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Scattering from charged macromolecules. I. Static structure factor

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Résumé. — Dans cet article, nous étudions la variation de la fonction cohérente de diffusion élastique $S(q)$ en fonction du vecteur transfert de moment q pour une solution de macromolécules chargées, à concentration finie, avec ou sans sel ajouté. Nous considérons en particulier les cas de macromolécules sous forme de sphère dure et de bâtonnet rigide. Nous introduisons un modèle de potentiel effectif pour tenir compte de la répulsion Coulombienne entre les ions macromoléculaires. Ceci nous permet d'interpréter le maximum observé expérimentalement dans la courbe de $S(q)$ à l'aide d'un argument simple de trou de corrélation.

Abstract. — In this paper we investigate the variation of the coherent static structure factor $S(q)$ with momentum transfer q for a solution of charged macromolecules at finite concentration with and without added salt. We consider in particular the cases of spherical and rodlike macromolecules. We introduce an effective potential model to account for the Coulomb repulsion between macromolecular ions and thence, we are able to interpret the peak observed experimentally in $S(q)$ using a simple correlation hole argument.

1. Introduction. — The properties of charged macromolecules such as latex spheres, micelles or other polyelectrolytes in solution have received a particular attention both from theoretical and experimental points of view. About thirty years ago, Kirkwood and Mazur [1] have investigated the radial distribution function $g(R)$, for a pair of charged spherical macromolecules in solution. They wrote :

$$g(R) = \exp[-U(R)/kT + \psi(R)/R] \quad (1)$$

where kT is the temperature in units of Boltzmann's constant k , and the function $\psi(R)$ is introduced to express the macromolecular ion concentration dependence of $g(R)$. $\psi(R)$ has been determined by solving the Born-Green-Yvon-Kirkwood (BGYK) hierarchy equations. In the low concentration limit $\psi(R)$ tends to vanish and we obtain :

$$g(R) \simeq \exp[-U(R)/kT] \quad (2)$$

where $U(R)$ is the potential of mean force between a pair of spherical macromolecular ions. The latter was approximated by the well known Verwey-Overbeek type of potential [2] i.e. :

$$U(R) = \infty, \quad \text{for } R < D \quad (3a)$$

$$U(R) = A \frac{e^{-KR}}{R}, \quad \text{for } R > D \quad (3b)$$

where A is a constant related to the potential of the diffuse electric double layer surrounding each macromolecular ion. D is the diameter of the macromolecule and K^{-1} , the Debye-Hückel screening length. If the macromolecular concentration is progressively increased, the pair distribution function $g(R)$ deviates from the simple form in equation (2) and shows an oscillatory behaviour which reflects an ordering of particles, typical of a liquid or even a crystal like structure.

Very recently, Hayter and Penfold [3] have reexamined the calculation of $g(R)$ for a solution of spher-

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rical macromolecular ions at a relatively high concentration using the potential of mean force in (3) and solving the Ornstein-Zernike (OZ) equation. Their results also indicate that the variation of $g(R)$ with the interparticle distance R at a relatively high concentration presents oscillations which are typical of an ordered structure. These theoretical results are largely corroborated by various scattering experiments using X-rays, light or neutrons techniques [3-6]. Furthermore, in X-rays and neutrons scattering experiments, the inverse momentum transfer q^{-1} may be comparable with the size of the macromolecular ions. In these events, the scattering signal will reflect not only the effect of interparticle correlations but also the effect of internal structure of the macromolecular ions. These combined effects may give rise to a peak in the form of the scattering signal [3, 7, 8, 9] which is different from the oscillations observed in $g(R)$ or equivalently in its Fourier transform. In view of the fact that this behaviour may sometimes lead to misinterpretation [10, 11], we believe it is worthwhile to emphasize once more the point that the maximum observed in many experiments [3, 7-11] may be interpreted using the idea of correlation hole effect. The latter was introduced by de Gennes [12] and Benoit [13] to explain a similar behaviour of the scattering signal observed with neutrons on partially deuterated polymers in solutions and in melts. This observation has already been made by Hayter *et al.* [7] and Hayter and Penfold [3].

The purpose of this paper is to introduce simple models to illustrate the above points in a simple way and without relying on heavy mathematical and numerical calculations. In particular, we introduce an effective potential model by assigning an effective size to the charged macromolecules, which is higher than the real geometric size to illustrate the hole of correlation produced by the Coulombic repulsion between the ions. This approximation has been originally introduced by Doty and Steiner [14] in their study of the light scattering of charged proteins. We are then able to show how this effect produces a peak in the scattering signal. We will use this effective potential model to calculate approximately the static structure factor for spherical as well as for rodlike macromolecular ions. We also suggest its extension to long coiled charged macromolecules.

2. Static structure factor. — 2.1 SPHERICAL MACROMOLECULAR IONS. — We consider a system of charged spherical macromolecules in solution. We assume that these macromolecules interact with each other via a hard sphere potential with an effective diameter D_{eff} which is higher than the real geometric diameter D . This means that the charges carried by the polymers produce a repulsive potential in the region surrounding them which would then be excluded to other neighbouring charges. This effect produces a correlation hole illustrated by the form of the pair

Fig. 1. — Pair distribution function $g(R)$ for spherical macromolecular ions in the effective potential model (dotted line, EHS, Eq. (6)), and as given by equations (2) and (3) (full line).

distribution function $g(R)$ represented by the dotted line in figure 1.

The static structure factor for spherical macromolecules of diameter D is well known [14, 15] :

$$S(q) = S_s(qD/2) \times \left[1 + 4\pi C_p \int_0^\infty dR R^2 [g(R) - 1] \frac{\sin qR}{qR} \right] \quad (4)$$

where $C_p = N_p/V$, N_p being the total number of macromolecules and V , the volume of the solution. $S_s(qD/2)$ is the form factor for spherical particles of diameter D . It is given by :

$$S_s(\alpha) = \left[3 \frac{(\sin \alpha - \alpha \cos \alpha)}{\alpha^3} \right]^2. \quad (5)$$

If we use in (4), the radial distribution function $g(R)$ displayed by the dotted line in figure 1, i.e. :

$$g(R) = 0, \quad \text{for } R < D_{\text{eff}} \quad (6a)$$

$$g(R) = 1, \quad \text{for } R > D_{\text{eff}} \quad (6b)$$

we obtain the following form for the static structure factor :

$$S(x) = S_s(x/2) \left[1 - 8 C_v r^3 \frac{3 J_1(xr)}{xr} \right] \quad (7)$$

where $x \equiv qD$, $J_1(\alpha) \equiv \frac{\sin \alpha - \alpha \cos \alpha}{\alpha^2}$ is the Bessel function of first order, C_v is the concentration of charged macromolecules, expressed in volume fraction :

$$C_v \equiv C_p \frac{4\pi}{3} \left(\frac{D}{2} \right)^3 \quad (8)$$

and r is given by :

$$r \equiv D_{\text{eff}}/D \quad (9)$$

which may be considered as a measure of the ionic strength of the solution. If the salt concentration is

Fig. 2. — Variation of $S(x)$ with $x \equiv qD$ for the classical hard sphere problem ($r = 1$) and for several values of C_v : (1) $C_v = 0.1$, (2) $C_v = 0.075$, (3) $C_v = 0.05$, (4) $C_v = 0.01$, (5) $C_v = 0$ or $S_s(x/2)$. This figure shows that $S(q)$ presents a maximum even in the classical hard sphere problem for sufficiently high concentrations.

low, r becomes large compared to 1 and may reach its upper limit $r_{\max} = C_v^{-1/3}/2$ determined by a zero isothermal compressibility of the solution (i.e. $S(q = 0) = 0$). On the other hand, in the presence of excess salt r becomes 1 and we obtain the classical bare hard sphere problem.

To illustrate graphically the behaviour of the scattering signal with momentum transfer q , we have plotted in figures 2, 3 and 4, the variations of $S(x)$ with $x \equiv qD$ as given by equation (7) for $r = 1$ (bare spherical macromolecules), $r = 2$ and $r = 4$ (strong correlation hole effect) respectively. In each of these three figures we have considered several values of the concentration C_v . We observe that even for bare macromolecules with $D_{\text{eff}} = D$, the shape of $S(q)$ may present a maximum as the volume fraction C_v increases. Furthermore, when r increases corresponding to lowering the ionic strength, the peak becomes

Fig. 3. — Variation of $S(x)$ with $x \equiv qD$ within the effective hard sphere (EHS) model for $r = 2$ and several values of C_v : (1) $C_v = 1.5 \times 10^{-2}$, (2) $C_v = 7.5 \times 10^{-3}$, (3) $C_v = 5 \times 10^{-3}$, (4) $C_v = 2.5 \times 10^{-3}$, (5) $C_v = 10^{-3}$, (6) $C_v = 0$ or $S_s(x/2)$. This figure illustrates the effect of concentration on the shape of $S(q)$ within the EHS model.

Fig. 4. — Variation of $S(x)$ with $x \equiv qD$ within the EHS model for $r = 4$ and several values of C_v : (1) $C_v = 2 \times 10^{-3}$, (2) $C_v = 10^{-3}$, (3) $C_v = 5 \times 10^{-4}$, (4) $C_v = 2.5 \times 10^{-4}$, (5) $C_v = 0$ or $S_s(x/2)$.

more pronounced even for relatively low values of C_v (e.g. $C_v = 10^3$). The oscillations with period π/r observed about $S_s(q)$ are due to the term involving the oscillating Bessel function $J_1(xr)$.

It would be certainly interesting to compare these predictions with those of other models developed for spherical macromolecules. In this respect, one may calculate $g(R)$ using for example, the procedure of Kirkwood and Mazur (BGYK) or the one used by Hayter and Penfold (OZ) or some other appropriate scheme. For our purpose here, we choose a crude model for $g(R)$ which will have the merit of keeping the manipulations simple and tractable analytically. We write :

$$g(R) = 0, \quad \text{for } R < D \quad (10a)$$

$$g(R) = e^{-U(R)/kT} \quad \text{for } R > D. \quad (10b)$$

This would correspond to the low concentration limit of the models developed by Kirkwood and Mazur or Hayter and Penfold. It is schematically represented by the full line in figure 1. Furthermore, for interparticle distances R larger than D , namely, away from the surface of the macromolecular ion, one may assume that $U(R) < kT$ and hence use the Debye-Hückel (DH) linearization approximation in (10b)

$$\text{i.e. } e^{-U/kT} \simeq 1 - U/kT = 1 - \frac{(Ze)^2}{\epsilon_0 kT} \frac{e^{-KR}}{R}, \text{ where } Ze$$

is the total charge carried by the macromolecule and ϵ_0 the dielectric constant of the solution. Therefore, by applying these considerations to equation (4), with some trivial integrations and rearrangements, we arrive at the following result, which is expressed conveniently in terms of dimensionless parameters :

$$S(x) = S(x/2) \left[1 - 8 C_v \frac{3 J_1(x)}{x} - y^2 e^{-s y} \frac{S y \sin x + x \cos x}{x(x^2 + S^2 y^2)} \right] \quad (11)$$

Fig. 5. — Variation of $S(x)$ with $x \equiv qD$ as given by equation (11) for $S = 1$ (no added salt), $y = 10 \sqrt{C_v}$ and several values of C_v : (1) $C_v = 5 \times 10^{-3}$, (2) $C_v = 10^{-3}$, (3) $C_v = 5 \times 10^{-4}$, (4) $C_v = 10^{-4}$, (5) $C_v = 0$ or $S_s(x/2)$.

where $y \equiv K_0 D$ and $S \equiv K/K_0$, K_0^{-1} being the Debye-Hückel screening length in the absence of added salt :

$$K_0^2 = 4 \pi \frac{Z^2 e^2}{\epsilon_0 kT} C_p \quad (12)$$

we must point out here that the use of DH approximation for $R > D$ implies that the spherical ions are regarded as pointlike particles at large distances. In the presence of added salt, the total screening length K^{-1} is given by :

$$K^2 = K_0^2 + K_s^2 \quad (13)$$

where K_s is the added salt contribution which in the case of a symmetric salt is :

$$K_s^2 = \frac{8 \pi}{\epsilon_0 kT} Z_{s+}^2 e^2 C_{s+} \quad (14)$$

$Z_{s+} e$ and C_{s+} represent the charge and the concentration of positive salt ions respectively (a factor 2 comes from charge neutrality of added salt). To illustrate the behaviour of $S(x)$ in this second model, we have plotted in figure 5 $S(x)$ as a function of x for $S = 1$ (no added salt), and for various values of C_v . Note that the parameter y can be written as $y = \alpha \sqrt{C_v}$ where $\alpha^2 \equiv 24 Z^2 (L_B/D)$, and

$$L_B = e^2 / \epsilon_0 kT$$

is the Bjerrum length. In the numerical calculations, we have let $\alpha = 10$ to ensure that $S(q = 0)$ remains positive for all concentrations considered. For a sphere of diameter $D = 100 \text{ \AA}$ and $L_B \simeq 7 \text{ \AA}$ (water at room temperature) $\alpha = 10$ would correspond to a total charge Ze no more than $8e$. Figure 5 shows again the dramatic effect of interactions in the lower range of q even for weakly charged macromolecules. For higher values of q (i.e. $qD > 3$) we recapture the form factor of a single spherical particle i.e. $S_s(qD/2)$.

Fig. 6. — Variation of $S(x)$ with $x \equiv qD$ as given by equation (11) for $C_v = 10^{-3}$, $y = 0.316$ and several values of salt parameters S : (1) $S = 1$ (no added salt), (2) $S = 1.25$, (3) $S = 1.5$, (4) $S = 1.75$, (5) $S = 2$, (6) $C_v = 0$ or $S_s(x/2)$. This figure illustrates the effect of added salt on the shape of $S(q)$.

Clearly, the maxima shown in these plots are not reminiscent of an order in the particle distribution [10, 11]. They are simply due to the correlation hole produced by the strong repulsive interaction both from hard sphere and electrostatic potentials. By adding salt to the solution one enhances the effect of screening between charged particles and S becomes greater than 1. To investigate this effect on the shape of the scattering signal, we have plotted in figure 6, $S(x)$ as a function of x for several values of S ranging from 1 to 2 and choosing $C_v = 10^{-3}$. We observe that, as the salt concentration increases, electrostatic interaction is progressively screened and may eventually disappear if C_s is high enough. These observations are consistent with the results of Hayter and Penfold [3] and with various other small angle neutron scattering experiments on polyelectrolyte solutions [7, 8, 9]. Without seeking a detailed expression

Fig. 7. — Variation of $S(x)$ with $x \equiv qD$ for spherical macromolecular ions : (1) as given by equation (7) (EHS) for $r = 3.6$ and (2) as given by equation (11) for $S = 1.586$ and $y = 0.316$, (3) $C_v = 0$ or $S_s(x/2)$. The parameters r , S , and y were chosen to give the same $S(q = 0)$ in both models. This figure shows that the two models yield qualitatively similar curves for $S(q)$.

of D_{eff} in terms of S and y , one may compare the curves of $S(x)$, for the two models by adjusting, for example, $S(q=0)$, or equivalently, the second virial coefficients to be the same in these two models. This is done in figure 7 by choosing the parameter as follows : $C_v = 10^{-3}$, $r = 3.6$, $S = 1.582$, and $y = 0.316$. Except for the tendency of oscillations around $S_s(q)$ in the EHS model, and a relatively small shift in the position of the maximum, the overall shape of the curves displaying a maximum is comparable in both cases.

2.2 RODLIKE MACROMOLECULAR IONS. — We propose now to apply the concept of effective potential to rodlike charged macromolecules. One must keep in mind, though, that a model which is suitable for spheres may not be good for rods. To our knowledge, however, nothing prevents from extending the idea of effective diameter to charged rods to simulate the long range Coulomb repulsion. In fact this idea was first suggested by Onsager [16] in 1949 and revived recently by Stigter [17] (1977). These authors calculated the second virial coefficient for a system of charged rods and found a result which is identical to the one derived earlier by Zimm [18] (1945) for a system of uncharged rigid rods. As in the case of spherical macromolecules, one must replace the rod bare diameter d by an effective diameter d_{eff} which is larger than d to simulate the long range electrostatic repulsion. Here d_{eff} is defined as the particular distance between two charged rods at right angles for which the electrostatic repulsive energy is equal to :

$$u_{12} = 0.462 \, 6 \, kT \quad (15)$$

d_{eff} is found to depend in particular on the screening length K^{-1} and the potential on the rod surface. The exact dependence of the effective diameter on relevant parameters such as K and Ze is not crucial for our purpose and we refer the reader to the papers by Onsager and Stigter for further details on this subject. In the present work we focus our attention on the calculation of the scattering signal one would obtain from a solution of charged rodlike macromolecules. For this purpose we use the expression derived by Zimm [18] in which we merely replace d in the expression of the second virial coefficient A_2 by d_{eff} to account for electrostatic repulsion. For rods of length L we have :

$$S(q) = S_s(qL) [1 - 2 A_2 Mc S_s(qL)] \quad (16)$$

(cf. Eq. (13b) of Ref. [18]). $S_s(qL)$ is the single rod form factor [14] :

$$S_s(qL) = \frac{2}{qL} \int_0^{qL} dx \frac{\sin x}{x} - \left(\frac{\sin(qL/2)}{qL/2} \right)^2 \quad (17)$$

A_2 is the second virial coefficient for rodlike macro-

molecules derived by Zimm, Onsager and Stigter as :

$$A_2 = N_0 \frac{\Pi d_{\text{eff}} L^2}{4 M^2} \quad (18)$$

where M is the molecular weight and N_0 Avogadro's number. In equation (16) the concentration c is expressed in weight per unit volume

$$c = \frac{N_p}{V} \frac{M}{N_0} \quad (19)$$

N_p is the number of rods in the volume V occupied by the solution. We must, however, emphasize the fact that the results in both equations (16) and (18) are only approximate in the sense that (16) is valid for relatively low concentrations and (18) is obtained in the limit where the length of the rod is much larger than its diameter. With this restriction in mind we propose to investigate the effect of correlation hole on the shape of the scattering function $S(q)$, with a magnitude proportional to $2 A_2 Mc$. It is interesting to note that the latter parameter combines both concentration, charge and added salt effects, whereas for spherical macromolecules, we had to consider these effects separately (see Eqs. (7) and (11)). In figure 8 we have plotted $S(q)$ as a function of qL for several values of the parameter $2 A_2 Mc$. In the high q region, all the curves tend to join the single rod form factor but in the lower q region, $S(q)$ is strongly affected as the quantity $2 A_2 Mc$ increases from 0 to its maximum value 1. The important factors involved in this quan-

Fig. 8. — Variation of $S(x)$ with $x \equiv qL$ for rodlike macromolecular ions, for several values of the parameter $2 A_2 Mc$: (1) $2 A_2 Mc = 0$, (2) $2 A_2 Mc = 0.1$, (3) $2 A_2 Mc = 0.25$, (4) $2 A_2 Mc = 0.5$, (5) $2 A_2 Mc = 0.75$, (6) $2 A_2 Mc = 1$ or $S_s(x/2)$. This figure illustrates the effect of C_v on the scattering signal.

tity are of course the concentration c , and the second virial coefficient A_2 which is a measure of the strength of repulsion between rods. Therefore, for a given finite concentration c , the shape of $S(q)$ may develop a maximum as A_2 increases reflecting a stronger correlation hole effect. One notes however that the maxima are not as sharp as in the case of spherical macromolecules. This is due to the specific large q -dependence of $S_s(q)$, which decays like q^{-1} for rods as compared to q^{-4} for spheres.

It is worth noting that the method developed by Zimm and summarized by equation (16) is of course not specific to rodlike macromolecules. It can be applied to coiled chains by choosing an appropriate form for $S_s(q)$. In particular it is widely used for Gaussian chains where $S_s(q)$ is given by the Debye function. For our purpose, since it is well known that charges produce a local stiffening of the coiled chain which is superposed to a long range excluded volume effect, we may borrow a form of $S_s(q)$ from sliding rod model [19] or wormlike chain model [20] or any other appropriate model that can incorporate local stiffness and excluded volume effects. We know that the stiffness of the chain decreases as we add more salt and ultimately reaches its intrinsic limit due to pure chemical bounding (i.e. bare persistence length). At the same time interaction between charges of different chains is progressively screened following a decrease of the effective depth of the potential surrounding each macromolecule. However, we do not reproduce these calculations here because we expect the results to be qualitatively similar to those of the effective rod model except perhaps for a more or less pronounced maximum due to the specific q -dependence of the single particle structure factor $S_s(q)$ at large q 's.

3. Conclusions. — In this paper we have investigated the properties of the elastic scattering signal one would obtain from a solution of charged macromolecules.

In particular we have focussed our attention on spherical and rodlike macromolecules because the models used in our calculations are perhaps more suitable for such particle shapes. Furthermore we have made some conjectures concerning coiled chains bearing electrostatic charges. There are two kinds of difficulties one faces in considering these problems.

(i) The first one has to do with the joint probability distribution function of particles belonging to different chains. That is to say, when two chains come close to each other (say within Debye length) so that

they start interacting with each other, the question one may ask is to what extent such an interaction perturbs the internal distribution of each chain? This problem is of course not specific to Coulomb interaction but it is related to the complexity of many body problems. It has been recently addressed by one of us [21] in calculating the first order concentration dependence of the diffusion coefficient for neutral polymers. In the case of spherical macromolecules this problem arises in a lesser critical degree since intra and intermolecular distributions are completely uncorrelated. In the case of rodlike macromolecules we have made use of a model proposed by Zimm which reduces the calculation of the interparticle scattering function to the much simpler calculation of the single particle form factor.

(ii) The second problem is inherent in the long range nature of Coulomb interaction and has been a subject of a large number of publications [22, 23, 24]. Unfortunately, until now this problem has not yet been completely solved. In this paper we do not address ourselves to this important problem. Our purpose here is to investigate the effect of Coulomb interaction on the shape of the scattering signal $S(q)$. We propose to treat charged macromolecules as if they were neutral but having effective sizes that depend on charge parameters such as K^{-1} and Ze . We have used this model explicitly for rodlike and spherical macromolecules and we have suggested its extension to sliding rod model or wormlike chains where both the persistence length and the depth of the effective potential surrounding the chains depend on K and Ze .

The main conclusion one can draw from this work is that the maximum observed in the scattering intensity which is obtained from a solution of charged macromolecules may have a different origin than a possible ordering due to long range Coulomb interaction. Such an interpretation based on de Gennes-Benoit correlation hole effect has been proposed for the first time for polyelectrolytes by Hayter *et al.* [7]. Here we have attempted only to put the argument in a quantitative framework using simple models hoping that it may serve in interpreting certain aspects of scattering experiments.

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