

Rescaled mean spherical approximation structure factor for an aqueous suspension of polystyrene spheres

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Abstract. Rescaled mean spherical approximation (RMSA) has been used to calculate the structure factor for the aqueous suspension of polystyrene macroions with the interaction potential taken according to Derjaguin and Landau (1941) and Verwey and Overbeek (1948) (DLVO) model. The effects of charge over the macroion and size on the surface potential and therefore, the structure factor have been studied. The breakdown of the DLVO potential with an excess charge over the macroion ($\geq 800e$) has been reported. The oscillation in the first peak height of structure factor versus wave vector curve with size has been correlated with the Debye length.

Keywords. Structure factor; surface potential.

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1. Introduction

The arrangement of charged macroions in suspension is governed mainly by the finite ion screened Coulomb interparticle pair potential (Tata *et al* 1986; Brown *et al* 1975). Hayter and Penfold (1981) solved the Ornstein–Zernike equation (Ornstein and Zernike 1914) under mean spherical approximation (MSA) (Lebowitz and Percus 1966) using DLVO potential to calculate the structure factor for the charged particles having a hard core. This has been used successfully in dense suspensions of charged micelles or colloidal particles (Hayter and Penfold 1981). It fails however, at low densities of highly correlated polystyrene spheres. Subsequently, Hansen and Hayter (1982) removed this limitation by a procedure known as rescaling. This rescaled MSA (RMSA) satisfactorily reproduces the results of an extensive numerical solutions of hypernetted chain equations (Schaefer 1977) as well as the experimentally determined structure factors (Tata *et al* 1987; Brown *et al* 1975; Sood 1987; Krause *et al* 1991). This theory has also been applied successfully to explain the temperature (Hartl and Versmold 1984) and impurity dependence (Verwey and Overbeek 1948) of the structure factor of mono disperse dilute colloidal suspensions. However, its application to a highly correlated spherical macroions at considerable densities in solution has not been done thoroughly to ascertain its validity.

An in depth study to understand particularly, the correlation between various parameters of the scatterer and the structure factor is essential to study the interparticle interaction potential by measuring the structure factor using light scattering method. The dependence of the structure factor on the variables such as number density (n_p) of macroion and impurity ion (n_i), charge over the macroion (z) and impurity ion

(z_i) have been studied by earlier workers (Tata *et al* 1987; Kesavamoorthy and Arora 1986; Sood 1987; Tata *et al* 1986) using the RMSA method. In the present work, it has been attempted to study the interparticle interaction potential amongst the aqueous suspension of polystyrene charged balls and the dependence of the structure factor on its charge (z) and size (diameter σ) using the RMSA formulation as given by Hayter and Penfold (1981). The break-down of the DLVO potential for highly charged ($z \geq 800e$) macroions has been reported. It is found that the peak height in the structure factor versus wave vector curve oscillates with size at fixed charge and particle density of the macroions. These oscillations are found to be correlated with the Debye length.

2. Theory and calculation

Hayter and Penfold (1981) reduced the DLVO pair potential (Verwey and Overbeek 1948) between highly charged polystyrene particles of diameter σ , dispersed in a screening continuum of dielectric constant ϵ , into the dimensionless form as given by

$$\beta U(x) = \gamma \exp(-kx)/x; \quad x > 1 \quad (1)$$

by defining $x = r/\sigma$, $k = \mathcal{H}\sigma$, $\beta = 1/k_b T$; where r is the interparticle centre-to-centre distance, k_b is the Boltzmann constant, T is the temperature, and \mathcal{H} is the Debye-Huckel inverse screening length obtained as follows

$$\mathcal{H}^2 = (n_p z e^2 + \sum n_i z_i e^2)/k_b T \epsilon \quad (2)$$

and γ is the dimensionless coupling constant given by

$$\gamma = \beta \pi \epsilon \sigma \psi_0^2 \exp(k) \quad (3)$$

ψ_0 is the surface potential of the particle given by

$$\psi_0 = ze/\pi \epsilon \sigma (2 + \mathcal{H}\sigma) \quad (4)$$

$\gamma \exp(-k) = \beta \pi \epsilon \sigma \psi_0^2$ is the contact potential for macroion pair in unit of $k_b T$. In colloidal system the Coulomb coupling is often large, i.e. $\gamma \gg 1$. Because of this the MSA yields reliable structure factors only for sufficiently high concentration i.e. $\eta \gg 0.2$, where η is the volume fraction and is given by

$$\eta = \pi \sigma^3 n_p / 6. \quad (5)$$

In case of the low density charged colloidal system such as polystyrene particles dispersed in water, where coulomb coupling is generally strong ($\eta \gg 1$) and η is less than 10^{-3} , the MSA yields unphysical negative contact values for the pair correlation function. Hansen and Hayter (1982) gave a rescaling procedure to overcome this difficulty by increasing the particle diameter from its actual value σ to an effective hard core value of σ^* while maintaining the coupling Γ_k a constant

$$\Gamma_k = 2\beta U(r = 2a), \quad (6)$$

where $2a = 2(3/4\pi n_p)^{1/3}$ is the mean interparticle spacing (Hayter and Hansen 1982).

The rescaling procedure consists of choosing a rescaled volume fraction $\eta^* = \pi\sigma^{*3}n_p/6$ at which MSA gives a non-negative contact potential value for correlation function. The expression for structure factor with modifications is given by (Hayter and Penfold 1981)

$$S(Q) = 1/[1 - 24\eta a(q)] \quad (7)$$

where $q = Q\sigma$ and

$$\begin{aligned} a(q) = & [A(\sin q - q \cos q) + B\{(2/q^2 - 1)q \cos q + 2 \sin q - 2/q\} \\ & + \eta A\{24/q^3 + 4(1 - 6/q^2)\sin q - (1 - 12/q^2 + 24/q^4)q \cos q\}/2]/q^3 \\ & + [C(k \cosh k \sin q - q \sinh k \cosh q) + F\{k \sinh k \sin q \\ & - q(\cosh k \cos q - 1) + \{(\cos q - 1) \cdot (q^2 + k^2)\}/q - \gamma \exp(-k)(k \sin q \\ & + q \cos q)\}/q(q^2 + k^2)]/q(q^2 + k^2) \end{aligned}$$

A , B , C and F are constants and are determined as given by Hayter and Penfold (1981). The structure factor for the aqueous suspension of charged polystyrene balls has been calculated using equation (7). The computer program as developed by Hayter and Hansen (1982) with slight modification to adopt for Mighty Frame II Machine has been used. The calculations have been performed in double precision.

3. Results and discussion

In order to see the effect of the interaction potential on the structure factor, the nature of the surface potential corresponding to different parameters viz. size of the macroion and charge on it are shown in figures 1a and 1b.

The variation of the structure factor with the size of the macroion having fixed particle charge (500e) and density ($4.0 \times 10^{18} \text{ m}^{-3}$) has been shown in figure 2. The first peak, which is prominently large, shifts towards larger Q with the size increase of the macroion. Further, for $\sigma \leq 1000 \text{ \AA}$, a peak smaller than the one mentioned above precedes it. The size increase reduces the strength of the surface potential (see figure 1a). The value of $k (= \mathcal{H}\sigma)$ however, increases. In fact, the nature of the variation of $S(Q)$ with Q turns out to be almost indistinguishable from each other for $k (= \mathcal{H}\sigma) \leq 0.5$ (Hansen and Hayter 1982). The surface potential decreases very slowly with particle diameter exceeding $\sim 1000 \text{ \AA}$ which corresponds to $k \geq 0.5$. This is the reason that the peaks of the structure factor get smeared giving rise to an almost constant value of it. The peak height is correlated with the size of the particle and also as size increases the difference between the two consecutive peak positions increases (see figure 2). In figure 3 the curve marked $S(Q)(I_{\max})$ shows the variation of the first peak height and the one marked $S(Q)(II_{\max})$ is that of the second peak height (of figure 2) with the size (σ) of the macroion. As σ increases beyond $\sim 800 \text{ \AA}$, the first peak height increases very rapidly up to $\approx 2400 \text{ \AA}$ whereafter its value oscillates. In case of the peak height of the second maxima however, $S(Q)$ almost remains constant except showing a small kink near $\sigma \approx 1000 \text{ \AA}$. This behaviour may be explained in terms of the effective hard sphere radius. Though the Debye length (λ_D) is constant, the effective hard sphere radius increases with the increase in particle

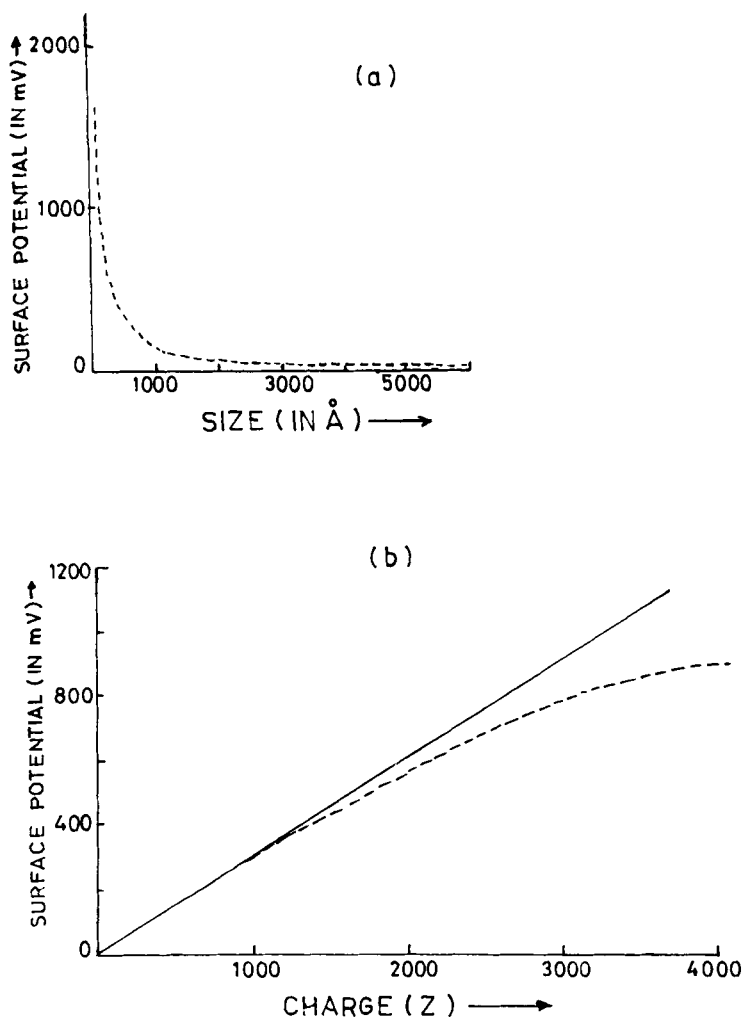


Figure 1. (a) Variation of surface potential with size for $z = 500$, $n_p = 4.00 \times 10^{18} m^{-3}$, $T = 294 K^\circ$, $\epsilon = 80$. (b) Variation of surface potential with charge (z) for $\eta = 0.001579$.

size (Pieranski 1983) viz; $\sigma^* = (\sigma + \lambda_D)$. Consequently, the effective volume fraction, $\eta^* = \eta \cdot (1 + 2\lambda_D/\sigma)^3$ also increases. This is perhaps the reason that the peak height in $S(Q)$ increases and shifts as well towards the higher wave vector side. It is also found that the first and second oscillation peaks in $S(Q)(I_{\max})$ vs σ occur nearly at λ_D ($\sim 2383 \text{ \AA}$) and $2\lambda_D$ ($\sim 4800 \text{ \AA}$), respectively.

The nature of the $S(Q)$ vs Q curve at different values of the surface charge viz; $z = 50, 100, 400, 800, 1200$ and $1600e$ for a given η is shown in figure 4. It is found that the amplitude of the structure factor increases but the peak positions remain nearly the same. Increase in charge on the macroions results in the increase of the interaction potential and decrease in the isothermal compressibility (Hayter and Penfold 1981). This in turn, causes an increase in the structure factor (see figure 4). Further, it is obvious from figure 4 that the structure factor at low scattering wave vector becomes oblivious beyond $z \gg 800e$. This corresponds to the fact that the surface potential (see figure 1b) for a given η deviates from its linearity after the

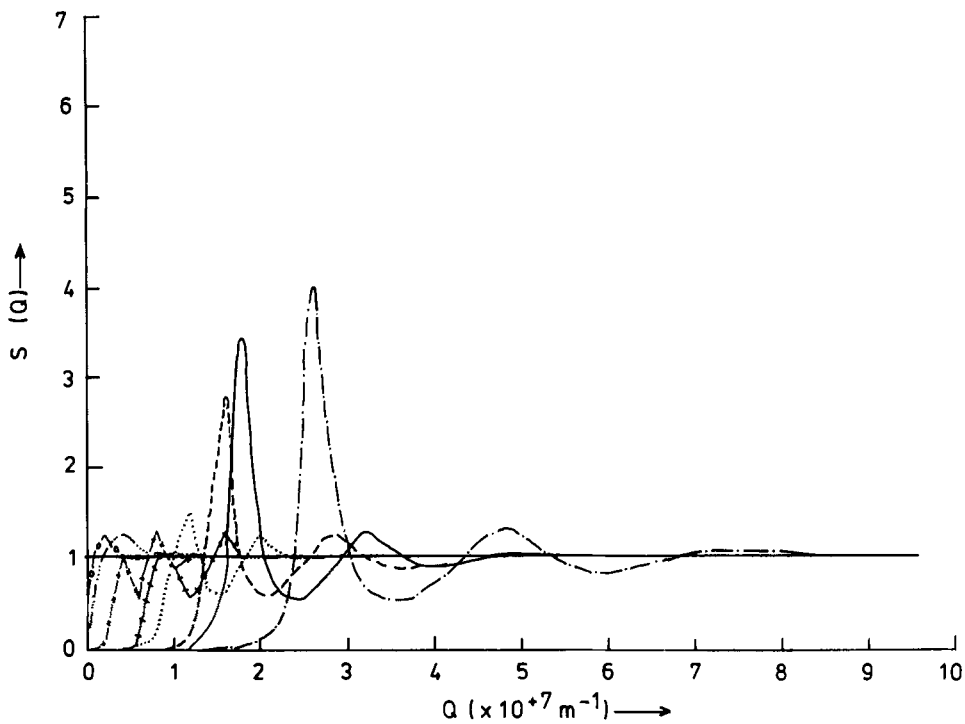


Figure 2. Structure factor for $z = 500$, $n_p = 4.00 \times 10^{18} \text{ m}^{-13}$, with $\sigma = 100$ (-o-o-), 200(-·-·-·-), 400(-*-*-*) , 800(+--+--+--+), 1000(·-·-·-·-), 1400(-·-·-·-), 1600(-·-·-·-), 2400(-·-·-·-) \AA .

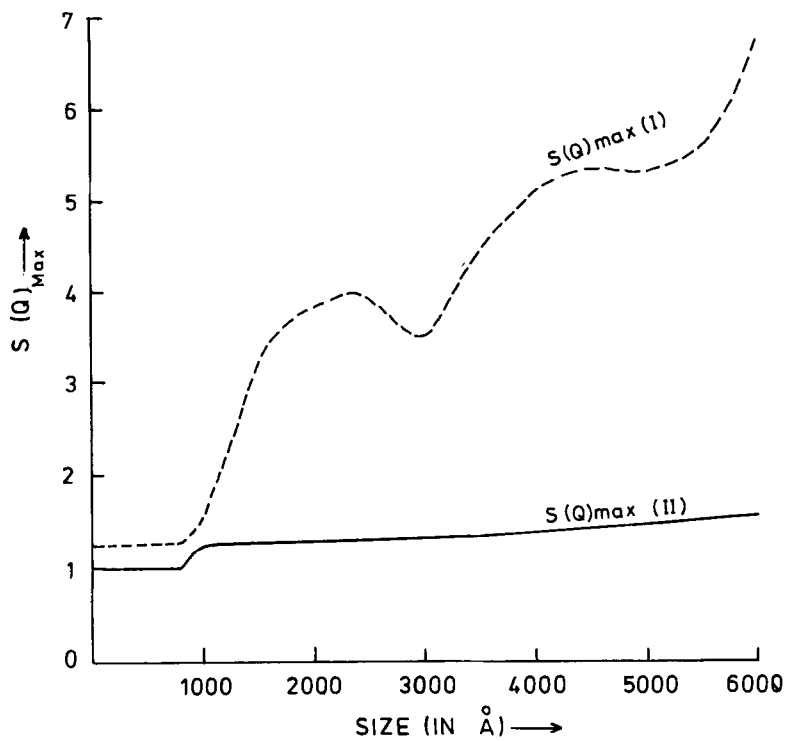


Figure 3. Variation of $S(Q)_{\text{max}}$ with size (σ) of the macroion.

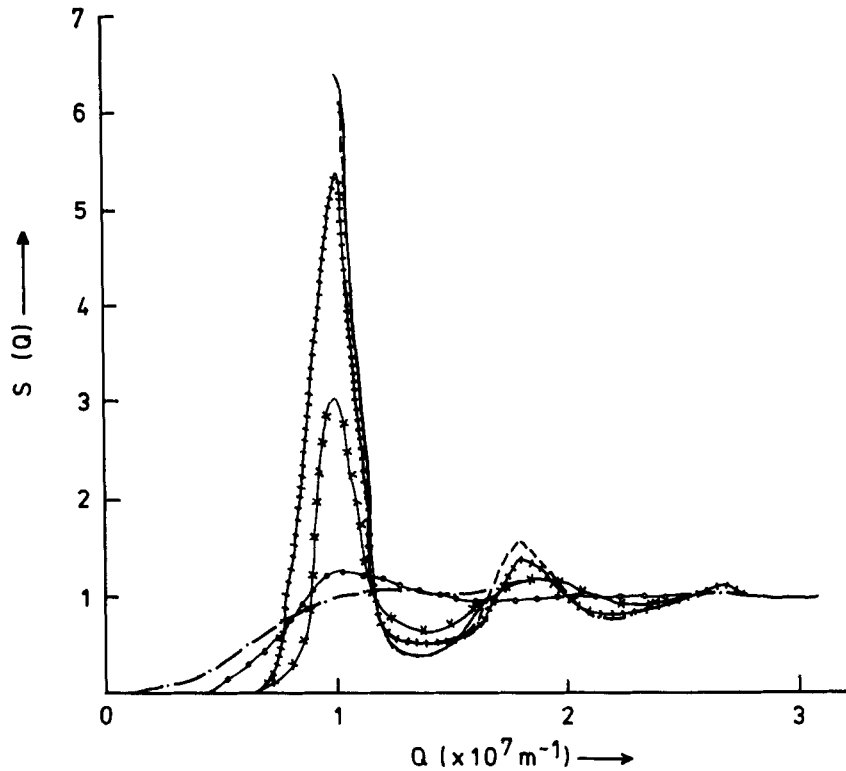


Figure 4. Nature of the structure factor $S(Q)$ for charge $z = 50$ (-·-·-·-), 100 (-○-○-), 400 (-·-·-·-·-·-·-), 800 (+·+·+·+), 1200 (-·-·-·-), 1600 (——) with $n_p = 4.00 \times 10^{18} \text{ m}^{-3}$, $\sigma = 910 \text{ \AA}$.

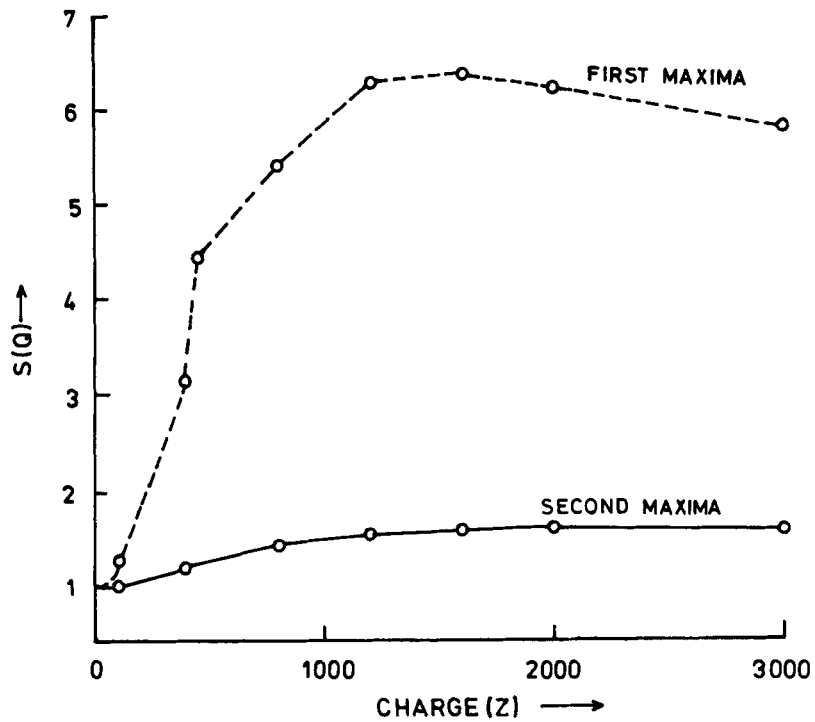


Figure 5. Variation of first and second peak heights with charge (z) on the macroion.

surface charge increases beyond 800e. The present results in this regard are in good agreement with that of the earlier workers (Tata *et al* 1986; Hansen and Hayter 1982). It is therefore, inferred that the DLVO surface potential and the RMSA model formulation need further modification for the surface charge exceeding $\sim 800e$. The variation of the first and second peak heights with the charge on the macroion is shown in figure 5. The height of the first peak increases rapidly with the charge up to $z \sim 1000e$ after which it becomes almost constant. The strength of the interaction with the nearest neighbour therefore, increases with the charge to a saturation point which becomes independent of it after that. For the next neighbour the increase in-charge does not affect the peak height due to the fact that there is a strong screening between them.

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