Structure and dynamics of screened-Coulomb colloidal liquids

R. O. Rosenberg

Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

D. Thirumalai

*Institute for Physical Science and Technology and Department of Chemistry and Biochemistry,
University of Maryland, College Park, Maryland 20742*

(Received 7 March 1986)

The pair correlation function and the velocity autocorrelation function of screened-Coulomb colloidal liquids, interacting via the Derjaguin-Landau-Verweg-Overbeek potential, are calculated using molecular dynamics. Examination of the structure reveals liquidlike behavior even at the lowest density which corresponds to a volume fraction less than 10^{-4}. The calculated radial distribution functions are in excellent agreement with experiment. The velocity autocorrelation function exhibits distinct oscillations at all densities, which indicates that the motion of a single particle is very strongly coupled to the collective modes of the screened-Coulomb colloidal liquid.

Suspension of electrically charged macroions exhibit a wide variety of physical phenomena.[1-7] The colloidal particles suspended in water are essentially spherical in shape and the interactions between them are strongly repulsive. The strength of the interaction between them is largely responsible for the variety of fascinating behavior of these systems. It is now known that these systems can mimic the collective structures seen in liquids[7] and solids.[8-10] These structures are quite delicate and can be easily disturbed, but will return to the original state if left alone. Mixtures of different size polystyrene spheres have been observed to form exotic colloidal alloys[11] and classical Wigner glasses.[4] These structures have been observed in various biological systems and in suspensions of colloidal polymers. The detailed study of the structural and dynamical aspects of these systems is not only of technological importance but may be useful in understanding the behavior of biological macromolecules. From the theoretical viewpoint these systems are intriguing because these strongly interacting many-body systems are classical and their interaction potential can be externally controlled by adjusting a few system parameters. These colloidal systems are ideal models to study features in the velocity autocorrelation functions, like the long-time tails, which are quite difficult to observe in simple liquids.

In this Rapid Communication we confine ourselves to the elucidation of the structural aspects and to the study of the self-motion in dilute concentration of polystyrene latexes. We assume that the direct interaction between two particles (referred to as polyballs from now on) can be modeled by the Derjaguin-Landau-Verweg-Overbeek (DLVO) potential. One should also include the effects of the direct interaction between the solvent (water) and the polyball as well as the hydrodynamic interaction mediated by the solvent. The direct interaction between the polyballs is expected to be the most dominant, and consequently we ignore both the hydrodynamic interaction[12] and the interaction between the solvent and the polyball. Furthermore, we treat the solvent as a dielectric continuum which is reasonable considering the disparity in the size of the polyball and the solvent. Although this is an approximate model for suspensions of polystyrene latexes (often used in colloid science), it is expected that one can predict fairly reliably the

structure of dilute suspensions of charged colloids using this simplified model. However, based on general physical arguments one can show that the neglect of hydrodynamic interactions will have profound effect on the dynamics of self-motion in colloidal suspensions. Thus, the dynamical aspects of our simulations of the polyball liquid cannot directly shed light on the self-motion in aqueous suspensions of charged colloids. The only previous simulations of these systems that we are aware of are due to Van Megen and Snook.[13] They used a smaller system and were only interested in determining the radial distribution function by Monte Carlo techniques. The simulations reported here are intended to complement this earlier work.

The advances in emulsion polymerization technique have enabled one to make suspensions of highly monodisperse polymer spheres of varying radii. When these spheres are suspended in water they become highly charged and the strength of the screened-Coulomb interaction is responsible for the large (few microns) interparticle separation. In this note we report the simulation of the structure and dynamics of charged polystyrene spheres at very low ionic strength with the view towards complementing the experimental investigation of Brown, Pusey, Goodwin, and Ottewill.[7] The experimental determination of the structure of the polystyrene spheres, at five densities, by light scattering technique, shows clear evidence of liquidlike behavior, with the short-range order extending over several particle diameters. They also observed that the reciprocal of the effective particle diffusion, which was determined from the initial decay of the nonexponential time-dependent autocorrelation function of the scattered light field, showed wave-vector dependence.

The simulations were carried out by integrating the classical equations of motion for a system of 864 polystyrene spheres. The potential energy of the N-particle system is taken to be a sum of pairwise potentials, $V(|r_i - r_j|)$ with $V(r)$ being the DLVO potential,[14]

$$V(r) = \frac{Z_{\text{eff}}^2}{\epsilon_0 r} \left[\frac{e^{qa}}{1+qa} \right]^2 e^{-qr} \; . \tag{1}$$

In Eq. (1) q^{-1} is the Debye screening length, Z_{eff} is the ef-

fective charge on the macroion, ϵ_0 is the dielectric constant of the medium (water), and a is the radius of the particle. We refer to a system of particles interacting through the DLVO potential given by Eq. (1) as a polyball liquid. The unit of length in these simulations is a, $k_B T$ is the relevant energy scale in the problem and the unit of time, $\tau = (ma^2/k_B T)^{1/2}$. The mass of the polyball, m, is 6.02×10^{-17} g. The present results are based on long molecular dynamics runs. Typically, the systems were equilibrated for about 10^4 time steps. Subsequently, the radial distribution functions were obtained by following a molecular dynamics trajectory for about 500 time steps. The velocity correlation functions of the polyball liquid were calculated by running a trajectory for about 1500 time steps. For all the cases considered here the inverse screening length is quite small which implies that the potential is long ranged. Despite the long-range nature of the potential we found that the use of Ewald summation was not necessary for this problem even at the lowest concentration considered here, for which the screening length is $25a$. We discuss this in detail elsewhere.[15] The simulations were done at the five experimental densities. Here we report our results at three of the densities and they correspond to the volume fractions $\phi_1 = 5.537 \times 10^{-4}$, $\phi_2 = 1.898 \times 10^{-4}$, and $\phi_3 = 8.116 \times 10^{-5}$.

In Fig. 1 we plot the radial distributions $g(r)$ as a function of r/a at the three densities. One of the problems in using the DLVO potential is that the effective charge on the polyball liquid is not easily determined. For this system the experimental value for Z_{eff} is estimated to be between 210 and 360. We have found that the $g(r)$ is extremely sensitive to Z_{eff}. By choosing $Z_{eff} = 211.234$ the results of our computer simulations for $g(r)$ were found to be in excellent agreement with the experimental work of Brown et al.[7] A minor change in Z_{eff} can introduce artificially long-range order, like that obtained in crystals. A value of $Z_{eff} = 272.56$ yields a dramatically different result for $g(r)$.[15] It is difficult to extract the precise numerical values of the experimental pair correlation functions which were obtained by Fourier transformation of the measured structure factors $S(k)$. However, a direct comparison of the peak heights, at all densities, between our simulations and the experimental

results shows agreement to within 5%. The location of the peak heights agree with the experimental values to within 10% at all the densities. Considering the possible experimental error 20% in the peak heights and about 4% error in the location of the peaks we can conclude that our simulation results are in excellent agreement with the experimental measurements. This suggests that the DLVO potential with the appropriate value for Z_{eff} may be reasonable in this concentration regime and one may not need many-body potentials to interpret the structure of the polyball liquid. It is quite remarkable that these colloidal systems seem to mimic liquidlike structures over several particle diameters. This is evident by the fairly pronounced first peak that is seen even at the lowest concentration. The width of first peak increases, and the height decreases as the concentration is lowered. At the higher concentrations one also sees the clear formation of second peaks corresponding to the formation of second "solvent shells." The position of this second shell corresponds to a distance of about $400a$. The persistence of such correlations over the long distance is due to the strength of the screened-Coulomb repulsion. One of the really unsolved issues in these systems is the precise determination of Z_{eff}. The good agreement between our results and the experimental measurements show that in this concentration regime Z_{eff} is not dependent on the concentration. Finally, for the DLVO interaction potential, one can approximate the thermodynamics of the system by an equivalent hard-sphere system. The diameter of the hard-sphere system can be determined using the Gibbs-Bogolibov inequality for the free energy.[16] The structure factors for the "best" hard-sphere system determined this way were calculated using the Percus-Yevick solution and they are in very good agreement with the experimentally determined $S(k)$.[15] It should be pointed out that recently Hansen and Haytor[17] have calculated $g(r)$ by solving the integral equation using a rescaled mean spherical approximation (MSA) and their results also compare favorably with experiment.

We now present our calculations of the velocity autocorrelation functions, $Z(t) = \langle V(0)V(t) \rangle / \langle V(0)^2 \rangle$, for the three densities. We should stress that, because our model neglects hydrodynamic interaction, the calculation of $Z(t)$ cannot be used to interpret the dynamics of self motion in aqueous suspension of charged colloids. Nevertheless, it is interesting to compute $Z(t)$ for the model polyball liquid considered here. The behavior we find in our simulations may be found in $Z(t)$ for charged colloids in very low-viscosity solvents. The velocity autocorrelation functions $Z(t)$ as a function of time are presented in Fig. 2. The most striking aspect of $Z(t)$ is the oscillatory behavior exhibited at all densities. These oscillations persist over a long period and the frequency of the oscillations increases with increasing concentration. The presence of the oscillations is an indication that the single-particle motion is very strongly coupled to the collective density fluctuations. The physical picture that is consistent with the behavior of $Z(t)$ emerges from observing that the tagged particle interacts strongly with the instantaneous cage formed by the neighboring polyballs. At relatively short times, i.e., times much shorter than some characteristic interaction time τ_I the dynamics of the particle is essentially that of a free particle. Because of the nature of the DLVO potential, the force acting on the tagged particle is very small and consequently the dynamics of the particle resembles that of the free particle. This was also reflected in the plot of the mean-square displacement
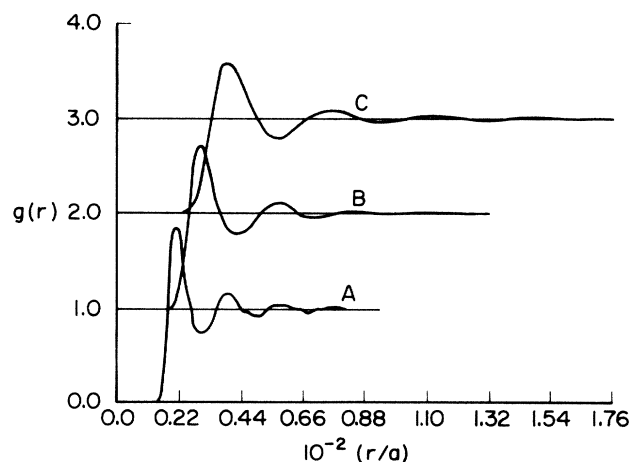

FIG. 1. Plot of the radial distribution function $g(r)$ as a function of r/a. Curve A is for $\phi_1 = 5.537 \times 10^{-4}$, while curves B and C correspond to $\phi_2 = 1.898 \times 10^{-4}$, and $\phi_3 = 8.116 \times 10^{-5}$, respectively. The value of $a = 250$ Å.
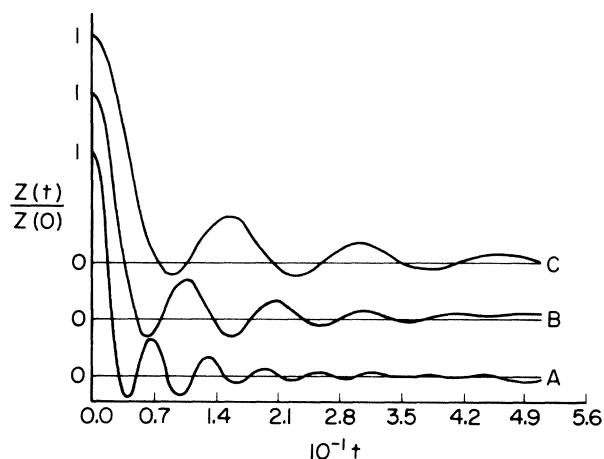
FIG. 2. Normalized velocity autocorrelation function $Z(t)$ as a function of t/τ, where τ is the unit of time. Refer to Fig. 1 for labels.

FIG. 3. Normalized power spectrum of the velocity autocorrelation function as function of ω/ω_{ps}. Refer to Fig. 1 for labels.

(MSD) $\langle \Delta R^2(t) \rangle$ as a function of time which indicated a t^2 behavior for short times. For intermediate time (comparable to several τ_I's) the particle can be viewed as rattling in a slowly evolving cage, and for times much larger than τ_I one recovers the long-time behavior of $Z(t)$. The value of the interaction time may be inferred by examining the velocity correlation functions and it turns out that τ_I varies from 4τ to 8τ for the three densities. The physical picture of the tagged particle being trapped in a cage made up of the nearest neighbors is further confirmed by the fact that the maximum in the power spectrum of the $Z(t)$ at nonzero frequency corresponds well with the frequency obtained from the second derivative of the potential evaluated at the mean interparticle distance. The possibility of the "repulsive cage" dictating the single-particle dynamics was put forth by Pusey for colloidal suspensions based on the experimental determination of $\langle \Delta R^2(t) \rangle$. It is unlikely that $Z(t)$ for aqueous suspensions of interacting charged macroions would show such distinct oscillations as reported here for the model polyball liquid.

The behavior of $Z(t)$ seen here is very reminiscent of the marked oscillations reported for strongly interacting one-component Coulomb plasma (OCP).[18-21] In fact, it proves quite convenient to analyze certain aspects of our results in direct analogy to OCP. Accordingly, we define a "plasma" parameter Γ_{ps} and a collective mode frequency ω_{ps} as

$$\Gamma_{ps} = Z^2 e^2/\epsilon_0 a_s k_B T , \qquad (2a)$$

$$\omega_{ps} = [4\pi(Ze)^2\rho/m\epsilon_0]^{1/2} , \qquad (2b)$$

where $a_s = (3/4\pi\rho)^{1/3}$. For the three densities considered here, the values Γ_{ps} lie in the range 56–110. In Fig. 3 we plot the power spectra $\tilde{Z}(\omega)/\tilde{Z}(0)$ as a function of ω/ω_{ps}, by directly Fourier transforming $Z(t)$. This figure clearly shows the existence of a peak near $\omega \sim \omega_{ps}$. The peak position corresponding to the maximum in $\tilde{Z}(\omega)/\tilde{Z}(0)$ is quite constant and occurs at $\omega_{max}/\omega_{ps} = 0.68 \pm 0.04$. This should be contrasted with the OCP results for $\tilde{Z}(\omega)$ which show that $\omega_{max}/\omega_p = 0.9 \pm 0.02$.[19] The comparison of $Z(t)$
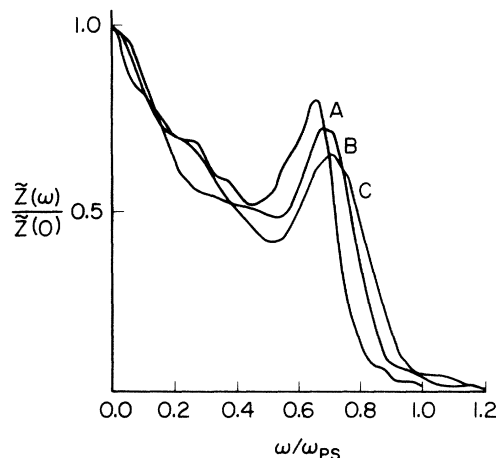
between the colloidal fluid and that of OCP suggests that the system considered may well be represented by the usual plasma parameter Γ in the range of 60–110. But for $\Gamma \sim 106$ (which is the value obtained for the highest density considered here) the OCP system shows a diffusive peak at a nonzero frequency which is not observed for the colloidal liquid. Based on general considerations one can expect such a peak to appear at slightly higher concentrations. Finally, we have evaluated the self-diffusion coefficient D, from the slope of the mean-square displacement at long times. A log-log plot of D as a function of Γ_{ps} is linear and one can fit it to a form $D = C\omega_p a^2\Gamma^{-n}$, where $C = 3.0$ and $n = 1.2$. Notice that a similar relation was proposed for the OCP by Hansen, McDonald, and Pollock.[19] The marked resemblance between OCP and the system studied here suggests that even for purposes of predicting the dynamical behavior of colloidal suspensions, OCP may serve as an appropriate reference state.

The structure of dilute concentration of polyball liquid shows remarkable similarity to that of simple liquids. The radial distribution functions obtained are in remarkable agreement with the experimental measurements for charged colloids. The single-particle dynamics of a polyball, as seen in the velocity autocorrelation function, clearly suggests OCP-like character and cannot be easily analyzed in terms of dynamics in dense simple liquids. It is interesting to note that varying the screening length (which can be arranged by adding dilute acid like HCl), that one can change the range of the DLVO potential. By continuously varying the q^{-1}, one can mimic the behavior of liquids that interact via short-range potential (Lennard-Jones potential) to those that have essentially infinite range, like the OCP. A more detailed account of these findings including simulations of interacting Brownian particles will be given elsewhere.

[1]B. J. Ackerman and N. Clark, Physica A **118**, 221 (1983).

[2]D. Hone, J. Phys. (Paris) Colloq. **46**, Suppl. 3, C3-21 (1985).

[3]P. M. Chaikin, P. Pincus, S. Alexander, and D. Hone, J. Colloid Interface Sci. **89**, 555 (1982).

[4]H. M. Lindsay and P. M. Chaikin, J. Chem. Phys. **76**, 3774 (1982).

[5]D. W. Schafer, J. Chem. Phys. **66**, 3980 (1977); D. W. Schafer and B. J. Berne, Phys. Rev. Lett. **32**, 1110 (1974).

[6]P. N. Pusey, J. Phys. A **11**, 19 (1978), and references therein.

[7]J. C. Brown, P. N. Pusey, J. W. Goodwin, and R. H. Ottewill, J. Phys. A **8**, 664 (1975).

[8]The possibility of ordering in these systems was anticipated by J. G. Kirkwood and J. Mazur, J. Polym. Sci. **9**, 519 (1952).

[9]P. A. Forsythe, S. Marcelja, D. J. Mitchell, and B. W. Ninham, Adv. Colloid Interface Sci. **9**, 37 (1978).

[10]F. Grüner and W. P. Lehman, J. Phys. A **15**, 2487 (1982), and references therein.

[11]S. Hachisu and Yoshimura, Nature **283**, 188 (1980).

[12]See S. Harris, J. Phys. A **9**, 1093 (1976).

[13]W. van Megen and I. Snook, J. Chem. Phys. **66**, 813 (1977); Faraday Discuss. Chem. Soc. **65**, 92 (1978).

[14]E. J. W. Verweg and J. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948). Note that Eq. (1) contains the geometrical factor $(1 + qa)^{-2}$ which is not contained in the usual DLVO potential. At the very low concentrations considered here $qa \ll 1$, and therefore Eq. (1) will be referred to as the DLVO potential.

[15]R. O. Rosenberg and D. Thirumalai (unpublished).

[16]B. Firey and N. W. Ashcroft, Phys. Rev. A **15**, 2072 (1977).

[17]J. P. Hansen and J. B. Hayter, Mol. Phys. **4b**, 651 (1982).

[18]J. P. Hansen, E. L. Pollack, and I. R. McDonald, Phys. Rev. Lett. **32**, 277 (1974).

[19]J. P. Hansen, I. R. McDonald, and E. L. Pollock, Phys. Rev. A **11**, 1025 (1975).

[20]For a review, see M. Baus and J. P. Hansen, Phys. Rep. **59**, 1 (1980).

[21]M. C. Marchetti and T. R. Kirkpatrick, Phys. Rev. A **32**, 2981 (1985).