langevin equation of motion,

$$m\ddot{\underline{r}}_i = \underline{F}_i^B(\zeta_i) - \zeta_i\dot{\underline{r}}_i + \underline{F}_{0i}, \tag{8}$$

The solution of which is,

$$P_i(\underline{r}_i, t, \underline{F}_{0i}) = \left(\frac{1}{4\pi D_i t}\right)^{3/2} \exp(-(\underline{r}_i - \underline{F}_{0i}t/\zeta_i)^2)/4D_i t), \tag{9}$$

for the particle i starting at time $t = 0$ with a delta function distribution function at $\underline{r} = \underline{0}$. Therefore a force field $\underline{F}_0$ combined with a local formulation for the diffusion coefficient gives an equilibrium stationary state corresponding to the interaction field U_0. Using this substitution we can treat the diffusion equation as if the local diffusion coefficients or equivalently the friction coefficients are treated as constants by the gradient operators. Therefore as,

$$\frac{\partial P_i}{\partial t} = D_i\underline{\nabla}_i^2 P_i - \frac{\underline{F}_{0i}}{\zeta_i}.\underline{\nabla}_i P_i, \tag{10}$$

we have,

$$\frac{\partial P_i}{\partial t} = \underline{\nabla}_i \cdot \left(D_i \underline{\nabla}_i \ln(P_i)P_i - \frac{\underline{F}_{0i}}{\zeta_i}P_i\right)$$

$$= \underline{\nabla}_i \cdot \left(D_i \underline{\nabla}_i \ln(P_i) - \frac{\underline{F}_{0i}}{\zeta_i} \right) P_i$$

$$= -\underline{\nabla}_i \cdot (\dot{\underline{r}}_i P_i), \tag{11}$$

where

$$\dot{\underline{r}}_i = -D_i \underline{\nabla}_i \ln(P_i) + \frac{\underline{F}_{0i}}{\zeta_i} \tag{12}$$

Phase space incompressibility is a typical condition for equilibrium stationary states. This can be written for the $N-$particle system as,

$$\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \dot{\underline{r}}_i = 0. \tag{13}$$

Substitute for $\dot{\underline{r}}_i$ from Eqn. (12) in Eq. (13) gives,

$$\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \dot{\underline{r}}_i = -\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \left(-D_i \underline{\nabla}_i \ln(P_i) + \frac{\underline{F}_{0i}}{\zeta_i} \right) \tag{14}$$

which on substituting of P_i from equation (9) into equation (14) gives,

$$\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \dot{\underline{r}}_i = -\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \left((\underline{r}_i - \underline{F}_{i0} t/\zeta_i)^2)/4D_i t - \frac{3}{2} \ln(4\pi D_i t) + \frac{\underline{F}_{0i}}{\zeta_i} \right). \tag{15}$$

This gives

$$\sum_{i=1}^{N} P_i \underline{\nabla}_i \cdot \dot{\underline{r}}_i = -\sum_{i=1}^{N} \frac{P_i}{2D_i t} (\underline{r}_i - \underline{F}_{i0} t/\zeta_i) = 0. \tag{16}$$

The latter equality arises because the distribution function of equation (9) represents random displacements about the mean $\langle (\underline{r}_i - \underline{F}_{i0} t/\zeta_i) \rangle = 0$. The expansion of P_i is solely in even powers of $(\underline{r}_i - \underline{F}_{i0} t/\zeta_i)$ therefore the term itself is a power series expansion in odd powers of $(\underline{r}_i - \underline{F}_{i0} t/\zeta_i)$, which is zero. Therefore the proposed equations of motion satisfy the incompressibility of phase space.

Turning now to the Brownian Dynamics algorithm derived from the equation of motion corresponding to the diffusion equation (3). We have,

$$\underline{r}(t+\Delta t) = \underline{r}(t) + (k_B T \zeta^{-1} \underline{\nabla} \zeta + \underline{F}(t)) \Delta t/\zeta + \Delta \underline{r}^B(\zeta(\underline{R})). \tag{17}$$

The $k_B T \zeta^{-1} \underline{\nabla} \zeta$ term in equation (17) distorts the distribution function, causing the algorithm not to generate a canonical ensemble for the configuration interaction field of U corresponding to the force field $\underline{F}$. However using,

$$\underline{F} = \underline{F}_0 - k_B T \zeta^{-1} \underline{\nabla} \zeta \tag{18}$$

then an algorithm of the Ermak form,

$$\underline{r}(t+\Delta t) = \underline{r}(t) + \underline{F}(t) \Delta t/\zeta(\underline{R}) + \Delta \underline{r}^B(\zeta(\underline{R})). \tag{19}$$

carried out with a force field $\underline{F}(t)$ will generate the canonical ensemble for the interaction field U_0 where $\underline{F}_{i0} = -\underline{\nabla}_i U_0$. Therefore the algorithm will generate states from the distribution function for an interaction field U_0. In our previous work we chose for $\zeta(\underline{R})$,

$$\zeta_i(\underline{R}) = \zeta_0\left(1 + C\sum_{j \neq i} \varepsilon\left(\frac{\sigma}{r_{ij}}\right)^m\right) \tag{20}$$

where r is the separation between the particle centres, C is a constant, m is an arbitrary exponent, and ε sets the energy scale. As yet we know little about the analytic form of ζ_i and how it depends on the configuration, $\underline{R}^N$. The analytic form adopted in equation (20) is reasonable in that (a) in the limit of zero volume fraction it goes to the correct limit, ζ_0 and increases strongly at high volume fraction, as would be expected to result from the crowding effects of the surrounding colloidal particles. The range of the interaction we expect not to extend typically beyond the first coordination shell of particles, which necessitates a large value for m in excess of ~ 12. (b) The analytic form chosen closely follows the interaction law, U_0 whose stationary distribution of states we seek to achieve in the simulations. This chosen analytic form for ζ_i, allows us to achieve this with some simplification of the equations, as revealed below.

The important point here is that we must construct a force field $\underline{F}$ to use in equation (19) to conduct the simulation that gives us a stationary distribution of states corresponding to an interaction field U_0. Therefore, for example, the simulation will produce a radial distribution function that is the same as that would be produced carrying out Ermak Rouse-level dynamics with the interaction field U_0. We can choose any form for U_0 we like, as this combined with the ζ term in equation (18) gives the F force field needed for the simulation algorithm of equation (19). It is convenient to choose for U_0 in a pair-wise additive form,

$$U_0(r,n) = \varepsilon(\sigma/r)^n, \tag{21}$$

then $\underline{F}_0(n) = -\underline{\nabla} U_0(n)$. Now as a result of eqn. (19) we also can write,

$$-k_B T \zeta^{-1} \underline{\nabla} \zeta = \zeta_0 C k_B T \zeta^{-1} \underline{F}_0(m). \tag{22}$$

At present we have no strong arguments of favour of particular values of m given a chosen value of n, so we adopt $m = n$, as this reduces somewhat the computational effort and leads to a more compact position update algorithm,

$$\underline{r}(t + \Delta t) = \underline{r}(t) + (1 + \zeta_0 C k_B T \zeta^{-1}(\underline{R}))\underline{F}_0(n, t)\Delta t/\zeta(\underline{R}) + \Delta \underline{r}^B(\zeta(\underline{R})). \tag{23}$$

It is important to emphasise that this algorithm generates a canonical ensemble for the potential field defined by particles interaction via equation (21) at equilibrium. In addition the parameter C in equation (20) and equation (23) can be adjusted to give the experimentally measured short-time self-diffusion coefficient, D_s, which fits well to the expression, [3]

$$\frac{D_s}{D_0} = (1 - 1.56\phi)(1.0 - 0.27\phi). \tag{24}$$

The relationship between the mean-square Brownian random displacements and D_s is,

$$\langle(\Delta \underline{r}^B)^2\rangle = 6k_BT\langle\zeta^{-1}(\underline{R})\rangle\Delta t = 6D_s\Delta t. \tag{25}$$

The time dependent self-diffusion coefficients, $D(t)$, were obtained from the force auto-correlation function, generalising the treatment of Åkesson and Jönsson, [14]

$$D(t) = D_0 - \frac{1}{3}\int_0^t (1 - t'/t)\langle(F(0)/\zeta(0))\cdot(F(t')/\zeta(t'))\rangle dt'. \tag{26}$$

The long-time self-diffusion coefficient, D_L, (*i.e.*, $D(t \to \infty)$) fitted to the experimental data [15] [16] between $0.04 < \phi < 0.5$ is,

$$\frac{D_L}{D_0} = 0.8(1.00 - 1.15\phi)(1.00 - 2.00\phi). \tag{27}$$

For the inverse power potentials considered here, the interaction energy, pressure and mechanical properties are trivially related [18]. The average interaction energy per particle, u, defines all first order thermodynamic quantities and is given by,

$$u = \frac{1}{2N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle U_{0ij}(r_{ij})\rangle. \tag{28}$$

For example, the osmotic pressure is given by,

$$P = n\rho\langle u\rangle/3. \tag{29}$$

What rôle does the so-called spurious flow term have on the dynamics of the model colloidal particles? As was shown in ref. [10] omission of the hydrodynamic force term causes the particles to approach too closely on average. Therefore the consequence of simply modifying the Ermak algorithm by introducing a local friction coefficient is to drive the particles more closely together. The hydrodynamic interaction term provides an additional repulsive 'force' that keeps the particles further apart, and in the process re-establishes the correct distribution function for the given interaction potential (labelled U_0 above). This additional term can be viewed as being derived from an effective hydrodynamic potential field, U_{hyd}, corresponding to an effective energy per particle i,

$$U_{\mathrm{hyd},i} = k_BT\ln(\zeta_i/\zeta_0). \tag{30}$$

The corresponding force is

$$F_{\mathrm{hyd},i} = -\underline{\nabla}\cdot U_{\mathrm{hyd},i} = -k_BT\zeta_i^{-1}\underline{\nabla}\cdot\zeta_i. \tag{31}$$

From this can be computed the hydrodynamic stress tensor, $\underline{\sigma}_{\mathrm{hyd}}$, for this model. As

$$\zeta_i(\underline{R}) = \zeta_0\left(1 + C\sum_{j\neq i} U_{0ij}(r)\right), \tag{32}$$

then

$$\underline{\sigma}_{\mathrm{hyd}} = \frac{k_BTC\zeta_0\rho}{N}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}(\underline{r}_i\zeta_i^{-1} - \underline{r}_j\zeta_j^{-1})\frac{\underline{r}_{ij}}{r_{ij}}U'_{0ij}, \tag{33}$$

following the procedure given in Allen and Tildesley [13]. The form of Eqn. (33) has the unusual term ($\underline{r}_i/\zeta_i - \underline{r}_j/\zeta_j$), which might suggest a dependence of the value of $\underline{\sigma}_{\text{hyd}}$ on the origin of the coordinate system. Let $\underline{r}_i = \underline{r}'_i + \underline{\Delta}$ and $\underline{r}_j = \underline{r}'_j + \underline{\Delta}$ represent a shift in the coordinate system by $\underline{\Delta}$. On substitution of these transformations in equation (33) we have,

$$\underline{\sigma}_{\text{hyd}} = \frac{k_B T C \zeta_0 \rho}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\underline{r}_i \zeta_j - \underline{r}_j \zeta_i) \frac{\underline{r}_{ij}}{r_{ij} \zeta_i \zeta_j} U'_{0ij}, \tag{34}$$

and

$$\begin{aligned} \underline{\sigma}_{\text{hyd}} = {} & \frac{k_B T C \zeta_0 \rho}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\underline{r}'_i \zeta_j - \underline{r}'_j \zeta_i) \frac{\underline{r}_{ij}}{r_{ij} \zeta_i \zeta_j} U'_{0ij} \\ & + \frac{k_B T C \zeta_0 \rho}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \underline{\Delta} (\zeta_i - \zeta_i) \frac{\underline{r}_{ij}}{r_{ij} \zeta_i \zeta_j} U'_{0ij}, \end{aligned} \tag{35}$$

The last term in Eqn. (35) will be zero on average on the grounds of symmetry, and consequently Eqn. (33) is independent of the origin of the coordinate system. The first term in Eqn. (35) is non-zero and is **not** trivially related to the thermodynamic stress (see below).

The thermodynamic contribution to the stress tensor, $\underline{\sigma}_{\text{therm}}$, in this model is given as usual as for any molecular system term

$$\underline{\sigma}_{\text{therm}} = \frac{\rho}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} (\underline{r}_{ij} \underline{r}_{ij} / r_{ij}) U'_{0ij}, \tag{36}$$

The total stress tensor is given by,

$$\underline{\sigma} = \underline{\sigma}_{\text{therm}} + \underline{\sigma}_{\text{hyd}} \tag{37}$$

The Newtonian viscosity and linear response dynamic moduli are obtained using the shear-stress time autocorrelation function, $C_s(t)$ defined as

$$C_s(t) = \frac{N}{\rho k_B T} \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \tag{38}$$

where $\langle \cdots \rangle$ indicates an average over time origins. The Green-Kubo formula can be used to obtain the Newtonian viscosity of the model colloidal liquid through

$$\eta_0 = \int_0^\infty C_s(t) dt. \tag{39}$$

3 COMPUTATIONAL DETAILS

We consider a cubic simulation cell interacting with an inverse power potential given in (21) with the values, $\varepsilon = k_B T$ and $n = 18, 36$ for this study. This interaction would represent a stabilised colloidal particle and is sufficiently hard to be equivalent to a hard-sphere system for many purposes. The number of molecules in the BD cell, N, is 256. The computations were carried out using a neighbourhood table list to speed up the search for interacting particles. Interactions were truncated for $r_{ij} > 1.3\sigma$ ($n = 36$) and $r_{ij} > 2.0\sigma$ ($n = 18$) because of the rapidly decaying nature of the pair potential interactions. The volume fraction, $\phi = \pi N\sigma^3/V$, where V is the volume of the simulation cell, is V. The volume fractions chosen for our simulations, 0.3403 and 0.450 are well within the fluid phase for the $n = 36$ and $n = 18$ fluids. We have for example the fluid-solid coexistence volume fractions of 0.494 – 0.534 for $n = 30$ and 0.488 – 0.534 for $n = 50$ [19]. Calculated properties are quoted in particle based reduced units, *e.g.*, σ for length, ε for energy, and $\sigma\,(m/\varepsilon)^{1/2}$ for time, where m is the mass of the model colloid particle. A summary of the system of units in the BD program is given in Appendix A.

The random displacement in the x–direction is given by the self-diffusion coefficient. Choosing a density independent reference value, the infinite-dilution self-diffusion coefficient, D_0,

$$\langle \delta_x^2 \rangle = 2\Delta t D_0(T), \tag{40}$$

where $D_0\,(T) = k_B T/\zeta$. The time step, Δt is maintained constant during each simulation (although there is no need to). We first select a desired root mean square displacement for each cartesian component, δ_m. This parameter is chosen to be small enough to prevent catastrophic overlap of particles and unrealistically large interaction forces, and yet large enough so that a sufficient region of phase space is explored without distorting the statistical averages. Equating $\langle \delta_m^2 \rangle$ to $\langle \delta_x^2 \rangle$ gives a formula for the time step,

$$\Delta t = \delta_m^2/2D_0(T). \tag{41}$$

We chose the value of $\langle \delta_m^2 \rangle$ on an empirical basis and investigated the dependence of the calculated properties on this value. In Table 1 we use u to assess the optimum value of the time step for the parameters: $N = 256$, $n = 36$, $\phi = 0.3403$ and $T^* = 3.0$. First at $\delta_m = 0.007$ we have u values that are statistically indistinguishable between Rouse-level and MFH simulation methods, supporting our assertion that the two algorithms produce the same ensemble for the interaction field U_0. With $\delta_m = 0.015$ the Rouse algorithm is not stable, whereas the MFH algorithm is stable although it shows some drift upwards in the value of u, which is significant at

Table 1 Average interaction energy per particle u calculated using equation (28) . Key: (a) Rouse denotes the Ermak algorithm of equation (23), (b) MFH denotes a MFH hydrodynamics simulation carried out using equation (23) with $C = 3.795$. Key: $T^* = 3.0$, $\phi = 0.3403$ $N = 256$. Standard errors in the last digit are given in brackets. A (–) indicates that the algorithm was not stable. We have, D_0 (1) $\equiv D_0$ ($T^* \equiv 1.0$).

δ_m/σ	$\Delta t D_o(1)a^{-2}$	u_{Rouse}	u_{MFH}
0.007	3.3×10^{-5}	0.879(4)	0.882(4)
0.010	6.7×10^{-5}	0.884(2)	0.889(4)
0.015	1.5×10^{-4}	–	0.895(2)
0.020	2.7×10^{-4}	–	0.919(2)

$\delta_m = 0.020$. Therefore the value $\delta_m = 0.007$ is a good compromise value, which corresponds to a time step of $\Delta t = 3.3 \times 10^{-5} a^2/D_0 (T^* = 1)$.

4 RESULTS AND DISCUSSION

In recent years there has been much interest in the analytic form of the time correlation functions in colloidal liquids. Based on a mode-coupling approximation Cichocki and Felderhof have predicted a power law time dependence to the time dependent self-diffusion coefficient, $D(t)$ which in the absence of hydrodynamic interactions goes as $\sim t^{1/2}$ for $t \to 0$ in the short-time limit and $\sim t^{-3/2}$ for $t \to \infty$ in the long-time limit [20]. They also assert that the shear stress relaxation function decays as $\sim t^{-7/2}$ asymptotically with time [21]. This differs from our previous results in which we found that the $C_s(t)$ can be represented very well by a so-called 'fractional' or 'stretched' exponential (except at very short times where this analytic form underestimates the simulation $C_s(t)$) [18]. The stretched exponential has the analytic form

$$C_s(t) = G_\infty \exp(-(t/\tau')^\beta), \tag{42}$$

where G_∞ is the infinite frequency shear rigidity modulus. The parameters τ' and β were found in that study by a least squares fit procedure. In this report we return to this discrepancy, making a more detailed examination of our time correlation functions. The difficulty with the previous least squares analysis is that, any departures from the presumed behaviour (*e.g.*, at very short time) are not characterised. Nor does it discern whether alternative functional forms apply in different regions of time. Another approach that does not have these deficiencies is to use a graphical manipulation of the computed **normalised** (*i.e.*, $C_{sn}(0) = 1$) functions. (This procedure has been suggested previously, *e.g.*, [22].) For an exponential decay $C_{sn}(t) = \exp(-t/\tau)$, for example, we have that $\ln(C_{sn}(t))$ is linear with slope $-\tau^{-1}$ when plotted against t. For a stretched exponential $\ln(-\ln(C_{sn}(t)))$ has a slope of β and an intercept of $-\beta\ln(\tau')$. An algebraic decay $C_{sn}(t) = At^{-\alpha}$ when plotted as $\ln(C_{sn}(t))$ *vs.* $\ln(t)$ has a slope of $-\alpha$. Therefore a graphical representation of these computed functions should indicate clearly which of these analytic forms (if any) the data conforms to.

In Figure 1 we show a $\ln(-\ln(C_{sn}(t)))$ *vs.* $\ln(t)$ plot for three Rouse-level state points (a) $\phi = 0.3403$ $n = 36$, (b) $\phi = 0.450$ $n = 36$, and (c) $\phi = 0.3403$ $n = 18$. These are the three upper curves at long time on the figure. At times less that 10^{-3} a^2/D_0 we found that for the same value of n all the curves coincide. (We were not able to find a simple analytic functional form that fitted this part of the curve.) There then follows a transition region for longer time which develops for $t > 10^{-2}$ a^2/D_0 into a good straight line, indicating the fractional exponential behaviour. This linear behaviour is the same for all volume fractions and the two potentials. If the correlation functions were power law analytic we would expect a linear curve when $\ln(C_{sn}(t))$ is plotted *vs.* $\ln(t)$. The three correlation functions are replotted on the same figure in this form, as the three lower curves at long time. There is a continouous decrease in slope with increasing time. At no point can a straight line justifiably be ascribed to

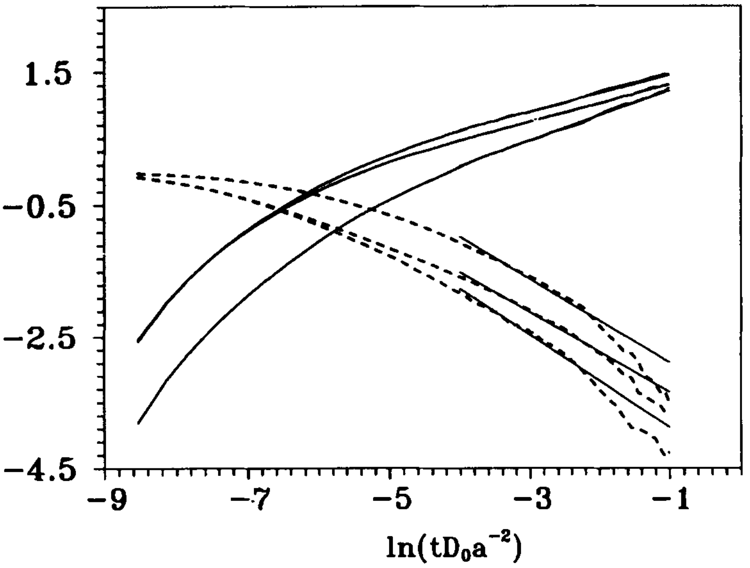

Figure 1 Volumes fraction and potential steepness dependence of the Rouse-level BD normalised shear stress autocorrelation functions, $C_{sn}(t)$. The three upper curves at long time (solid lines) are ln $(-\ln(C_{sn}(t)))$ *vs.* ln (t) from top to bottom: (a) $n = 36$ and $\phi = 0.3403$, (b) $n = 36$ and $\phi = 0.450$, and (c) $n = 18$ and $\phi = 0.450$. A linear regression was made in the interval $[-4, -1]$. The lower dashed curves are the same data plotted as ln $(C_{sn}(t))$ *vs.* ln (t), in the reverse order from top to bottom.

these curves. Therefore we maintain our previous assertion that at long times the shear stress autocorrelation function decays as a fractional exponential.

There appears to be two quite distinct regimes in the stress relaxation process. The first is essentially independent of density and presumably corresponds to the equivalent of the 'free-flight' short time regime observed in molecular systems. Although here the dynamics is always diffusive, even in the $t \rightarrow \Delta t$ limit. (Phenomena on time scales $<\Delta t$ are beyond the scope of the current algorithm.) In Figure 2 we compare the decay of D (t) with ln $(-\ln$ $(C_{sn}(t)))$, *vs.* ln (t). The volume fractions 0.3403 and 0.450 using $n = 36$ are considered. It shows that $D(t)$ still has an appreciable proportion left to decay by the time the stress autocorrelation function has entered the fractional exponential regime (upper linear regime on the figure). Therefore we can only ascribe at this stage the linear regime in the stress autocorrelation function to be associated with the *approach* towards the long-time asymptote of $D(t)$.

In Figure 3 we show the thermodynamic contribution to $C_{sn}(t)$ for the Rouse and MFH models at the $\phi = 0.3403$ and 0.450 states with $n = 36$. Interestingly, although both manifest the same two-time regime behaviour, the MFH case is more clearly linear in the first regime, so that the MFH model appears to produce two regimes of fractional exponential behaviour.

In Figure 4 the stress autocorrelation function derived from a MFH simulation with the parameters: $\phi = 0.3403$, $n = 36$, $N = 256$, $C = 3.80$ and $T^* = 1.0$ is given. This value for C gives a computed $D_s/D_0 = 0.42$ which is statistically the same as the experimental value from eqn. (24). As revealed in the figure, the

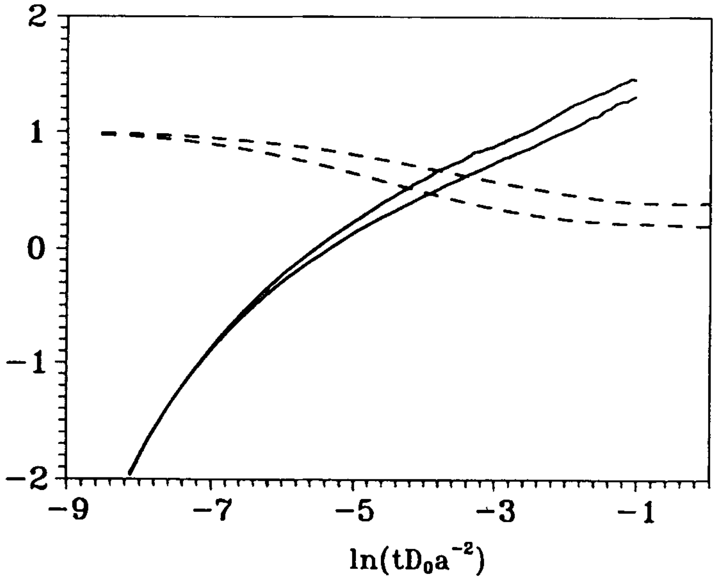

Figure 2 A comparison between ln $(-\ln(C_{sn}(t)))$ (solid lines) and (dashed lines) $D(t)$ *vs.* ln (t) for the Rouse-level $n = 36$ data. Key: Upper solid curve (upper dashed curve) $\phi = 0.3403$, and lower solid curve (lower dashed curve) $\phi = 0.450$.

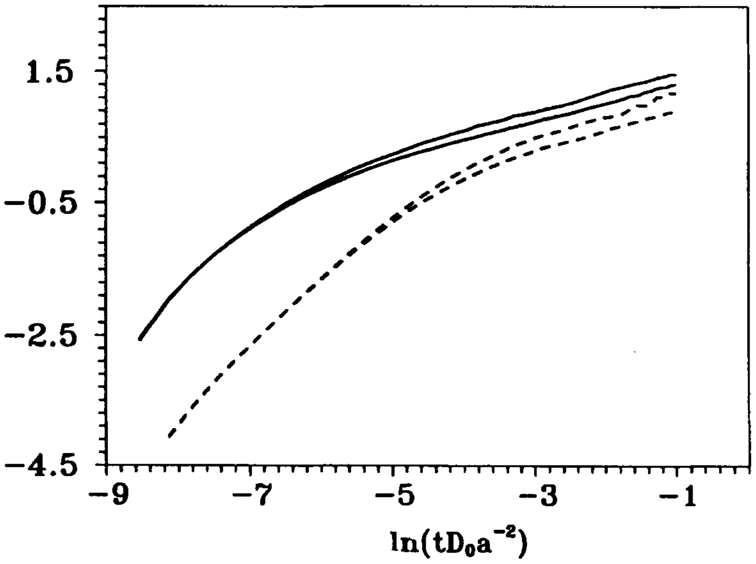

Figure 3 A comparison between Rouse-level (solid lines) and MFH (dashed lines) ln $(-\ln(C_{sn}(t)))$ *vs.* ln(t) for $n = 36$ and at two volume fractions 0.3403 (upper solid and dashed lines) and 0.450 (lower solid and dashed lines).

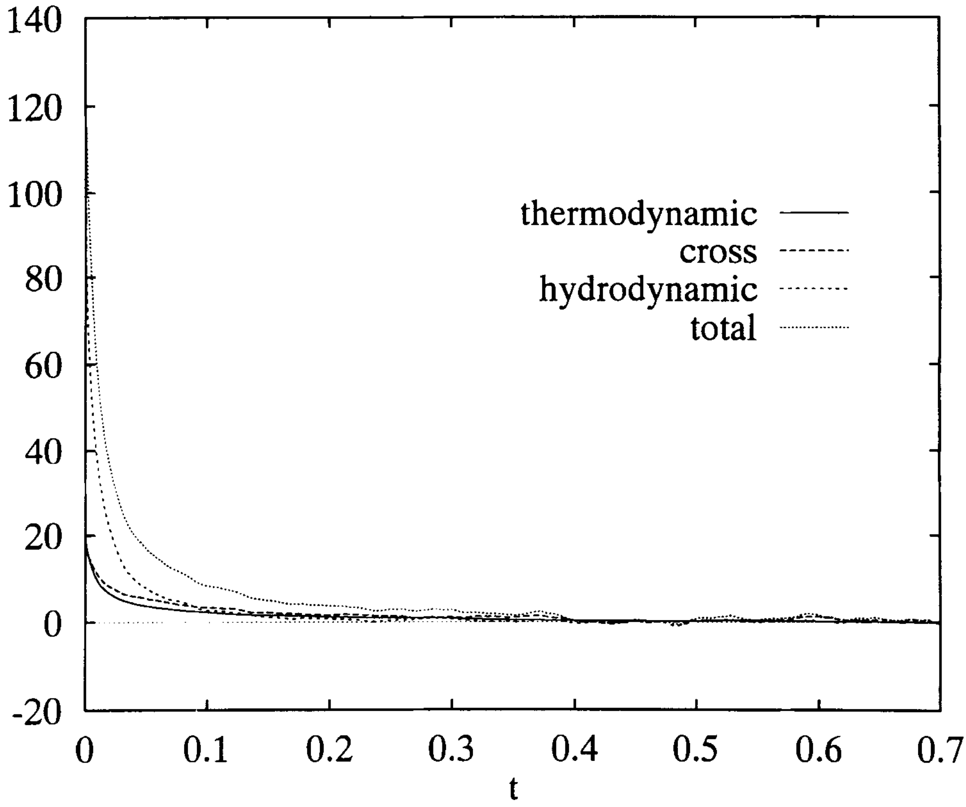

Figure 4 The shear stress autocorrelation function derived from a MFH simulation with the parameters: $\phi = 0.3403$, $n = 36$, $N = 256$, $C = 3.80$ and $T^* = 1.0$. The three components (thermodynamic, hydrodynamic and cross) are indicated on the figure.

hydrodynamic contribution, $\langle \sigma_{\mathrm{hyd},xy}(0)\ \sigma_{\mathrm{hyd},xy}(t)\rangle$ dominates over the thermodynamic $\langle \sigma_{\mathrm{therm},xy}(0)\ \sigma_{\mathrm{therm},xy}(t)\rangle$, and cross, $2\langle \sigma_{\mathrm{therm},xy}(0)\ \sigma_{\mathrm{hyd},xy}(t)\rangle$ contributions. The integrated viscosity is $\eta_0/\eta_s = 8.5\ (1)$, while the experimental value from the Krieger-Dougherty equation is 4.7. One of the deficiencies of the current algorithm is that the local friction coefficient is optimised for the self-diffusion behaviour, and the definition of the shear stress and hence viscosity is rather poorly specified by comparison. The algorithm makes no attempt to follow the solvent flow patterns in the host liquid phase. Therefore it is to be expected that the shear stress of the system is deficient. This is an area that needs improving in future developments of the model.

5 CONCLUSIONS

One of the current goals of discrete particle simulation is to generate a realistic time evolution of a dense suspension in a computationally efficient manner. Here we have continued our development of a new approach to this difficult problem. Following traditional Brownian Dynamics techniques, we include non-trivial hydrodynamic effects. Rather than through a poorly converging expansion of the Oseen far-field limit, we use a semi-empirical dense fluid reference state chosen to achieve the correct short-time diffusion behaviour.

We have established the formulae for the stress tensor in these systems, and computed the components from the hydrodynamic and thermodynamic parts to the shear stress autocorrelation function. We have also investigated further the time dependence of the shear stress autocorrelation function, confirming our previous observation that for times in excess of $t > 10^{-2}\ a^2/D_0$ the decay is of the fractional exponential form and not power law in time.

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APPENDIX A

The program units for length (L), mass (M) and energy (E) are $L^* = L/\sigma$, $M^* = M/m$ and $E^* = E/\varepsilon$ where σ and ε are defined in the pair potential of eqn. (21). Mass is the mass of the colloidal particle. Mass plays no significant role in a BD program in the creeping flow limit, which is the case here. It remains to express the solvent related properties in these basic units. The friction coefficient, $\zeta_0 = 3\pi\sigma\eta_s$ is the viscosity of the solvent. Then $\zeta_0^* = 3\pi\sigma^*\eta_s^* = 3\pi\eta_s^*$. It is convenient to engineer that $\zeta_0^* = 1$ which means that $\eta_s^* = 1/3\pi$.

The infinite dilution value for the self-diffusion coefficient, $D_0^*\ (T) = k_BT/\zeta_0^*$. Therefore in reduced units, $D_0^*(T) = k_BT/\zeta_0^* = T^*$. If we define $D_0^*\ (T^* = 1) = D_0^*\ (1)$ then $D_0^*(1) = 1$. From this a reference reduced relaxation time can be defined as $\tau_r = a^2/D_0\ (1)$ where a is the radius of the colloidal particle. We have $\tau_r^* = a^{*2}/D_0^*\ (1) = 1/4$. The particle-based unit for time is $\sigma\ (m/\varepsilon)^{1/2}$ and therefore $\tau_r = 4^{-1}\ \sigma\ (m/\varepsilon)^{1/2}$. An alternative reduced time and self-diffusion coefficient would be also to scale out the temperature as well. However, this would complicate the interpretation of situations in which temperature effects are of importance and non-trivial, such as in the study of flocculation.

References

[1] D. L. Ermak, "A Computer simulation of charged particles in solution. I. Technique and equilibrium properties", *J. Chem. Phys.*, **62**, 4189 (1975).

[2] D. M. Heyes and A. C. Brańka, "Molecular and Brownian Dynamics Simulations of Self-diffusion in Inverse Power Fluids", *Phys. Chem. Liqu.*, **28**, 95 (1994).

[3] R. A. Lionberger, and W. B. Russel, "High frequency modulus of hard sphere colloids", *J. Rheol.*, **38**, 1885 (1994).

[4] P. J. Mitchell, D. M. Heyes and J. R. Melrose, "Brownian-dynamics simulations of model stabilised colloidal dispersions under shear", *JCS Farad. Trans.*, **91**, 1975 (1995).

[5] P. Lindner, I. Markovič, R. C. Oberthür and A. R. Rennie, "Small angle neutron scattering studies of polymer latices under sheared conditions", *Progr. in Coll. and Polym. Sci.*, **76**, 47 (1988).

[6] D. L. Ermak and J. A. McCammon, 'Brownian dynamics with hydrodynamic interactions', *J. Chem. Phys.*, **69** 1352 (1978).

[7] L. Durlofsky, J. F. Brady and G. Bossis, "Dynamic simulation of hydrodynamically interacting particles", *J. Fluid. Mech.*, **180**, 21 (1987).

[8] W. van Megen and I. Snook, 'Brownian dynamics simulation of concentrated charge-stabilized dispersions', *J. Chem. Soc. Faraday Trans.*, **80**, 383 (1984).

[9] X. F. Yuan, and R. C. Ball, "Rheology of hydrodynamically interacting concentrated hard disks", *J. Chem. Phys.*, **101**, 9016 (1994).

[10] D. M. Heyes "Many-body hydrodynamics brownian simulations of viscosity and self-diffusion of near hard-sphere colloidal liquids", *J. Phys.: Condensed Matter*, submitted.

[11] N. G. van Kampen, 'Stochastic processes in physics and chemistry' (North-Holland, 1981, Amsterdam). pp 291.

[12] W. Hess and R. Klein, "Generalized hydrodynamics of systems of Brownian particles", *Adv. in Phys.*, **32**, 173–283 (1983) (see pp. 274).

[13] M P. Allen and D. J. Tildesley, 'Computer Simulation of Liquids' (Clarendon Press, 1987, Oxford) pp. 48.

[14] Åkesson, T. and Jönsson, B. "Brownian dynamics simulation of interacting particles", *Molec. Phys.*, **54**, 369 (1985).

[15] J. W. Goodwin, and R. H. Ottewill, "Properties of concentrated dispersions", *JCS Farad. Trans.*, **87**, 357 (1991).

[16] M. Medina-Noyola, "Long-time self-diffusion in concentrated dispersions", *Phys. Rev. Lett.*, **60**, 2705 (1988).

[17] H. Löwen, "Melting, freezing and colloidal suspensions", *Phys. Rep.*, **237**, 249 (1994).

[18] D. M. Heyes and P. J. Mitchell, "Self-diffusion and viscoelasticity of dense hard-sphere colloids", *JCS Farad. Trans*, **90**, 1931 (1994).

[19] R. Agrawal and D. A. Kofke, "Thermodynamic and structural properties of model systems at solid-fluid coexistence. I Fcc and bcc soft spheres", *Mol. Phys.*, **85**, 23 (1995).

[20] B. Cichocki and B. U. Felderhof, 'Time-dependent self-diffusion coefficient of interacting Brownian particles', *Phys. Rev.*, **A44**, 6551 (1991).

[21] B. Cichocki and B. U. Felderhof, 'Linear viscoelasticity of colloidal suspensions', *Phys. Rev.*, **A46**, 7723 (1992).

[22] C. P. Lindsey and G. D. Patterson, "Detailed comparison of the Williams-Watts and Cole-Davidson functions", *J. Chem. Phys.*, **73**, 3348 (1980).