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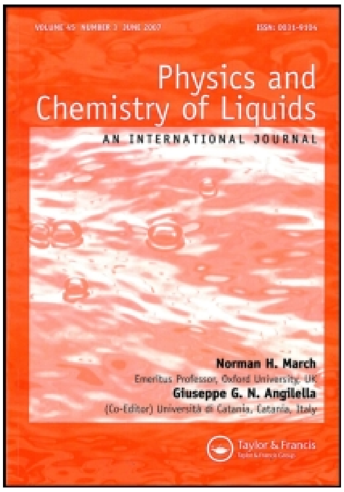

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The Bhatia-Thornton Partial Structure Factors of Polyelectrolyte Solutions

F. Ould Kaddour[a]; M. Silbert[b]; M. J. Grimson[c]
[a] Departement de Physique, Institut des Sciences Exactes, Tlemcen, A/gerie [b] School of Mathematics and Physics, University of East Anglia, Norwich, UK [c] AFRC Institute of Food Research, Norwich Laboratory, Norwich, UK

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The Bhatia–Thornton Partial Structure Factors of Polyelectrolyte Solutions

F. OULD KADDOUR

Institut des Sciences Exactes, Département de Physique,
I.N.E.S. de Tlemcen, Tlemcen, Algerie

M. SILBERT

School of Mathematics and Physics, University of East Anglia,
Norwich, NR4 7TJ, UK

and

M. J. GRIMSON

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

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We have calculated the Bhatia–Thornton partial structure factors for a two component system of charged hard spheres in solution, using the mean spherical approximation for the computation of the Ashcroft–Langreth structure factors. Our results show that for electrolytes which are highly asymmetrical in size and charge, the charge-number partial structure factor $S_{NQ}(q)$ is very sensitive to the distribution of the ions. The Bhatia–Thornton structure factors exhibit clearly the effects of charge ordering and condensation of the small ions around the large ions in concentated solutions.

KEY WORDS: Bhatia–Thornton structure factors, polyelectrolytes, condensation, solutions.

1 INTRODUCTION

In the study of binary liquid alloys the Bhatia–Thornton[1] structure factors have been very successful in providing a ready link between the thermodynamic properties of the alloy and the scattering functions. These three structure factors which, for charged systems, are named as the number–number, charge–charge and number–charge partial structure factors relate the fluctuations in particle number and charge and the correlation between these two fluctuations in the system. Furthermore they are linearly related to the better known Ashcroft–Langreth[2] structure factors which characterise the species–species correlations. The Bhatia–Thornton partial structure factors both in their long-wavelength limit, where they relate to the thermodynamic properties of the system, as well as for finite wavevectors, have been extremely successful in advancing our understanding of chemical short-range order in liquid binary alloys.[3,4] It is a straightfoward matter to evaluate these structures factors for electrolyte and polyelectrolyte solutions in which the Ashcroft–Langreth structure factors have been computed[5,6,7] for several cases. Whereas it appears that the Ashcroft–Langreth partial structure factors are not very illuminating, we shall show in this work that the Bhatia–Thornton structure factors exhibit clearly the effects of charge ordering and the onset of charge condensation as a function of the ionic charge and size difference and concentration of the ions in the solution. In this work we consider a two component system of charged hard spheres, immersed in a continuous background, interacting via a direct coulomb potential i.e. the primitive model (PM) of electrolytes. This model has been frequently applied to polyelectrolyte solutions such as some biological systems, micellar solutions and colloidal suspensions.[8,9,10] We use the mean spherical approximation (MSA) for the computation of the Ashcroft–Langreth structure factors. In Section 2 we define the Bhatia–Thornton structure factors and proceed to their evaluation for arbitrary sizes, charges and concentration of the ions. In Section 3 we give a discussion of the results.

2 STRUCTURE FACTORS

We adopt the following definitions and conventions. The two ions have diameter σ_1 and σ_2, valence Z_1 and Z_2, with σ_2 being larger than σ_1 and Z_2 being higher than Z_1 in absolute value. The concentration fraction of ions of type i is defined by

$$C_i = \frac{n_i}{n}, \tag{1}$$

where n_i is the number density of ions of species i and n is the total number density. We choose the dielectric constant as $\varepsilon = 78.3$ and the temperature $T = 298°\mathrm{K}$. The MSA for the interionic direct correlation function for the primitive model of a multicomponent system of charged hard spheres has been solved analytically by Blum.[11] We use Hiroike's[12] results for the determination of the direct correlation function $C_{ij}(q)$. The Ashcroft-Langreth structure factors are given by

$$\begin{aligned} S_{11}(q) &= (1 - n_2 C_{22}(q))/D(q) \\ S_{22}(q) &= (1 - n_1 C_{11}(q))/D(q) \\ S_{12}(q) &= (n_1 n_2)^{1/2} C_{12}(q)/D(q), \end{aligned} \tag{2}$$

where q is the scattered wavevector and

$$D(q) = (1 - n_1 C_{11}(q))(1 - n_2 C_{22}(q)) - n_1 n_2 C_{12}^2(q).$$

The Bhatia-Thornton structure factors are given in terms of (2) as

$$\begin{aligned} S_{NN}(q) &= C_1 S_{11}(q) + 2(C_1 C_2)^{1/2} S_{12}(q) + C_2 S_{22}(q) \\ S_{QQ}(q) &= C_2 S_{11}(q) - 2(C_1 C_2)^{1/2} S_{12}(q) + C_1 S_{22}(q) \\ S_{NQ}(q) &= S_{11} + \frac{(C_2 - C_1)}{(C_1 C_2)^{1/2}} S_{12}(q) - S_{22}(q), \end{aligned} \tag{3}$$

where S_{NN} denotes the number-number, S_{QQ} the charge-charge and S_{NQ} the charge-number partial structure factors.

3 RESULTS AND DISCUSSION

Figures 1-4 show the three Bhatia-Thornton partial structure factors $S_{NN}(q)$, $S_{QQ}(q)$ and $S_{NQ}(q)$ for different combinations of the ionic diameters, charges and concentrations. They are intended to display the characteristic physical features which arise from variations of the adjustable quantities rather than mimic any particular system.

In Figure 1, as a reference point, we have chosen an ionic hard sphere diameter ratio $\sigma_1/\sigma_2 = 5$ Å/10 Å and a small asymmetry in the ionic charges of $Z_1/Z_2 = -1/+6$. The total number density of ions in solution was set at $n = 6.02 \times 10^{25}$ m^{-3} which corresponds to a 0.1 M solution. For this diameter ratio, which is not very large, we find that within the MSA there is little cross correlation between the charge and number fluctuations, since $S_{NQ}(q)$ shows only small departures from a constant zero value. Note that within the MSA solution for the primitive model with equal diameters of the two ionic species (i.e. the restricted primitive model of electrolyte) there is no cross correlation at all between the charge and number fluctuations so that $S_{NQ}(q) = 0$ for all q. The figure shows that $S_{NN}(q) \simeq 1$ which indicates that we have a very dilute system with regard to simple excluded volume consider-

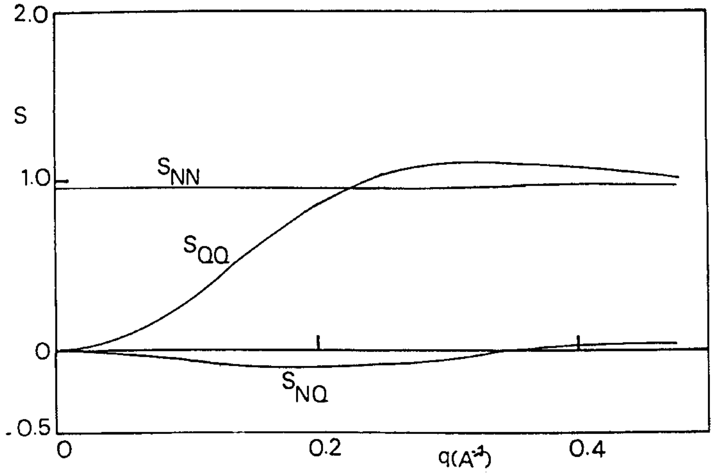

Figure 1 The Bhatia-Thornton structure factors $S_{NN}(q)$, $S_{QQ}(q)$, $S_{NQ}(q)$ of a solution of charged hard spheres with $\sigma_1 = 5$ Å, $\sigma_2 = 10$ Å, $Z_1 = -1$, $Z_2 = +6$. The total number density of the ions $n = 6.02 \times 10^{25}$ m^{-3}; $\varepsilon = 78.3$, $T = 298$°K and q is the wavevector.

ations. The charge-charge structure factor $S_{QQ}(q)$ shows more structure than any other partial structure factor which implies that there is some degree of charge ordering within the solution.

The effects on the Bhatia-Thornton structure factors of increasing the asymmetry of the small and large ions is shown in Figure 2, where the electrolyte has the same concentration as in Figure 1, i.e. a 0.1 M

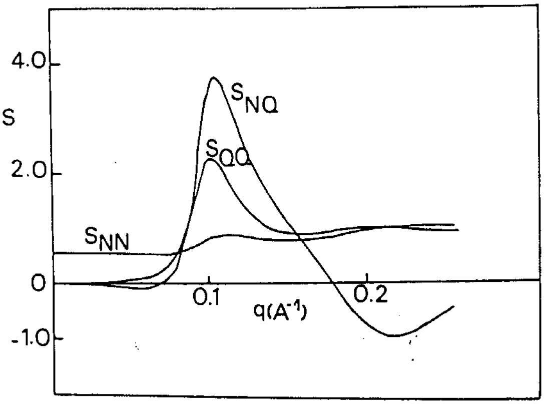

Figure 2 The Bhatia-Thornton structure factors $S_{NN}(q)$, $S_{QQ}(q)$, $S_{NQ}(q)$ of a solution of charged hard spheres with $\sigma_1 = 5$ Å, $\sigma_2 = 50$ Å, $Z_1 = -1$, $Z_2 = +20$. The total number density of the ions $n = 6.02 \times 10^{25}$ m^{-3}, $\varepsilon = 78.3$, $T = 298$°K and q is the wavevector.

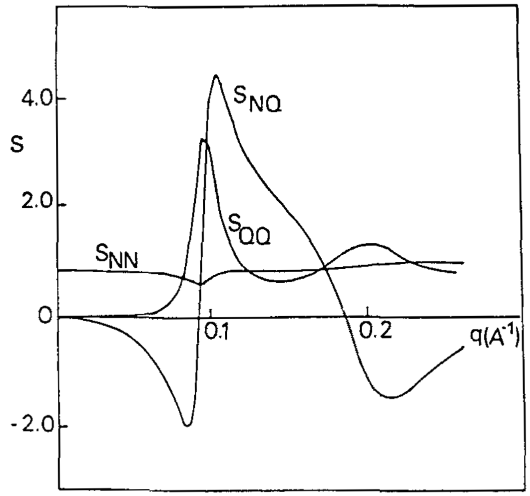

Figure 3 The Bhatia–Thornton structure factors $S_{NN}(q)$, $S_{QQ}(q)$, $S_{NQ}(q)$ of a solution of charged hard spheres with $\sigma_1 = 5$ Å, $\sigma_2 = 50$ Å, $Z_1 = -1$, $Z_2 = +50$. The total number density of the ions $n = 6.02 \times 10^{25}$ m^{-3}, $\varepsilon = 78.3$, $T = 298$°K and q is the wavevector. Note that only the asymmetry in charge has been changed with respect to Figure 2.

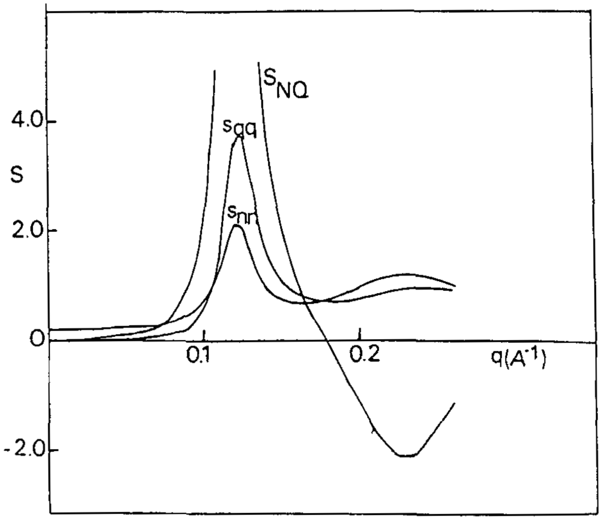

Figure 4 The Bhatia–Thornton structure factors $S_{NN}(q)$, $S_{QQ}(q)$, $S_{NQ}(q)$ of a solution of charged hard spheres with $\sigma_1 = 5$ Å, $\sigma_2 = 50$ Å, $Z_1 = -1$, $Z_2 = +20$, the total number density of the ions $n = 12.04 \times 10^{25}$ m^{-3}; $\varepsilon = 78.3$, $T = 298$°K and q is the wavevector. The parameters have the same values as in Figure 2 except that the concentration of the ions is doubled.

solution. The ion size asymmetry has been increased with $\sigma_1/\sigma_2 = 5\ \text{Å}/50\ \text{Å}$ and a corresponding increase in the charge asymmetry has been made to ensure the stability of the MSA solution. Here we have taken $Z_1/Z_2 = -1/+20$. When compared with the results of Figure 1, we note that there is a small but noticeable change in $S_{NN}(q)$ that is a result of the increased excluded volume of the ions. But $S_{NN}(q)$ still shows very little structure. The increase in charge asymmetry between the ions has significantly sharpened the structure of $S_{QQ}(q)$ and moved the location of the principal peak to smaller wavevectors. This can be interpreted as an enhanced charge ordering in the solution due to the increased electrostatic interactions. Most dramatic has been the alteration to the form of the cross correlation structure factor $S_{NQ}(q)$ which now displays a strong oscillatory structure and signifies a strong coupling of the charge and number fluctuations in the sample.

Figure 3 shows that the Bhatia–Thornton structure factors have the ability to distinguish the effects of charge asymmetry from those of size asymmetry. Here we have kept all of the parameter values the same as in Figure 2, except for the ionic charge asymmetry which has been increased to $Z_1/Z_2 = -1/+50$. Comparing Figures 2 and 3 it is immediately apparent that there has been little alteration to the form of $S_{NN}(q)$ which supports our hypotheses that $S_{NN}(q)$ is principally determined by excluded volume considerations. The increase in charge asymmetry is clearly reflected in the enhanced structure of $S_{QQ}(q)$. The enhancement of $S_{NQ}(q)$ that has resulted from an increase of the ion charge asymmetry is also notable. But the most interesting aspect of this curve is the appearance of secondary maximum or "shoulder" on the high angle side of the principal peak of $S_{NQ}(q)$ which is located at a wavevector corresponding to the inverse Debye screening length.

The effect of the electrolyte concentration is illusrtrated in Figure 4 for which we have chosen the same parameter values as in Figure 2 except for the electrolyte concentration which has been doubled, i.e. a 0.2 M electrolyte solution. It can be seen that the amplitudes of the oscillations in $S_{NQ}(q)$ have increased dramatically, by a factor of nearly three, although the shape of the curve is similar in both figures. At the same time $S_{NN}(q)$, the fluctuation in particle number, starts to display some significant topological order that follows from increases in the excluded volume of the ions. The charge ordering, indicated by $S_{QQ}(q)$, also shows enhancement with increases in the electrolyte concentration as expected.

The sensitivity of the cross correlation Bhatia–Thornton structure factor, $S_{NQ}(q)$, to details of the ion size and charge asymmetry is remarkable; all the more so, since earlier studies of similar systems through the Ashcroft–Langreth partial structure factors showed no such dramatic features.[5,6,7] From the results obtained here, a physical picture follows in which the large highly charged ions are surrounded by a condensed layer of the small ions which are constantly jumping from one large ion to another, a picture that is consistent with the concepts of counterion condensation from polyelectrolyte theory.[13] Thus we conclude that the Bhatia–Thornton structure factors provide a useful and physically appealing method for studying scattering from electrolyte and polyelectrolyte solutions in which the size and charge asymmetry of the ions is large.

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