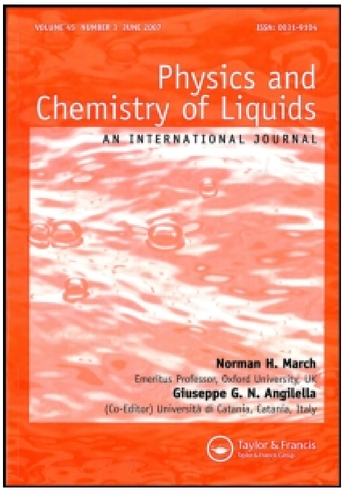

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Elastic Scattering from Charged Colloidal Dispersions

L. Baba-ahmed[a]; M. Benmouna[a]; M. J. Grimson[b]
[a] Physics Department, Institute of Sciences, Tlemcen, BP, Algeria [b] AFRC Institute of Food Research, Norwich Laboratory, Colney Lane, Norwich, England

To cite this Article Baba-ahmed, L. , Benmouna, M. and Grimson, M. J.(1987) 'Elastic Scattering from Charged Colloidal Dispersions', Physics and Chemistry of Liquids, 16: 3, 235 — 238
To link to this Article: DOI: 10.1080/00319108708078524
URL: http://dx.doi.org/10.1080/00319108708078524

Phys. Chem. Liq., 1987, Vol. 16, pp. 235–238
0031-9104/87/1603-0235$18.50/0

Printed in the United Kingdom

Letter

Elastic Scattering from Charged Colloidal Dispersions

L. BABA-AHMED, M. BENMOUNA

Physics Department, Institute of Sciences, Tlemcen BP 119, Algeria.

and

M. J. GRIMSON

AFRC Institute of Food Research, Norwich Laboratory,
Colney Lane, Norwich, NR4 7UA, England.

(Received 28 August 1986)

The static structure factor for a dispersion of charged colloidal particles is calculated in the Random Phase Approximation. The effects of the electrostatic repulsion between the particles is split into two parts; a strong short range repulsion which is included in the reference system through an enhanced effective hard sphere diameter and a long range interaction of DLVO type that is treated as a perturbation.

Recently, Hayter and Penfold[1] have calculated the static structure factor $S(q)$ for a dispersion of charged colloidal particles using the Mean Spherical Approximation (MSA) and the resulting analytic expression for $S(q)$ has been used extensively to interpret experimental scattering data.[2] Although useful, their calculation is difficult to extend to multicomponent systems and not convenient for the description of dynamical properties. Since our aim is to examine these problems in the near future, we propose a simple and hopefully useful model based on liquid state perturbation theory using the well known Random Phase Approximation (RPA).[3,4,5] Normally in this approximation scheme, the electrostatic interaction between the colloidal particles would be treated as a perturbation to the reference hard sphere fluid arising from the "bare" excluded volume interaction between the colloidal particles. The modification to this description introduced here consists of assuming that for strong electrostatic repulsions, two spheres cannot come closer to each other than a certain effective hard sphere diameter $D_{\text{eff}} = RD$, where $R \geq 1$ and D is the "bare" hard sphere diameter. The original Hayter–Penfold calculations are known to lose their validity for dispersions of both low densities and high surface potentials[6] and the Rescaled Mean Spherical Approximation (RMSA) was proposed by Hayter and Hansen[7] to extend the validity of the calculations to lower densities. But when the surface potential ψ_0 is large, the validity of the model is still unclear. The effective hard sphere argument introduced here is consistent with the spirit of the RMSA. But we include the rescaling argument as an integral part of the physical model independent of the density as opposed to Hayter and Hansen who introduced rescaling only when unphysical results are obtained from the MSA at low densities.

The scattering intensity $I(q)$ from a colloidal dispersion represented as a one-component macrofluid is given by

$$I(q) \propto P(q)S(q) \tag{1}$$

where $P(q)$ is the macroparticle form factor. The structure factor $S(q)$ can be written[8] in terms of the fourier transform of the direct correlation function $C(q)$ with

$$S(q) = \frac{1}{1 - nC(q)} \tag{2}$$

where n is the number density of macroparticles and another equation relating $C(q)$ to the pairwise interaction potential is needed to solve the problem completely. For this we propose to use a perturbation theory based on the RPA[3,4,5] with

$$C(q) = C_{0\,\text{eff}}(q) - \beta U_{\text{eff}}(q) \tag{3}$$

where $\beta = (k_B T)^{-1}$, $C_{0\,\text{eff}}(q)$ is the direct correlation function for the hard sphere reference fluid whose hard sphere diameter is $D_{\text{eff}} \equiv RD$ $(R \geq 1)$ and $U_{\text{eff}}(q)$ is the fourier transform of the perturbation potential. We may use the well known Percus–Yevick[8] expression for the hard sphere reference fluid which gives

$$\begin{aligned} nC_{0\,\text{eff}}(q) = {} & \Big[A(\sin x - x\cos x) \\ & + B\left[\left(\frac{2}{x^2} - 1\right)x\cos x + 2\sin x - \frac{2}{x}\right] \\ & - \frac{\eta A}{2}\left[\frac{24}{x^3} + 4\left(1 - \frac{6}{x^2}\right)\sin x - \left(1 - \frac{12}{x^2} + \frac{24}{x^4}\right)x\cos x\right]\Big]x^{-3} \end{aligned} \tag{4}$$

where $x = qD_{\text{eff}}$, $n = \pi n D_{\text{eff}}^3/6$ is the effective volume fraction and

$$A = -24\eta\frac{(1+2\eta)^2}{(1-\eta)^4}, \quad B = 36\eta^2\frac{(2+\eta)^2}{(1-\eta)^4} \tag{5}$$

Again we stress that by replacing D by its effective value, $D_{\text{eff}} = RD(R \geq 1)$, we hope to simulate reasonably well the strong short range repulsion of charged spheres and the structure factor for the hard sphere reference fluid $S_0(q)$ should model the real structure factor $S(q)$ for wavevectors greater than q_p, the wavevector of the principle peak in $S(q)$,[3] i.e.

$$S(q) \simeq S_0(q) \quad \text{for} \quad q \geq q_p \tag{6}$$

The perturbation correction which is significant for small wavevectors, $q \leq q_p$, is represented by $U_{\text{eff}}(q)$ which is usually assumed to arise from the classical DLVO potential:

$$U_{\text{eff}}(r) = \pi\varepsilon D_{\text{eff}}^2 \psi_{0\,\text{eff}}^2 \frac{\exp(-k_D(r - D_{\text{eff}}))}{r}, r > D_{\text{eff}} \tag{7}$$

where k_D is the inverse Debye screening length, ε is the dielectric constant of the medium and $\psi_{0\,\text{eff}}$ is an effective surface potential. The DLVO interaction potential known to be invalid for $r \sim D$, but the effective potential of this model avoids this difficulty by not allowing the spheres to come into true contact with each other so that the DLVO potential need only be used for large r with an effective interaction strength.[9] If we assume the $U_{\text{eff}}(r) = 0$ for $r < D_{\text{eff}}$,[5] then by taking the Fourier transform of Eq. (7) one finds

$$nC(q) = nC_0(q) - 24\eta\gamma e^{-s}(x\cos x + s\sin x)/[x(x^2 + s^2)] \tag{8}$$

where $s \equiv k_D D_{\text{eff}}$ and γ is a constant depending on $\psi_{0\,\text{eff}}$ with

$$\gamma = \beta\pi\varepsilon D_{\text{eff}} \psi_{0\,\text{eff}}^2 \exp(s) \tag{9}$$

This model can easily be shown to reproduce the essential features of the MSA and RMSA results as obtained by Hayter *et al.*[1,7] when R is chosen to ensure that the principle peak in $S(q)$ is correctly located and $\psi_{0\,\text{eff}}$ is chosen to give correct values of the osmotic compressibility. To illustrate this last point, we consider the forward scattering intensity which is obtained by letting $q = 0$, when

$$S(q=0)^{-1} = \frac{(1+2\eta)^2}{(1-\eta)^4} + 24\eta\gamma\frac{(1+s)}{s^2}\exp(-s) \tag{10}$$

We recall that η represents here the effective volume fraction which is fixed when R has been chosen, so that if the Debye screening length is calculated from the concentration of added salt (assumed to be very much greater than the counterion concentration), $\psi_{0\,\mathrm{eff}}$ is the only free parameter available to fix the osmotic compressibility. This model is in principle good for any density as long as the hard sphere system constitutes an accurate reference system. This limits applicability to charged dispersions with added salt where the charge screening effects are dominant. In systems with no added salt an alternative approach based on a one component plasma reference fluid is more appropriate.[10]

The simplicity of this model makes it suitable for the study of dynamical properties of charged colloidal dispersions and this will be the subject of a future communication.

Acknowledgement

One of us (M.B.) thanks the Institute of Food Research, Norwich Laboratory for their hospitality and the AFRC for financial support through the Underwood Fund during the course of part of this work. We thank Dr. M. Silbert for many interesting discussions and helpful remarks.

References

1. J. B. Hayter and J. Penfold, *Mol. Phys.*, **42** (1981); 109, ibid. *J.C.S. Faraday 1*, **77**, 1851 (1981).
2. D. Benedouch and S. H. Chen, *J. Phys. Chem.*, **87**, 1473 (1983).
3. M. J. Grimson, *J.C.S. Faraday 2*, **79**, 817 (1983).
4. M. J. Grimson and A. T. Augousti, *Phys. Chem. Liq.*, **14**, 53 (1984).
5. M. J. Grimson and P. Richmond, *J. Physique*, **46**, 447 (1985).
6. B. Svensson and B. Jönsson, *Mol. Phys.*, **50**, 489 (1983); D. J. Gonzalalez, M. J. Grimson and M. Silbert, *Mol. Phys.*, **54**, 1047 (1985).
7. J. P. Hansen and J. B. Hayter, *Mol. Phys.*, **46**, 561 (1982).
8. J. P. Hansen and I. R. McDonald, *Theory of simple liquids* Academic Press, London, (1976).
9. S. Alexander, P. M. Chaikin, P. Grant, G. Morales, P. Pincus and D. Hone, *J. Chem. Phys.*, **80**, 5776 (1984).
10. M. J. Grimson, *J. Chem. Phys.*, **79**, 5070 (1983).