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A. T. Augousti^a; M. J. Grimson^b

^a Physics Laboratory, University of Kent, Canterbury, Kent ^b ARC Food Research Institute Colney Lane, Norwich, Norfolk

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Shouldered Hard Sphere Model for Charged Colloidal Dispersions

A. T. AUGOUSTI

Physics Laboratory, University of Kent, Canterbury, Kent, CT2 7NR.

and

M. J. GRIMSON

ARC Food Research Institute Colney Lane, Norwich, Norfolk, NR4 7UA.

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The experimentally determined structure factor for an aqueous dispersion of charged polystyrene spheres is analyzed in terms of a system of particles interacting through a shouldered hard sphere potential. The fit of the model system to the experimental data is sufficiently good that the fluid represents a suitable reference system for perturbation studies of the small-angle scattering.

Light and neutron scattering studies of the static structure factor $S(q)$ for aqueous dispersions of charged colloidal particles bear a strong resemblance to similar studies of simple liquids.^{1,2} This has led authors to try to interpret experimentally determined structure factors with models that are familiar from theories of simple liquids. In particular, the well-known hard sphere fluid and one-component plasma (OCP) have been used with varying degrees of success. For all of the models used, the free parameters of the interaction potential between the particles are chosen to ensure that the principal peak in $S(q)$ for the model fluid matches that of the dispersion. But it has been found that the second peak in $S(q)$ for the hard sphere fluid is located at too small a wavevector to model the experimental data after the principal peak has been fitted (see, for example, Figure 1). The OCP³ is considerably better than the hard sphere fluid at locating the positions of the peaks of $S(q)$ in agreement with experiment, but significantly underestimates the magnitude of the second peak in $S(q)$. Perhaps the most successful model to date in terms of fitting experimental data for charged dispersions has been the rescaled mean spherical approximation (RMSA) of Hansen and Hayter.⁴

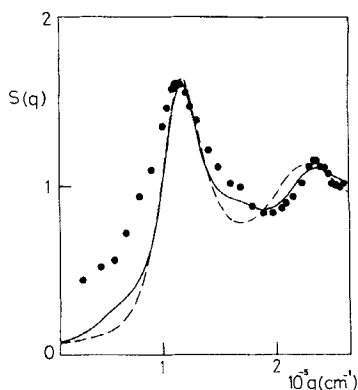


FIGURE 1 Structure factors for an aqueous dispersion of polystyrene spheres of nominal density $\rho = 2.53 \times 10^{12} \text{ cm}^{-3}$. The solid line represents the shouldered hard sphere fluid, the dashed line corresponds to a hard sphere fluid and the experimental data (\bullet) is due to Grüner and Lehmann.¹ The relevant parameters for the model fluids are given in the text.

This model involves a rescaling procedure to extend the range of applicability of a fluid of particles interacting through a hard sphere plus long-ranged repulsive Yukawa potential in the MSA.⁵ This model is as successful as the OCP in locating the position of the peaks in $S(q)$, but is noticeably better in reproducing the magnitude of the second peak. The major deficiency of the RMSA is its inability to reproduce accurately the trough between the principal and second peaks in $S(q)$ with regard to the position of the minimum and asymmetry of the trough.

As an example of the asymmetry of the trough in $S(q)$ we show in Figure 1 the structure factor for an aqueous dispersion of polystyrene spheres of nominal density $\rho = 2.53 \times 10^{12} \text{ cm}^{-3}$ obtained by Grüner and Lehmann¹ in a light scattering experiment. This asymmetry of the trough in $S(q)$ is not unique to colloidal dispersions, a similar problem arises in some liquid metals which exhibit a shoulder on the high angle side of the principal peak of $S(q)$. Silbert and Young⁶ have shown that this feature is consistent with a fluid whose pair potential has the form of a shouldered hard sphere,

$$\varphi_{\text{SHS}}(r) = \begin{cases} \infty & r < d \\ \varepsilon & d < r < \lambda d \\ 0 & r > \lambda d \end{cases} \quad (1)$$

with suitable choices for the constants d , ε and λ . While the study of Silbert and Young was performed using an approximate analytic theory, the results have been confirmed by Monte Carlo simulations due to Levesque and Weis⁷ and an exact study of a one-dimensional analogue due to Kincaid and Stell.⁸

In this letter we follow Silbert and Young in using a simple analytic approximation for the structure factor of this shouldered hard sphere fluid based on the random phase approximation (RPA). This formalism has been described elsewhere⁹ and consists of writing the direct correlation function of the shouldered hard sphere fluid $c_{\text{SHS}}(r)$ as the sum of the direct correlation function for a fluid of hard spheres of diameter d , $c_{\text{HS}}(r)$, and a perturbation potential arising from the shoulder in $\varphi_{\text{SHS}}(r)$. The structure factor for the shouldered hard sphere fluid is then given by

$$S_{\text{SHS}}(q) = (1 - c_{\text{SHS}}(q))^{-1} \quad (2)$$

where the Fourier transform of $c_{\text{SHS}}(r)$ is given by

$$c_{\text{SHS}}(q) = \int dr 4\pi r^2 \frac{\sin qr}{qr} [c_{\text{HS}}(r) - \beta\epsilon\theta(\lambda d - r)] \quad (3)$$

When the analytic form of $c_{\text{HS}}(r)$ from the Percus–Yevick approximation⁹ is used, the integral in Eq. (3) is straightforward. Although the RPA formalism has its limitations at high momentum transfers, previous work^{6,7} suggests that it should be adequate for the present study.

For a system of particles of packing fraction $\eta = \pi\rho d^3/6$, the shouldered hard sphere fluid represents a model with four adjustable parameters (η , d , ϵ , λ) and it is difficult to be sure that a unique solution has been found in a search to obtain the combination of parameters to satisfy the observed data. But in Figure 1 we show the structure factor for a shouldered hard sphere fluid with $\eta = 0.27$, $d = 5.2 \times 10^{-5}$ cm, $\beta\epsilon = 0.28$ and $\lambda = 2.1$ in relation to the experimental data of Grüner and Lehmann¹ for an aqueous dispersion of polystyrene spheres of nominal density $\rho = 2.53 \times 10^{12}$ cm⁻³. It is reasonable to treat η as a variational parameter, since doubts exist as to the correct value of the density.³ For comparative purposes Figure 1 also shows the best fit to experiment that can be obtained with a hard sphere fluid by varying the two parameters η and d ($\eta = 0.34$ and $d = 5.6 \times 10^{-5}$ cm). It can be seen that the shouldered hard sphere fluid is significantly superior to the hard sphere fluid in modelling the observed data. Indeed the shouldered hard sphere fluid is very successful in regard to its ability to locate and model the second peak in $S(q)$ in addition to the reproduction of the asymmetry of the trough between the first and second peaks of $S(q)$. Further note that the shoulders on the low and high angle sides of the principal peak in $S(q)$ for the shouldered hard sphere fluid mimic corresponding features in the experimental data. Thus the shouldered hard sphere fluid represents a useful model system for interpreting experimental data that will complement the RMSA of Hansen and Hayter⁴ which also contains four free parameters.

The primary aim of this study is to produce a model system that can represent the experimentally observed structure factor at high momentum

transfers accurately enough to perform perturbation treatments on the available small angle scattering data. Given the success of the shouldered hard sphere fluid above, we may use this model as a reference system in a RPA calculation of the interaction potential from the observed $S(q)$.^{10,11} In this treatment the effective interparticle pair potential $\varphi(r)$ for the colloid is given by Ref. 10.

$$\varphi(r) = \varphi_{\text{SHS}}(r) + \frac{k_B T}{(2\pi)^3} \int dq 4\pi q^2 \frac{\sin qr}{qr} \left[\frac{1}{S(q)} - \frac{1}{S_{\text{SHS}}(q)} \right] \quad (4)$$

This technique has been seen to be semi-quantitatively accurate when applied to simple liquids and liquid metals [10, 12] and the results of a calculation based on the shouldered hard sphere fluid and experimental data shown in Figure 1 are given in Figure 2.

The effective pair potential shown in Figure 2 displays a cusp at the hard core and a discontinuity at larger particle separations due to the form of the shouldered hard sphere reference potential. Thus we may expect the calculated $\varphi(r)$ to be only an approximation to the true effective pair potential. But it is interesting to note that the oscillatory nature of the calculated pair potential is consistent with a similar study of high density dispersions.¹¹ As noted in the analysis of the result in Ref. 11, the shallow primary minimum in $\varphi(r)$ at the hard core is too deep to be of van der Waals origin so the calculated form of $\varphi(r)$ differs qualitatively from the form given by DLVO theory. The deficiencies of DLVO theory in predicting the structure of concentrated dispersions of charged particles are evident from the work of Hansen and Hayter. Hansen and Hayter use a fluid of particles interacting via a hard core plus repulsive Yukawa pair potential that is equivalent to a

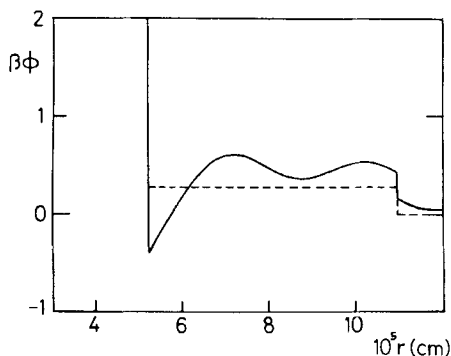


FIGURE 2 Effective interparticle pair potential for aqueous dispersion of polystyrene spheres with structure factor depicted in Figure 1. The dashed line shows the reference shouldered hard sphere fluid used to obtain the structure factor in Figure 1.

DLVO theory pair potential in the absence of van der Waals interactions, which are thought to be negligible in these systems,^{4,11} and fail to accurately reproduce the large wavevector form of $S(q)$. The failure of the Hansen and Hayter model in the small angle scattering regime is far more serious and questions the long-range form of the DLVO pair potential. However, the status of DLVO theory from these scattering measurements may appear to be artificially bad for two reasons. Firstly the simple DLVO pair potential is derived in the dilute dispersion limit and is not strictly valid for the concentrated systems studied in the light and neutron scattering experiments. Second, the samples used in the experiments are known to be polydisperse to a small extent and it can be shown that polydispersity of the sample around some representative monodisperse system may be regarded at the level of the RPA as an additional contribution to the effective pair potential.¹³ Thus a study of the polydispersity of the samples used in the experiment is essential if structure factor measurements are to provide information on colloid interaction potentials.

It must be emphasized that the model presented for the large wavevector form of the structure factor is by no means unique, but given the simplicity of the shouldered hard sphere model it may provide a guide for the interpretation of experimental data. Much more work is required on the possible degree of polydispersity of the polystyrene sphere system used in the experiments if the physical origin of the shoulder in the interaction potential is to be attributed to either an intrinsic softness of the core in the pair potential, polydispersity of the hard cores or some other effect.

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References

1. F. Grüner and W. Lehmann, *J. Phys. A*, **13**, 2155 (1980).
2. J. B. Hayter and J. Penfold, *JCS Faraday 1*, **77**, 1851 (1981).
3. M. J. Grimson, *J. Chem. Phys.*, to be published.
4. J.-P. Hansen and J. B. Hayter, *Mol. Phys.*, **46**, 651 (1982).
5. J. B. Hayter and J. Penfold, *Mol. Phys.*, **42**, 109 (1981).
6. M. Silbert and W. H. Young, *Phys. Lett. A*, **58**, 469 (1976).
7. D. Levesque and J. J. Weis, *Phys. Lett. A*, **60** 473 (1977).
8. J. M. Kincaid and G. Stell, *Phys. Lett. A*, **65**, 131 (1978).
9. M. J. Grimson, *JCS Faraday 2*, **79**, 817 (1983).
10. I. L. McLaughlin and W. H. Young, *Phys. Chem. Liq.*, **11**, 263 (1982).
11. M. J. Grimson and W. H. Young, to be published.
12. I. Yokoyama and S. Ono, *Phys. Chem. Liq.*, to be published.
13. G. Rickayzen, private communication.