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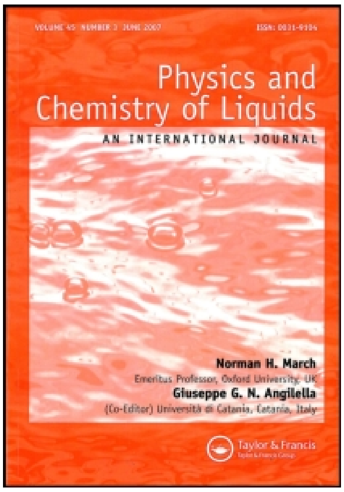

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Effective Interparticle Pair Potential in Electrostatically Stabilized Colloidal Dispersions at Melting

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A method based on the random phase approximation (RPA) is used to calculate the effective interparticle pair potential $\varphi(r)$ in a concentrated charged colloidal dispersion from an observed structure factor $S(q)$. By using Monte Carlo simulation results for inverse power potential fluids at their melting points as reference systems, the perturbation scheme determines $\varphi(r)$ at the melting point of the colloid from experimental data. The resulting $\varphi(r)$ is found to be oscillatory and differ qualitatively from the form predicted by DLVO theory.

1 INTRODUCTION

In two earlier papers[1,2] one of us (MJG) introduced a perturbation theory based on the random phase approximation (RPA) which enabled the small wavevector behaviour of the static structure factor $S(q)$ in colloidal dispersions to be analyzed in terms of the interparticle pair potential from the DLVO theory of colloid stability.[3] Application of the theory to microemulsions showed that experimentally observed osmotic compressibilities lead to values for the Hamaker constants consistent with other experiments.[1] However, when used to study highly charged aqueous dispersions of polystyrene spheres the values of the electrostatic surface potential for the macroions given by the theory were found to be an order of magnitude smaller than the zeta potentials normally associated with this system.[2] The electrostatic component of the interparticle pair potential in DLVO theory is obtained from a Debye–Hückel (DH) theory of screening and in

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light of the above results doubts must exist as to the validity of DH screening in concentrated electrostatically stabilised dispersions.

This letter aims to tackle the inverse problem to that of Refs. 1 and 2 and determine the effective interparticle pair potential $\varphi(r)$ from observed data. This problem has been of continuing interest in the study of simple liquids and liquid metals since the initial work of March and co-workers[4,5] and many different schemes,[6] all approximate to some degree, have been proposed for the task. Here we concentrate on the method developed by McLaughlin and Young[7] which uses the RPA to calculate the perturbation correction to a reference potential from the observed $S(q)$. Recently Yokoyama and Ono[8] have used this method to determine $\varphi(r)$ for liquid metals with inverse power potentials for the reference system. This is of special interest as Monte Carlo (MC) simulation data is available at the melting point for the reference fluid[9,10] and the introduction of errors through analytic approximations on the reference system is avoided. Yokoyama and Ono have shown that the RPA is capable of producing pair potentials from observed data on liquid metals that are fully consistent with the accepted forms from pseudopotential theory. They have further shown that while the RPA is often deemed to be only semi-quantitative, due to its inability to fully incorporate long wavelength fluctuations, it can work very well indeed when an accurate reference system is used. Here we use Yokoyama and Ono's treatment to determine $\varphi(r)$ for an aqueous dispersion of polystyrene spheres at their melting transition from the experimental measurements of Grüner and Lehmann.[11,12]

2 THEORY

Perturbation theories of liquid structure assume that the effective interparticle pair potential may be divided into a 'reference' part $\varphi_0(r)$ and a 'perturbation' part $\varphi_1(r)$ with

$$\varphi(r) = \varphi_0(r) + \varphi_1(r) \tag{1}$$

The RPA consists of writing the direct correlation function $c(r)$ as

$$c(r) = c_0(r) - \beta\varphi_1(r) \tag{2}$$

where $\beta = (k_B T)^{-1}$ and $c_0(r)$ is the direct correlation function of the reference fluid, a fluid at the same temperature T and density ρ as the true fluid with a pair potential $\varphi_0(r)$. The Fourier transform of $c(r)$ is related to $S(q)$ through the relation

$$S(q) = (1 - \rho c(q))^{-1} \tag{3}$$

Thus denoting the structure factor of the reference fluid by $S_0(q)$, from Eqs. (2) and (3) we may write the perturbation potential as

$$\varphi_1(r) = \frac{k_B T}{\rho(2\pi)^3} \int_0^\infty dq\, 4\pi q^2 \frac{\sin qr}{qr} \left[\frac{1}{S(q)} - \frac{1}{S_0(q)}\right] \tag{4}$$

It is well known that the main features of $S(q)$ in simple liquids are determined by the short ranged repulsive forces between particles.[13] So when the reference potential $\varphi_0(r)$ is chosen to include the essential details of the short range repulsive forces, we expect $S(q) \simeq S_0(q)$ for $q > q_p$ where q_p is the wavevector of the principal peak in $S(q)$. This assumption allows the integral in Eq. (4) to be truncated and $\varphi_1(r)$ evaluated when $S(q)$ and $S_0(q)$ are known for $q < q_p$. The effective interparticle pair potential is then given by Eq. (1).

In this letter the reference fluid is taken to be a fluid of particles interacting via an inverse power potential of the form

$$\varphi_0(r) = \varepsilon \left[\frac{\sigma}{r}\right]^n \tag{5}$$

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This type of fluid has been studied by Hoover *et al.*[9] and Hansen and Schiff[10] using MC simulation methods with the thermodynamic and structural properties being available at the melting point for $n = 12, 9, 6, 4, 1$. The case of $n = 1$ corresponds to the one-component plasma (OCP) used earlier,[2] where we saw that while $S_0(q)$ for the OCP was able to fit $S(q)$ for the polystyrene sphere dispersion in regard to the location of the peaks in $S(q)$, it underestimated the magnitude of the secondary peak after the primary peak had been fitted. A simple scaling of $S_0(q)$ for Percus–Yevick hard spheres[13] shows that a hard sphere fluid ($n \to \infty$) can also correctly locate the peak positions in $S(q)$, but overestimates the magnitude of the secondary peak. So particular interest has been shown in reference inverse power potential fluids with intermediate values of n, namely $n = 12$ and $n = 6$. The case of $n = 9$ has been excluded as discrepancies exist between the two sets of MC data.[8]

Grüner and Lehmann have measured $S(q)$ for polystyrene sphere dispersions at several densities,[11] but as MC data is only available at melting we are restricted to studying the system at the melting transition.

3 RESULTS

Figure 1 compares the experimentally observed $S(q)$ for the polystyrene sphere dispersion at melting[12] with the MC simulation results for inverse power potential fluids with $n = 12$ and $n = 6$[10]. Several important points are relevant to this comparison. First, the MC simulations were

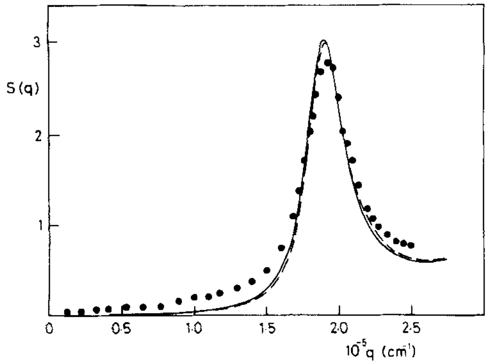

FIGURE 1 The structure factors for inverse power potential reference fluids at melting from Monte Carlo simulations[10] are plotted together with the experimental data of Grüner and Lehmann[12] (●) for an aqueous dispersion of polystyrene spheres at melting. The solid line corresponds to a fluid with pair potential $\varphi_0(r) = \varepsilon(\sigma/r)^{12}$ and the dashed line to $\varphi_0(r) = \varepsilon(\sigma/r)^6$. The potential parameters are listed in Table I.

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performed for a dimensionless density $\rho\sigma^3 = 1$. So as the value of σ for the reference fluid was chosen to locate the principal peak in $S_0(q)$ at the corresponding position in the experimental data, the particle density was not adjustable. However, the values for ρ obtained in both the $n = 12$ and $n = 6$ cases was in fact very close to the value $\rho = 1.95 \times 10^{13}$ cm^{-3} experimentally obtained by Grüner and Lehmann.[12] (The values for ρ and σ in the inverse power potential fluids is shown in Table I).

TABLE I

Inverse power potential parameter values for Figure 1

$\varphi_0(r)$	σ(cm)	ρ(cm^{-3})	ε/k_BT
$\varepsilon(\sigma/r)^{12}$	3.71×10^{-5}	1.96×10^{13}	1.75
$\varepsilon(\sigma/r)^{6}$	3.67×10^{-5}	2.02×10^{13}	4.74

Secondly, unlike Ref. (2), we are unable to tune the interaction strength ε to provide a good fit for the magnitudes of the principal peaks in $S(q)$ and $S_0(q)$, since the MC simulations were performed under the restriction that the system be at melting. For inverse power potential fluids this implies that ε satisfies the relation[9]

$$\rho^*(\beta\varepsilon)^{3/n} = \text{constant} \tag{6}$$

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where ρ^* is the ratio of the density to the close packing density and the constant $= 0.844$ when $n = 12$ and constant $= 1.75$ when $n = 6$. The consequent values for ε relevant to Figure 1 are given in Table I. However despite the constraints the fit of the MC curves to the experimental points is still good and the form of Eq. (4) ensures that small discrepancies between $S(q)$ and $S_0(q)$ at large q, $q > q_p$, are not significant. It is also reasonable to further assume that $S(q) = S_0(q)$ for all wavevectors outside the measured range on the same basis.

The effective interparticle pair potentials obtained from the results of Figure 1 and Eqs. (1) and (4) are displayed in Figure 2. The similarity between the curves obtained by using reference potentials with $n = 6$ and $n = 12$ is striking. Both potentials show strong repulsive cores for

$$r \simeq 1.5\,\sigma \simeq 5.5 \times 10^{-5}\ \text{cm},$$

which is considerably larger than the particle diameter of $d = 9.1 \times 10^{-6}$ cm, and attractive wells with minima at $r \simeq 2\sigma$. A secondary repulsive contribution to the potential is shown by both cases at $r \simeq 2.6\sigma$, but this is small in magnitude with $\varphi(r = 2.6\,\sigma) \simeq 10^{-2}k_BT$. Results for $r > 3\sigma$ are not to be relied upon due to inaccuracies in the experimental and simulation data in addition to the errors introduced by numerical integration over a finite number of data points.

The calculated potentials of Figure 2 have a form which is strongly reminiscent of classic DLVO theory which represents the superposition of DH repulsive screening and an attractive van der Waals interaction.[3] But if

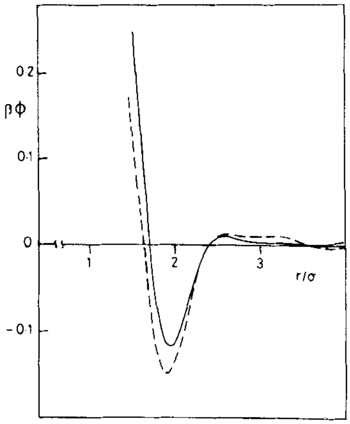

FIGURE 2 The effective interparticle pair potential in an aqueous dispersion of polystyrene spheres at melting. The solid line corresponds to a calculation with an r^{-12} reference fluid and the dashed line to one with an r^{-6} reference fluid.

we use the standard expression for the van der Waals interaction φ_{vw} between spherical particles of diameter d given by[14]

$$\varphi_{vw}(r) = -\frac{A}{12}\left[\frac{d^2}{r^2 - d^2} + \frac{d^2}{r^2} + 2\ln\left[1 - \frac{d^2}{r^2}\right]\right] \tag{7}$$

where A is the Hamaker constant, then at the location of the minimum r_m in potentials of Figure 2 (where $r_m \sim 2\sigma \sim 6d$) we find $\beta\varphi_{vw}(r_m) \sim -10^{-3}\beta A$. While accurate measurements of Hamaker constant are not available, we expect values for βA of order unity. So the van der Waals interaction potential is negligibly small compared to the calculated $\varphi(r)$ of Figure 2 and the attractive component of $\varphi(r)$ cannot originate from van der Waals forces between the macroions.

A comparison of the calculated $\varphi(r)$ in Figure 2 and the potential given by DH screening theory is not quantitatively possible due to the lack of knowledge regarding the surface potential. But, since DH screening theory gives rise to a Yukawa type of interaction potential which is monotonically repulsive,[3,15] the calculated $\varphi(r)$ in Figure 2 differs qualitatively from a DH potential.

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4 DISCUSSION

The effective interparticle pair potential calculated here from experimental scattering data is oscillatory in sign and differs qualitatively from the monotonic repulsive interaction given by the DH theory of screening. This helps to explain why an earlier analysis of the same data in terms of the potential from DLVO theory gave anomalous low values for the surface potential of the macroion.[2] However, the failure of the DH theory of screening in electrostatically stabilized colloidal dispersions at melting should not be unexpected since the DH theory is derived in the dilute limit where interparticle correlations are negligible. At melting this is not valid as may be seen from the form of $S(q)$.

While this simple theory based on the RPA may not be very accurate for a quantitative evaluation of $\varphi(r)$, applications of the theory to other systems have shown the results to be very good in a qualitative sense[7] and semi-qualitative when the reference system is accurately known.[8] So we may have some confidence in the existence of an attractive component to the pair potential of polystyrene sphere dispersions at melting. A simple analysis suggests that this attractive component does not originate from van der Waals interactions between the macroparticles. In future work we hope to extend the present analysis to dispersions away from their melting transition in order to understand the density dependence of $\varphi(r)$. But due to the scarcity of MC data for inverse power potential reference fluids, it may prove necessary to use alternative reference systems to proceed further.

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