

Effect of size and charge on ordering of a highly charged concentrated macroions in suspension

R K PANDEY and D N TRIPATHI

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

MS received 15 January 1993; revised 19 October 1994

Abstract. An efficient fast Fourier transform method has been employed to determine correlation function [$g(r^*)$] using the structure factor [$S(Q^*)$] calculated with the rescaled mean spherical approximation (RMSA) and the DLVO potential. Based on this function a parametric (size and charge) study of the ordering in a highly charged and concentrated macroions (an ideal colloid) has been made. The strength of the correlation increases with the increase in the charge on macroions and it saturates after a certain value. Similarly, a critical diameter of the particle depending on the charge on it has been found at which normal feature of the ordering disappears.

Keywords. Correlation function; rescaled mean spherical approximation; DLVO.

PACS Nos 82·70; 61·20

1. Introduction

Colloids define a range of systems containing dispersed particles that are larger than atomic dimensions but small enough to exhibit Brownian motion, which prevents appreciable sedimentation in normal gravity. The particles have typical dimensions in the range 10^2 – 10^5 Å and have of the order of 10^2 – 10^4 surface ionizable groups [1, 2]. These ubiquitous dispersions fall into two categories, namely lyophilic (solvent loving) and lyophobic (solvent fearing) [3, 4].

In a recent work [5] we have analyzed the nature of the structure factor for a highly charged concentrated monodisperse macroions in aqueous suspension as obtained using the DLVO interaction potential [3] and rescaled mean spherical approximation (RMSA) [6]. The limitations regarding the applicability of the DLVO model interaction potential and the theoretical framework of RMSA for such a system have been examined.

It is well-known that the number density and hence the volume fraction and the excess ion concentration (counterions + impurity ions) are the two important parameters which govern the ordering process in such systems. Tata *et al* [7] have found that as the impurity ion concentration (n_i) increases the peak height of $g(r^*)$ decreases and its position shifts towards lower values of r^* and finally it becomes zero for $n_i > 3z\rho$. Because, an addition of ionic impurity reduces Coulomb screening length and so the particles can penetrate deeper into the value of r^* at which $g(r^*)$ becomes zero. The influence of the particle concentration on pair distribution function has been studied by Hartl and Versmold [8]. It is pointed out that height of the first peak of $g(r^*)$ increases very slowly and its position also shifts towards lower side of r^* .

However, the number density remaining constant, increase in size of the macroions also results in the increase of the volume fraction η . Further, the increase in the surface charge of the particles is bound to affect the interaction potential. Therefore, these two factors viz the size and the charge of the suspension are also expected to play an important role in the process of ordering. In this work we examine the nature of the radial correlation function (which is a Fourier transform of the structure factor) and hence the ordering process, in respect of these two parameters in the case of an ideal charged colloidal suspension.

2. Theory

An outline of the RMSA method is given by Hayter and Penfold [6]. The radial distribution function is defined as

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^\infty [S(Q) - 1] Q \sin Qr dQ \quad (1)$$

where ρ is the number density, Q is the momentum transfer (or scattering wave vector) and $S(Q)$ is the structure factor at Q . Equation (1) may be expressed in terms of dimensionless variable by defining

$$\begin{aligned} r^* &= \frac{r}{\sigma} \\ Q^* &= Q\sigma \end{aligned} \quad (2)$$

where σ is the particle diameter, as

$$g(r^*) = 1 + \frac{1}{12\pi\eta r^*} \int_0^\infty [S(Q^*) - 1] Q^* \sin Q^* r^* dQ^* \quad (3)$$

where

$$\eta = \frac{\pi\alpha^3 \rho}{6} \quad (4)$$

is the volume fraction. The upper limit of the integration is replaced by a finite value of 128, i.e., nearly 100 times that of the first peak position Q_{\max}^* of the structure factor $S(Q^*)$ to evaluate $g(r^*)$ to sufficient accuracy. In the calculation of $g(r^*)$ we have calculated $S(Q^*)$ (see [5]) at an interval of $dQ^* = 0.1$. All calculations are carried out in double precision on Mighty Frame(II) Computer of the Computer Centre, BHU, Varanasi, using a program developed by Hayter and Hansen [9] and Hayter [10].

3. Results and discussion

The radial correlation function $g(r^*)$ for various values of ze viz. 1200, 800, 200, 100, 50 with $\sigma = 600 \text{ \AA}$, 910 \AA and 1600 \AA for $\rho = 4.0 \cdot 10^{18} \text{ m}^{-3}$ have been shown in figure 1a, 1b and 1c, respectively in order to see the change in its nature and hence the ordering due to the charge on different sizes of macroions. The first peak amplitude in $g(r^*)$ vs. r^* curve increases with the increase of charge on macroions. Its position also shifts slightly towards higher r^* value. The number of peaks increases indicating thereby, the increase in the range as well as strength of the interaction potential and

Radial correlation function

the decrease in isothermal compressibility [11]. This implies that the strength of the interaction potential between nearest neighbor, next-nearest neighbor, next-to-next nearest neighbor and so on, increases with the increase of charge on macroions at a given volume fraction. Further, for $\sigma = 600 \text{ \AA}$ and $z \geq 200e$ (volume fraction $\eta = 4.52 \cdot 10^{-4}$) a peak smaller than the one mentioned above, precedes it at lower value of r^* (see figure 1a). The position of the second and third peaks however, remain unaltered.

The variation of the pair correlation function $g(r^*)$ with r^* for different size (σ) with $z = 500e, 800e$ and $1000e$ for $\rho = 4.0 \cdot 10^{18} \text{ m}^{-3}$ have been shown in figures 2a, 2b and 2c, respectively. The first peak height increases with size increase of the macroions indicating an increase in the strength of the correlation.

It is important to note that for particles having a critical diameter, which is a function of the charge over the macroion ($\sigma \leq 200 \text{ \AA}$ for charge $z = 500e$, $\sigma \leq 400 \text{ \AA}$ for $z = 800e$ and $\sigma \leq 800 \text{ \AA}$ for $z = 1000e$), the normal shape of the function $g(r^*)$ gets distorted and it acquires an unphysical negative contact values [6]. Except these critical diameter, the position of the first maximum of $g(r^*)$ occurs in the range of r equal to 5 to 10 times of the diameter (σ). In this case RMSA gives reasonably good results with the variation of charge and size. It is to be noted that Hartl and Versmold [8] have also reported a similar result in this range with the different particle densities. However, below the critical size, which is a function of the particles density and charge, the ordering in the colloidal suspension has not been observed. This is a most likely condition of Brownian motion of the suspensions in the medium. This may also be an indication of the failure of the RMSA method for such a system. Further, it is noticed that the number of peaks increases and its position shifts as well towards lower value of r^* . This behavior may be explained in terms of the increase in effective volume fraction [12, 13], i.e., $\eta^* = \eta(1 + (2/k))^3$ and effective charge [14], i.e., $z^* = z/(1 - \eta)$. The centre-to-centre distance between charged macroions remain unaltered at fixed particle concentration (ρ). The interparticle separation however, decreases as size increases. Therefore, an increase in effective volume fraction and effective charge result an increase of the interactions between nearest neighbor next-to-next nearest neighbor and so on. This may be the reason that the peak height as well as number of peaks increase and their positions shift as well towards the lower value of r^* . The effective charge and therefore, the interaction potential increases with the increase in charge and size of the macroions. This causes decrease in the width and increase in the height of the peaks in $g(r^*)$ (see figures 1 and 2). That is the strength of binding between the layer increases and the interlayer spacing decreases.

In both the cases i.e. increase in size as well as charge, the interaction potential causes a change in the shape and size of the pair correlation function $g(r^*)$. The variation in peak $g(r^*)_{\max}$ and dip $g(r^*)_{\min}$ magnitudes and relative shift in their positions may therefore, provide an estimate of the change in it due to a change in these two factors. The variation of $g(r^*)_{\max}$ and $g(r^*)_{\min}$ with charge and size are shown in figure 3. The curves marked $g(r^*)_{\max}(I)$ and $g(r^*)_{\max}(II)$ and $g(r^*)_{\min}(I)$ and $g(r^*)_{\min}(II)$ show the variation of height and depth of first and second peaks of $g(r^*)$ vs r^* with charge and size, respectively. It is noticed that both the height as well as depth of first two peaks increases with the charge up to $z \approx 1000e$ (see figure 3a) which, thereafter acquires a plateau region. That is, the increase in charge in excess of $\sim 1000e$ has no effect on them. This behavior may be understood in terms of the maximum charge [1] at a given volume fraction (η), i.e., $z^{\max} = 7.5\sigma/\lambda$; (where

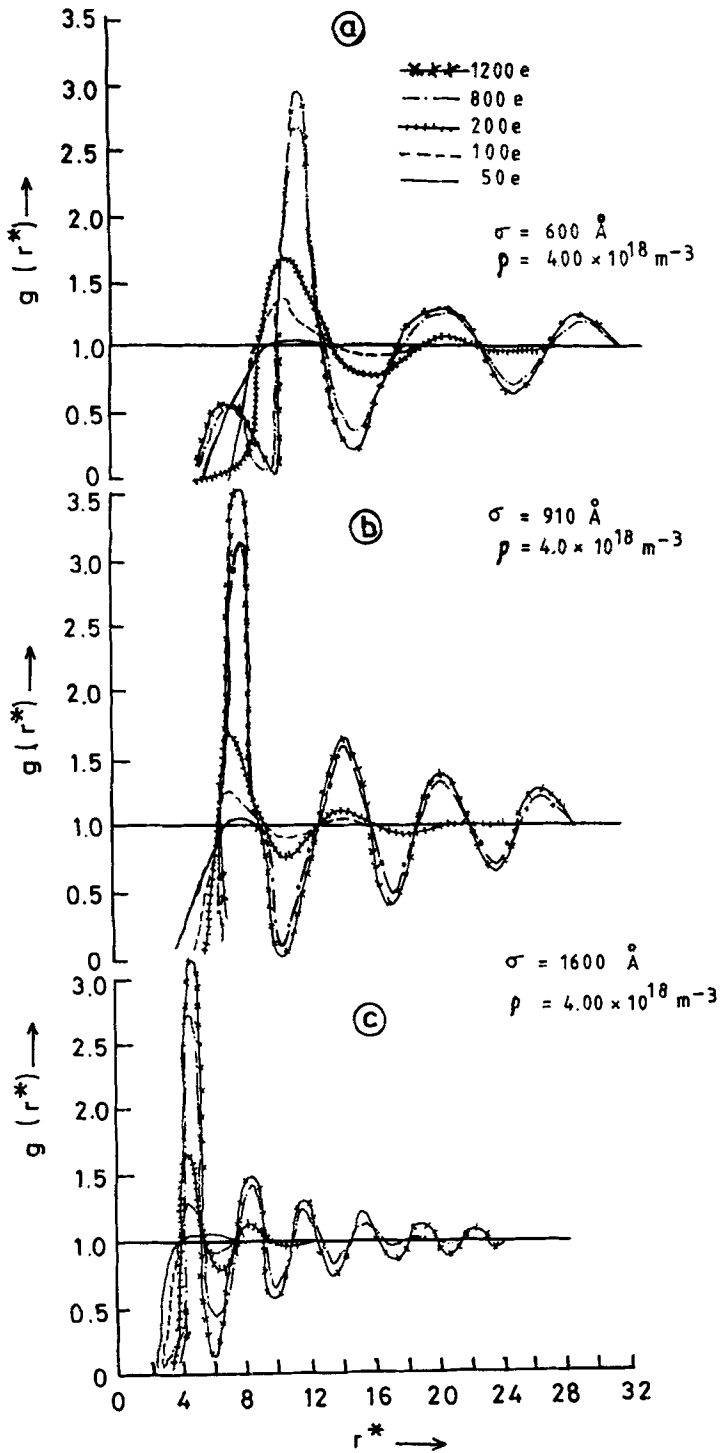


Figure 1. Variation of $g(r^*)$ with r^* for $z = 50 \text{ e}$ (—), $z = 100 \text{ e}$ (---), $z = 200 \text{ e}$ (++++), $z = 800 \text{ e}$ (-·-·-·-·-·-·-), $z = 1200 \text{ e}$ (-*-*-*-*) at (a) $\sigma = 600 \text{ \AA}$, (b) $\sigma = 910 \text{ \AA}$ and (c) $\sigma = 1600 \text{ \AA}$.

Radial correlation function

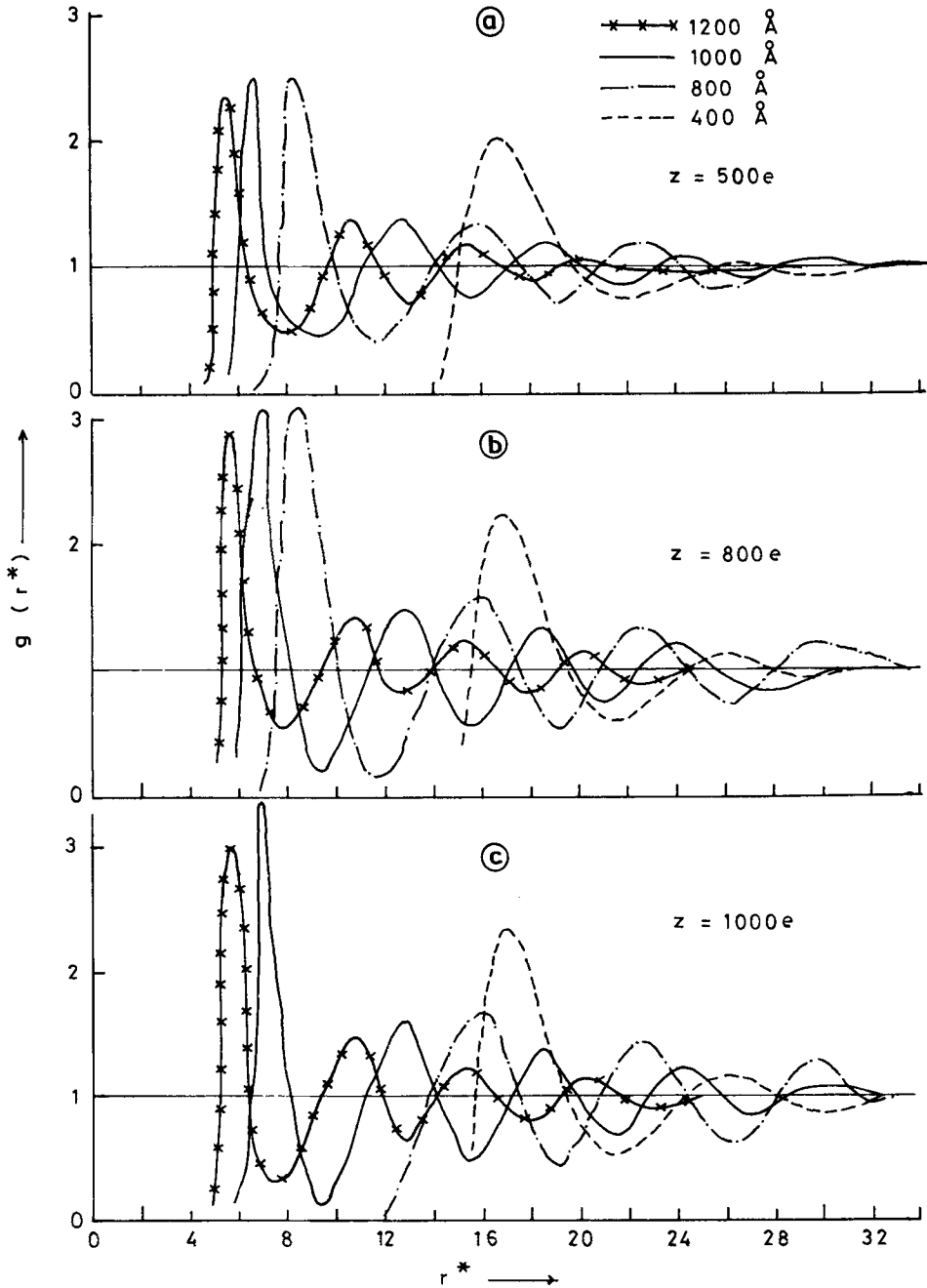


Figure 2. Variation of $g(r^*)$ with r^* for a given charge (a) $z = 500e$, (b) $z = 800e$ and (c) $z = 1000e$ and size $\sigma = 400 \text{ \AA}$ (---), $\sigma = 800 \text{ \AA}$ (-·-·-), $\sigma = 1000 \text{ \AA}$ (—) and $\sigma = 1200 \text{ \AA}$ (*-*-*)).

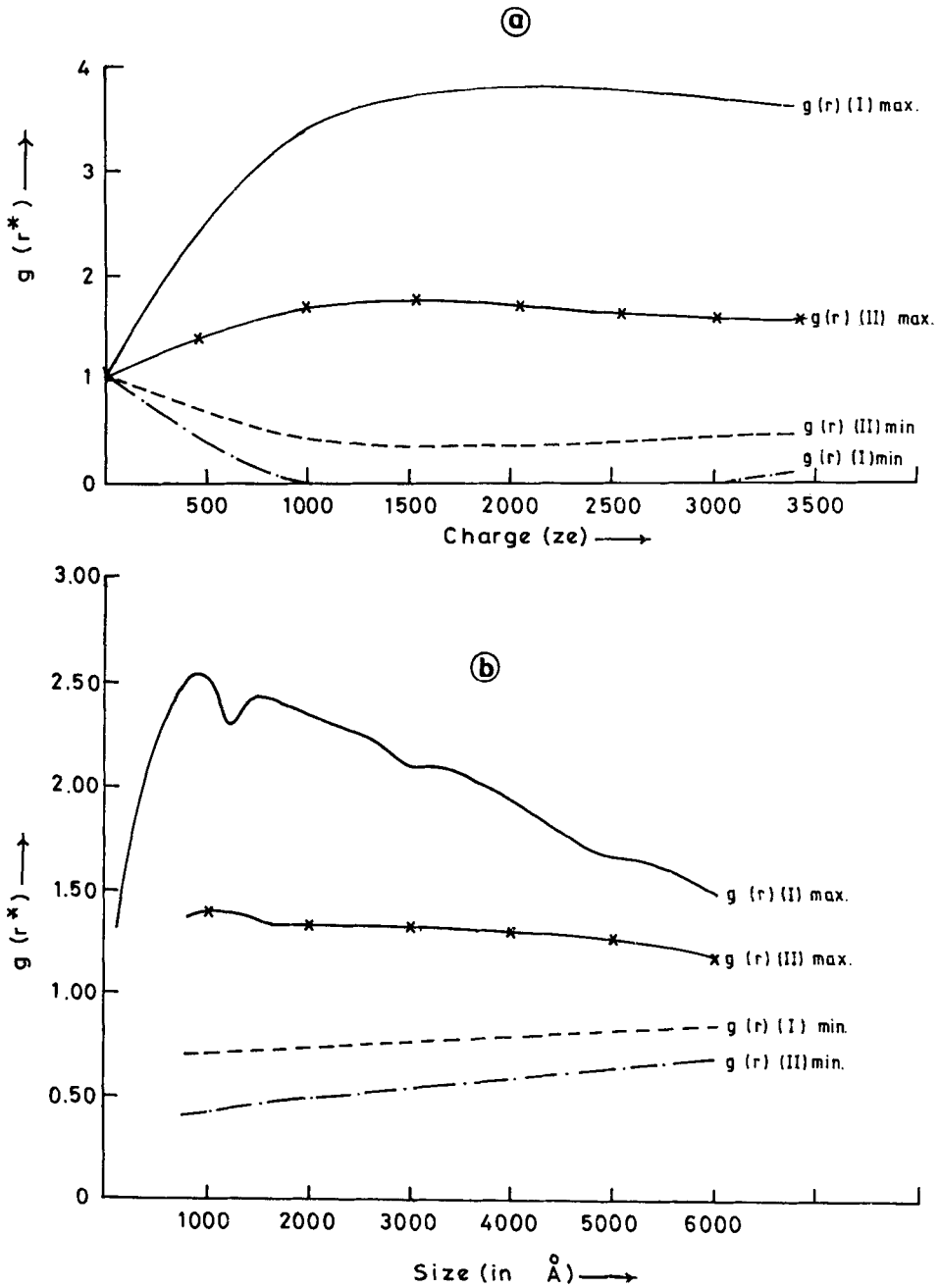


Figure 3. Variation of $g(r^*)_{\max}$ and $g(r^*)_{\min}$ with (a) charge for size $\sigma = 910 \text{ \AA}$ and (b) size for $z = 500 e$.

$\lambda = e^2/4\pi\epsilon_0\epsilon k_b T$) on the macroion that is effective in ordering. In the present case the value of z^{\max} is found to be $\approx 975 e$. Thus the expression given by Alexander *et al* [1] confirms our results.

$g(r^*) \text{ (I) }_{\max}$ increases in the beginning with an increase in particles diameter up to $\sigma = 1000 \text{ \AA}$, then after it oscillates (see figure 3b). $g(r^*) \text{ (II) }_{\max}$ on the other hand,

Radial correlation function

remains nearly constant. The first two dips depth $[g(r^*)_{\min}]$ increases very slowly with size increase of the macroions. All of the heights and dips viz. $g(r^*)(I)_{\max}$, $g(r^*)(II)_{\max}$, $g(r^*)(I)_{\min}$ and $g(r^*)(II)_{\min}$ converge to a value of $g(r^*)$ equal to 1.0 indicating thereby, a decrease in the interaction potential from nearest neighbor to next nearest neighbor and so on amongst the charged particles in suspension.

Acknowledgements

Authors are grateful to Profs D K Rai and K N Upadhyay for fruitful discussions with them. One of the authors (RKP) is thankful to UGC for the financial support during the course of this work.

References

- [1] S Alexander, P M Chaikin, P Grant, G J Morales, P Pincus and D Hone, *J. Chem. Phys.* **80**, 5776 (1984)
- [2] R D Groot, *J. Chem. Phys.* **94**, 5083 (1991)
- [3] E J W Verwey and J Th G Overbeek, *Theory of the stability of lyophobic colloids* (Elsevier 1948)
- [4] B V Derjaguin and L D Landau, *Acta Phys. Chim. URSS* **14**, 633 (1941)
- [5] R K Pandey and D N Tripathi, *Pramana – J. Phys.* **39**, 589 (1992)
- [6] J P Hansen and J B Hayter, *Mol. Phys.* **46**, 651 (1982)
- [7] B V R Tata, R Kesavamoorthy and Akhilesh K Arora, *Mol. Phys.* **57**, 369 (1986)
- [8] W Hartl and H Versmold, *J. Chem. Phys.* **88**, 7157 (1988)
- [9] J B Hayter and J P Hansen, *The structure factor of charged colloidal dispersion at any density* (Institute Lave-Langevin Report, 1982)
- [10] J B Hayter, *A program for fast bi-directional transform between $g(r)$ and $s(Q)$* (Institute Laue-Langevin Report, 1979)
- [11] J B Hayter and J Penfold, *Mol. Phys.* **42**, 109 (1981)
- [12] J P Hansen, *J. Phys.* **C14**, L151 (1981)
- [13] P Pieranski, *Contemp. Phys.* **24**, 25 (1983)
- [14] N J Wagner, R Krause, A R Rennie, B D'Aguanno and J M Goodwin, *J. Chem. Phys.* **95**, 494 (1991)