Structure factor of charged colloidal suspensions using Brownian–dynamics simulation: Comparison of Yukawa and Sogami pair potentials

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Abstract. Static structure factors $S(Q)$ are obtained for dilute charged colloidal systems using Brownian dynamics simulation method for the widely used screened Coulomb repulsive Yukawa potential and the recently proposed Sogami pair potential. The latter potential has, in addition to the usual repulsive part, an attractive term which is necessary to understand the reentrant phase transition reported in these colloids. It is shown for the first time that $S(Q)$ obtained using the Sogami potential for parameters favourable for liquid-like order agrees well with that measured experimentally. Thus it appears that the Sogami potential explains features of a homogeneous liquid as well as phase separated states, whereas Yukawa potential does not.

1. Introduction

Electrostatically stabilized aqueous colloidal systems can develop structural orders similar to those in atomic liquids (Pusey 1979; Tata *et al* 1987), crystalline solids (Williams and Crandall 1974) and even glasses (Pusey and van Megen 1987; Lindsay and Chaikin 1982; Kesavamoorthy *et al* 1988) when suitably deionized. The unique feature of these systems is that one can alter the strength and range of interparticle interaction simply by changing the impurity ion concentration n_i and the particle (also called polyball or macroion) concentration n_p, making them model systems to study the co-operative behaviour in condensed matter. It is widely believed that the particles interact predominantly via repulsive screened Coulomb Yukawa potential $U(r) \simeq \exp(-Kr/r)$, (for a review, see Castillo *et al* 1984). Here K is the inverse Debye screening length. There also exists a primary minimum (Castillo *et al* 1984) in the inter particle interaction due to London-van der Waals attraction, which gives rise to irreversible aggregation (flocculation), when n_i is large. However, for suspensions with low n_i this minimum is not important due to Coulomb barrier. So far Yukawa potential is used to explain ordering phenomena in colloids. Using this potential it has been shown that the static structure factors for liquid like ordered suspensions, computed using rescaled-mean spherical approximation (RMSA) (Hansen and Hayter 1982) and hypernetted chain (HNC) approximation (Schaefer 1977) agree well with the experiments (Hartl *et al* 1983; Tata *et al* 1986). The Monte Carlo (MC) (van Megen

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and Snook 1977) and Brownian dynamics (BD) simulations (Gaylor *et al* 1981) have been done with Yukawa potential to calculate static and dynamic properties of these colloids and the results agree with the light scattering experiments. Recently Arora *et al* (1988) have observed a reentrant phase transition in these colloids, wherein a non-interacting homogeneous suspension phase separates into a rare (low polyball concentration) and a dense (high polyball concentration) phases as the impurity concentration n_i is reduced. This suspension once again becomes homogeneous (with liquid or crystalline-like order) on further reduction of n_i. This phenomena cannot be explained on the basis of the pure repulsive interparticle interaction. Since a purely repulsive interaction between particles confined in a given volume cannot lead to inhomogeneous phases except the crystalline-liquid transition observed in a system of hard spheres, an attractive part in $U(r)$ is a must. Based on free energy calculation, Arora *et al* (1988) showed that the observed phase transition can be understood by considering Sogami potential (Sogami 1983; Sogami and Ise 1984) which has the usual screened Coulomb repulsion and also an attractive part leading to a secondary minimum. The formalism of Sogami and Ise (1984) has been questioned by Overbeek (1987), subsequently Ise *et al* (1988a) have in turn shown flaws in the treatment of Overbeek. A number of other experimental results viz. the coexistence of ordered and disordered phases (Ise 1986), observation of Ostwald ripening in the growth of colloidal crystals (Ito *et al* 1989) and the existence of stable voids in colloidal crystals (Ise *et al* 1988b) also suggest the existence of a secondary minimum in the effective pair potential (Ise *et al* 1988).

As pointed out earlier, apart from the phase separated states colloidal suspensions also exhibit homogeneous liquid-like and crystalline-like ordered states. To confirm whether Sogami potential leads to these structural orders (for some physically reasonable parameters), we obtain $S(Q)$ of a suspension of colloidal particles interacting via Sogami potential. As analytical calculations of $S(Q)$ using Sogami potential on the lines similar to that of RMSA (routinely used for Yukawa potential) is difficult, we use BD simulation to obtain pair correlation function ($g(r)$) and mean square displacement ($r^2(t)$). $S(Q)$ is obtained by Fourier transforming $g(r)$. Yukawa potential is also used in simulation for the sake of comparison. $S(Q)$ obtained using Sogami potential agrees equally well with the experimental $S(Q)$. MC simulations are also carried out for the same parameters and compared with the BD results.

This paper is organized as follows. In §2 we present both Yukawa and Sogami pair potentials with a brief discussion of their origin. Details of BD simulation is presented in §3. Section 4 deals with the results and discussion. We end this paper with conclusions given in §5.

2. Pair potentials

2.1 *Yukawa potential*

For the aqueous monodispersed colloidal system consisting of polystyrene spheres (polyballs) of radius a, charge Ze, the screened Coulomb Yukawa pair potential between ith and jth particles is given by (Verwey and Overbeek 1948)

$$U_Y(r_{ij}) = Z^2 e^2 [\exp(Ka)/(1 + Ka)]^2 \exp(-Kr_{ij})/\varepsilon r_{ij} \tag{1}$$

where K is inverse screening length given by

$$K^2 = 4\pi e^2 \left(n_p Z + \sum_\beta n_\beta Z_\beta^2 \right) \bigg/ \varepsilon k_B T. \qquad (2)$$

The first term in (2) arises due to $n_p Z$ counter-ions coming from particles with concentration n_p and the second term is the contribution of the impurity ions of βth type with the concentration n_β and charge eZ_β. In all our calculations the impurities are considered as monovalent ($Z_\beta = \pm 1$), hence $n_i = \sum_\beta n_\beta$. ε is the dielectric constant of the medium and taken to be equal to 78·0 at room temperature $T(=298°\,\text{K})$. A detailed discussion on the range of validity of this potential is given in the recent work of Robbins *et al* (1988).

2.2 *Sogami potential*

For the system considered above Sogami obtained an effective pair potential $U_s(r)$ given by (Sogami 1983; Sogami and Ise 1984)

$$U_s(r_{ij}) = Z^2 e^2 (\sinh Ka/Ka)^2 [A \exp(-Kr_{ij})/r_{ij} - B \exp(-Kr_{ij})]/\varepsilon \qquad (3)$$

where $A = 1 + Ka \coth(Ka)$, $B = K/2$ and K is given by (2).

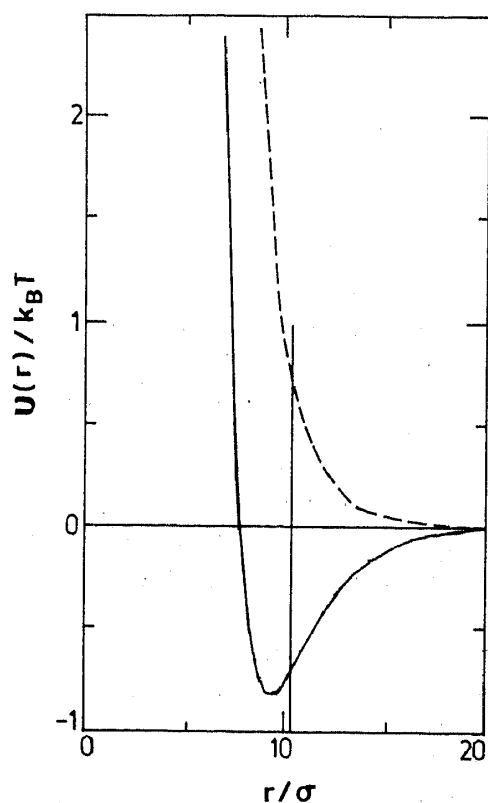The attractive term leads to a secondary minimum in $U_s(r)$ whose position ($R_{\min}$)

Figure 1. Pair potential $U(r)$ in units of $k_B T$ vs distance of separation r in units of σ. Continuous line is Sogami potential for $\sigma = 0.109\,\mu\text{m}$, $n_p = 1.33 \times 10^{12}\,\text{cm}^{-3}$, $Z = 600$ with $n_i = 1.75 \times 10^{15}\,\text{cm}^{-3}$ and dotted line is Yukawa potential for $n_i = 2.1 \times 10^{15}\,\text{cm}^{-3}$ with n_p and Z same as above. The vertical line is at interparticle separation $2a_s = 10.35\sigma$.

depends on n_p and n_i and is given by

$$R_{min} = [C + 1 + \{(C + 1)(C + 3)\}^{1/2}]/K \tag{4}$$

where $C = A - 1$. Sogami potential has been derived from the Gibbs free energy which takes into account counterion-counterion and polyball-polyball interaction. The degrees of freedom of counterions are integrated out to give an effective pair potential $U_s(r)$. Figure 1 shows the $U_y(r)$ and $U_s(r)$ used in the calculation. Marked on figure 1 is the line at $r = 2a_s$. It can be noted that the interaction at $r = 2a_s$ is repulsive in one case and attractive in the other case.

3. Simulation details

Simulations at constant volume and constant temperature are performed for a colloidal system with particle density n_p. N particles are taken in a cubic cell with cube length L given by $L^3 = N/n_p$. The periodic boundary conditions are used to remove the surface effects and simulate an infinite system. The number of particles chosen in the simulation were $N = 128$ and 250. The results are same for both the values, consistent with the earlier observation that $N > 100$ does not change the results (Gaylor et al 1981). All the results presented in this paper correspond to $N = 250$. The potential is cut-off at $r = L/2$ at which $U(r = L/2) \leqslant 10^{-4} k_B T$, which is comparable to the cut-off value used in simulation of Lennard-Jones systems (Rahman 1964). The small value of $U(r)$ at the cut-off suggests that the Ewald summation is not required for computing the total energy. The initial configuration is that of the particles arranged on the body centered cubic(bcc) lattice. Simulation with starting configuration being random also gave the same results. The simulations are performed on Norsk Data 560CX computer.

3.1 *Brownian dynamics simulation*

Based on BD algorithm of Ermak and Yeh (1974), Gaylor et al (1981) have applied the BD computer simulation to dilute aqueous colloidal dispersions. For these dilute suspensions, many body hydrodynamic interactions are not significant (Gaylor et al 1981, van Megen et al 1985). The dynamics of each particle is governed by the Langevin equation in which the random force is related to viscous damping of the medium through the fluctuation dissipation theorem. Ermak and Yeh (1974) formalism allows one to obtain the new positions of the particles by integrating the Langevin equation over a time step Δt, which is large compared to the momentum relaxation time τ_R but is small compared to the time τ_e over which the configuration of the particles appreciably changes. The momentum relaxation time $\tau_R = m/f$, where m is the mass of particle and the friction coefficient $f = 6\pi\eta a$, η is the viscosity of the medium. For polystyrene particle of diameter $\sigma(=2a) = 0.109$ μm and $\eta = 0.01089$ Poise, $\tau_R = 6.4 \times 10^{-10}$ s.

We have used the algorithm of Ermak and Yeh (1974) which provides the following equations to generate the particle trajectories and velocities

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{R}_i(\Delta t) + \mathbf{F}_i(t)\Delta t/\gamma \tag{5}$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) \exp(-\Delta t/\tau_R) + \mathbf{V}_i$$
$$+ [\mathbf{F}_i(t + \Delta t) - \mathbf{F}_i(t) \exp(-\Delta t/\tau_R)]/\gamma \qquad (6)$$

where $\mathbf{r}_i(t)$, $\mathbf{v}_i(t)$ are the position and velocity of the ith particle at time t respectively. The $\mathbf{R}_i(\Delta t)$ is the Gaussian random displacement representing the net effect of the collisions of the ith particle with other particles in the time interval Δt, and $\mathbf{V}_i$ is the Gaussian random velocity of the ith particle. $\mathbf{F}_i(t)$ is the direct force on the ith particle due to remaining particles in the system i.e.,

$$\mathbf{F}_i = -\sum_{j \neq i} \frac{\partial U(r_{ij})}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}}. \qquad (7)$$

The random displacements $\mathbf{R}_i$ and the random velocities $\mathbf{V}_i$ are generated by employing central limit theorem. Here M random numbers having uniform distribution in the range 0 to 1 are selected and their sum S is calculated. This sum S is Gaussian distributed with mean $M/2$ and variance $M/12$ and the required Gaussian variate $\zeta(t)$ (here $\zeta = X$, Y or Z component of $\mathbf{R}_i$ or $\mathbf{V}_i$) with zero mean and variance α is obtained as

$$\zeta(t) = \sqrt{\alpha}\{(S/\sqrt{M/12}) - \sqrt{3/M}\}. \qquad (8)$$

The variance for random displacement is $\alpha_R = 6D_0\Delta t$, where D_0 is the diffusion coefficient of the particle $(D_0 = k_B T/f)$ and the variance in random velocity $\alpha_v = 3 k_B T/m$.

As discussed above the time step chosen in BD algorithm should be such that $\tau_R \ll \Delta t \ll \tau_e$. For our system $\tau_R = 6\cdot4 \times 10^{-10}$ s. Since there is no unambiguous way of estimating τ_e, we tried time steps from $\Delta t = 10^{-7}$ to 10^{-3} s and monitored the total energy. It was found that for $\Delta t \leqslant 10^{-4}$ s the total energy is conserved with root mean squared deviation of $\sim 0\cdot7\%$ whereas for $\Delta t > 10^{-4}$ s the total energy is not conserved and showed wide excursions. Hence $\Delta t = 10^{-4}$ s has been chosen in our simulations. Using the value of D_0 it can be seen that the particle on the average moves $\sim 4\%$ of the average interparticle distance $2a_s$ $(=2(3/4\pi n_p)^{1/3})$ in time Δt. After reaching equilibrium $g(r)$ was obtained (for $r = L/2$) using the standard methods (Rahman 1964). The structure factor $S(Q)$ is calculated using

$$S(Q) = 1 + 4\pi n_p \Delta r \sum_{l=1}^{l_{max}} (g(l\Delta r) - 1) l\Delta r \sin(Ql\Delta r)/Q \qquad (9)$$

for those values of wavevector Q which satisfy

$$Q = 2\pi(n_1, n_2, n_3)/L \qquad (10)$$

where n_1, n_2, n_3 are integers and $l_{max} = L/(2\Delta r)$. This constraint on Q is introduced by the finite size of the system. The same constraint limits the range of $g(r)$ to $r \leqslant L/2$ and can introduce spurious oscillations or distortions in the small Q region of the computed $S(Q)$ using (9).

4. Results and Discussion

The parameters entering the pair potentials, (1) for Yukawa and eq (3) for Sogami are σ, n_p, n_i and Z. The particle diameter σ is $0\cdot109$ μm, and the particle concentration

in the suspension can be determined accurately by weight method (Tata *et al* 1987) and was found to be $n_p = 1.33 \times 10^{12}\,\text{cm}^{-3}$ for which we have measured $S(Q)$ by angle resolved Rayleigh scattering (Tata *et al* 1987). The accurate determination of the quantities n_i and Z are experimentally difficult (Robbins *et al* 1988). The charge Z for the diameter $0.109\,\mu\text{m}$ particle has been reported to be 600 ± 100 (Lindsay and Chaikin 1982) and hence $Z = 600$ is taken in all our calculations. The experimental $S(Q)$ was fitted to the calculated $S(Q)$ using RMSA for the Yukawa potential (Hansen and Hayter 1982; Härtl *et al* 1983) with n_i as the fitting parameter. The peak position and peak height of the first peak in $S(Q)$ are chosen as criteria for judging the best fit. The best fit of calculated $S(Q)$ to the experimental data was obtained for $n_i = 2.1 \times 10^{15}\,\text{cm}^{-3}$. The impurity ion concentration was estimated from the conductivity measurements and found to be $(1.9 \pm 0.4) \times 10^{15}\,\text{cm}^{-3}$. It is interesting to note that the fitted value of n_i matches well with the measured one.

The same value of n_i in the Sogami potential (eq (3)) was used to compute $g(r)$ and $S(Q)$ by BD simulation. It was found that the calculated $S(Q)$ does not match well with the experiment. But a good agreement with the experiment was obtained for $n_i = 1.75 \times 10^{15}\,\text{cm}^{-3}$. A small difference in n_i (note this n_i value is also within the experimental accuracy) for Yukawa and Sogami potentials is not surprising since K enters both the potentials in slightly different ways. Hence the results will be presented for Sogami potential with $n_i = 1.75 \times 10^{15}\,\text{cm}^{-3}$.

In BD simulation the total potential energy is monitored to find out whether equilibrium has been reached or not. Typically 700 time steps have taken to reach the equilibrium. The relative error in the energy after reaching equilibrium is 0.85%. In addition to energy the virial pressure and velocity distribution of particles are also monitored as a check for equilibrium state. After 700 time steps the virial pressure remained constant with relative error being 0.53% and velocity distribution remained Maxwellian. The interval $\Delta r = 0.16$ was used to calculate $g(r)$ and particle coordinates generated from 350 time steps were used for averaging. The $g(r)$s thus obtained for Sogami (continuous line) as well as Yukawa (dotted line) pair potentials are shown in figure 2(a). Since Δr chosen is very small the $g(r)$ obtained looks almost continuous curve. Figure 2(b) presents $S(Q)$s calculated using (9). Also shown are the experimental data with error bars. One can see from figure 2(b) that the calculated $S(Q)$ for Yukawa potential (dotted line) matches with the experiment. Also note that the calculated $S(Q)$ for Sogami potential (continuous line) also agrees equally well with the experimental $S(Q)$. To compare the equilibrium BD results with other simulation techniques conventional Monte-carlo simulations (based on Metropolis method, see for example Binder 1979; Hansen and McDonald 1986) were also carried out for same parameters of the suspension. The step size of 0.56 was chosen such that trial rejection rate was $45 \pm 5\%$. The calculations are started with initial configuration being the particles occupying a bcc lattice and first $100{,}000$ configurations are discarded to allow the system to equilibrate. The total potential energy and virial pressure of the system is monitored to find out whether equilibrium has been reached or not. After reaching equilibrium typically $150{,}000$ configurations are generated to determine $g(r)$. The relative error in energy as well as in virial pressure are same as that in BD simulation. The errors of this magnitude are normal for a liquid-like ordered suspension. Figure 3 shows calculated $S(Q)$s for the Sogami potential using MC and BD simulations. It is not surprising to find that both the calculated $S(Q)$s agree. At this stage one can compare the total computation time needed to calculate
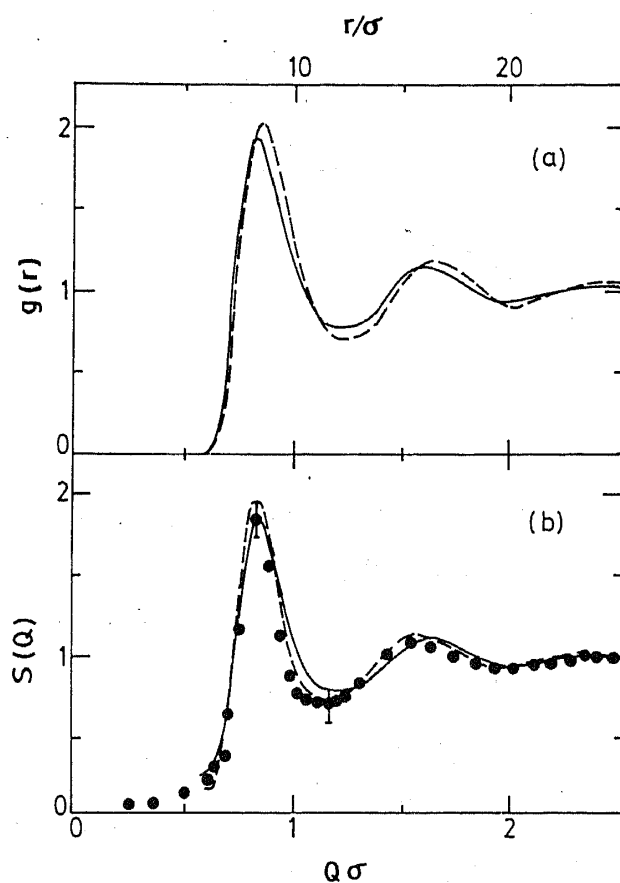
Figure 2. (a) Pair distribution functions $g(r)$ vs r (in units of σ) calculated from BD simulation for Sogami potential (——) with $n_i = 1·75 \times 10^{15}$ cm^{-3} and Yukawa potential (———) with $n_i = 2·1 \times 10^{15}$ cm^{-3}. n_p and Z as mentioned in figure 1. (b) Structure factors $S(Q)$ vs Q (in units of σ^{-1}) calculated using eq. (9) and $g(r)$s of figure 2(a) for Sogami (——) and Yukawa (———) potentials. The parameters are same as for figure 2a. Experimental $S(Q)$ (······) is also shown for comparison.
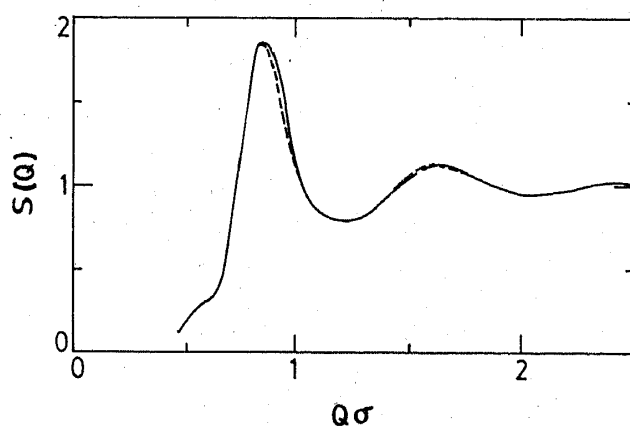
Figure 3. Comparison of structure factors $S(Q)$ vs Q (in units of σ^{-1}) calculated from MC (——) and BD (———) for Sogami potentials with $n_i = 1·75 \times 10^{15}$ cm^{-3}, n_p and Z as in figure 1.

$S(Q)$. The CPU time for MC was 5 h and for BD was 3 h, on Norsk Data System, which clearly demonstrates that BD simulation saves a lot of computation time.

The dynamic light scattering experiments give a direct estimate of mean square
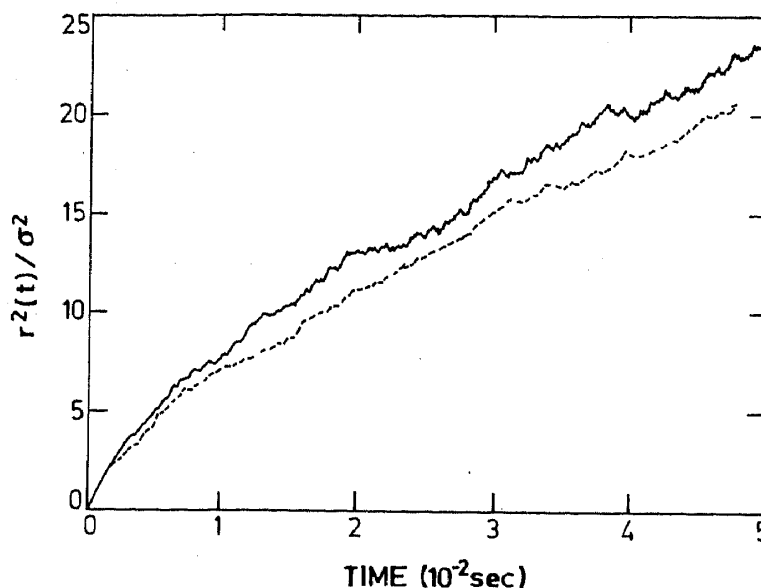
Figure 4. Mean square displacement $r^2(t)$ (in units of σ^2) vs t (in seconds) calculated from BD simulation for Sogami potential (——) with $n_i = 1.75 \times 10^{15}\,\text{cm}^{-3}$ and for Yukawa potential (———) with $n_i = 2.1 \times 10^{15}\,\text{cm}^{-3}$, n_p and Z as in figure 1.

displacement defined as $r^2(t) = \sum_{i=1}^{N} (r_i(t) - r_i(0))^2/N$. For interacting system the short time ($t < \tau_c$, where τ_c is the mean collision time) behaviour of $r^2(t)$ is like free diffusion and the long time behaviour ($t > \tau_c$) exhibits saturation (Pusey 1979). The short and long time diffusion constants D_S and D_L respectively can be obtained from the slope of $r^2(t)$ vs t plot in the short and long times (Pusey 1978). Using 500 time steps of BD simulation data $r^2(t)$ is calculated for both the potentials and is shown in figure 4. This behaviour of $r^2(t)$ is expected for a liquid-like ordered suspension (Gaylor et al (1981)). One can notice from figure 4 that $r^2(t)$ calculated for a colloidal system interacting with Sogami potential also agrees well qualitatively and the difference in long time behaviour of $r^2(t)$ is due to the difference in the magnitude of interaction strengths of the two potentials. We report here D_S and D_L obtained from figure 4. $D_S = 2.4 \times 10^{-8}\,\text{cm}^2/\text{s}$ for both potentials. $D_L = 0.66 \times 10^{-8}\,\text{cm}^2/\text{s}$ for Yukawa potential (from dashed curve of figure 4) and $D_L = 0.71 \times 10^{-8}\,\text{cm}^2/\text{s}$ for Sogami potential (from continuous curve of figure 4). D_0 for $0.109\,\mu\text{m}$ particle in aqueous medium is $3.68 \times 10^{-8}\,\text{cm}^2/\text{s}$ (from Stokes–Einstein relation). The D_0 value goes as input in generating particle trajectories (see eq. 5). Here $D_S \neq D_0$, because the time scale used here is $10^{-4}\,\text{s}$. However we confirmed if smaller time scale is chosen ($\Delta t = 10^{-6}\,\text{s}$) we obtain $D_S \simeq D_0$. Lower value for D_S for $\Delta t = 10^{-4}\,\text{s}$ is because the particles start experiencing the interaction in this time scale. D_S and D_L obtained are comparable with macroscopic values reported in the literature (Pusey 1978; Gaylor et al 1981). D_L value for both the potentials are of same order, the small difference in D_L value for both potentials could be due to difference in the interaction strengths of the potentials. Careful dynamic light scattering measurements and accurate determination of n_i can perhaps be used to find out which potential fits better to the experiment.

5. Conclusions

We have shown that the static structure factor $S(Q)$ obtained based on the Sogami

pair potential, which has a secondary minimum, agrees well with the experimental data. It is also shown that the mean square displacement calculated for Sogami potential agrees qualitatively. The two features viz. the earlier mentioned reentrant phase transition and above mentioned homogeneous liquid like ordering can be understood using Sogami potential. Although Yukawa can explain the second feature it cannot explain the first feature. This suggests that Sogami potential is perhaps a better choice for the charged colloidal systems. It will be interesting to examine some more dynamical as well as static properties of the colloids with Sogami potential and compare with the experiments. Such calculations are underway.

Acknowledgements

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