Charge Structure in Electrolytes and Polyelectrolytes. Experimental Evidence and Interpretation

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The question is raised if a wave vector dependent dielectric structure function significantly describes electrolyte and polyelectrolyte solutions. Experimental results for the charge-charge structure function in electrolytes and in polyelectrolytes are presented at concentrations beyond the Debye-Hückel range. A dielectric structure function and a macroscopic dielectric constant are derived from scattering experiments. The time decay of the dynamical charge structure function is related to the Debye-Falkenhagen relaxation time. Effects of dissymmetry in charge and size are examined. Beyond a certain dissymmetry, the concentration fluctuations of the interacting counterions lower the energy of the system. We test these predictions first given by F. Oosawa and S. Marčelia, by analyzing the q dependence of the charges structure function. We compare experimental results on DNA rods and Polystyrene sulfonate coils.

1 Introduction

The presence of electrical charges in neutral solutions increases the complexity of these systems in several ways. Charges are known, for instance, to homogenize molecular structures and this is used to stabilize [1] colloidal suspensions. On the other hand, charge coupling can induce concentration profiles and mesomorph structures [2]. More characteristic is the fact that dielectric and charge transport properties are themselves modified by the structure transformations. There is an important feedback between molecular organization and electric properties. This relationship is well unterstood only in limited cases, where the inherent nonlinearity can be reduced to a linear response. In very dilute electrolyte solutions, the charge structure and its implication on the electric conductivity are described by the Debye screening length [3]. Other well identified effects are the counterion condensation [4] on a linear polyion and the electric persistance length [5] along flexible polyions. However, one does not know how these effects vary with solute concentration.

Here we wish to examine further the relation between molecular structure and electric properties. For this we propose an experimental investigation, based

on the observation of the charge-charge structure function $S_{zz}(q,t)$. The latter is directly derived from concentration fluctuations in $\pm$ charges:

$$\rho_z(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) \tag{1}$$

The relation to electric properties is given by Gauss' Law

$$\frac{4\pi\rho_z(r)}{\varepsilon} = div\, grad\, \phi(r) \tag{2}$$

where ε is the relative dielectric constant and ϕ the electric potential. Equation (2) is fundamental for our purpose.

The charge-charge structure function $S_{zz}(q,t)$ can be determined directly in a scattering experiment if conditions for zero average contrast [6] (also called Θ optical method) are met: Here the collision amplitude associated with a positive charge should be of opposite sign and same magnitude as a negative charge [7]. The possibility to label molecular structures without introducing physical perturbation (for instance by isotopic substitution) has allowed true correlation functions to be derived instead of apparent correlation, and the labelling pattern associated to zero average contrast is one of them.

The idea to apply such techniques was suggested by recent studies of Benoit [8], Borsali et al. on (neutral) block polymers in dilute solutions. When the contrasts of the two blocks with respect to the solvent are equal in magnitude but opposite in sign, the observed structure function $S_{zz}(q)$ reads

$$S_{zz}(q) = \frac{q^2}{3}\frac{R_G^2}{2}, \qquad qR_G^2 < 1 \tag{3}$$

where R_G is the radius of gyration of the copolymer. Further, for the relaxation time of the diffusive modes, the dispersion relation reads

$$\frac{1}{\tau(q)} = D(1/R_G^2 + q^2), \qquad qR_G < 1 \tag{4}$$

where D is the diffusion coefficient. Equations (3) and (4) are very suggestive of what is expected in electrolytes (see also earlier work by Nallet [9] et al.). We recognize namely in (3) an expression of Stillinger and Lovett's second sum rule [10], and in (4) an expression of Debye and Falkenhagen's relaxation time. The analogy between the two situations is discussed in section 3.

The use of the charge-charge structure function

$$S_{zz}(q) = \frac{1}{\rho V}\int d^3r \int d^3r' e^{iq(r-r')}\langle\rho_z(r)\rho_z(r')\rangle \tag{5}$$

in ionized systems is not new. Detailed accounts are found in the studies of molten salts, metal alloys and two-component plasmas. The authors were already concerned with the relation between the molecular structure and the electrical resistivity. For instance Bhatia and Thornton [11] suggest that an enhancement of the concentration structure function, $S_{cc}(q)$ (similar to the charge-charge structure function $S_{zz}(q)$) is responsible for a "rise in the resistivity-versus-temperature curve".

In two-component plasmas, J. P. Hansen and I. R. McDonald [12] find a negative deviation from the Nernst-Einstein conductivity which is due to cooperative effects between charges.

The new aspect in our study of the charge-charge structure functions is the presence of a large quantity of neutral solvent. This is of course a major complication, and the question is raised wether the solute charge-charge structure function in such a situation still has some significance. The rotation and deformation of solvent molecules also contribute to the dielectric structure [13]. It is not obvious that solute and solvent effects can be clearly identified.

When a dissymmetry is introduced between positive and negative charge carriers as in polyelectrolytes, the charge structure is modified. The coupling constants are higher and part of the counterions accumulates in a frozen profile along the polyions. The charge-charge function acquires a new significance. Polyions are quasi static in comparison to counterions, and the concentration fluctuations of the counterions tend to lower the energy of the system. Interesting consequences have been predicted by F. Oosawa [14] and S. Marčelia [15].

Finally, we compare the charge-charge structure function of rigid rods and flexible coils.

2 Formal Relations and Sum Rules

We give expressions for the charge-charge structure function and the sum rules in the limit $q \to 0$.

A) For a solution containing point charges of concentration $\rho_\pm(r)$, the charge structure function is given by equation (5).

B) The sum rules are obtained by expanding the exponential in (5) about $q = 0$. In our case of simple point charges

$$\langle \rho_z(r)\rho_z(r')\rangle = \langle \delta\rho_z(r)\delta\rho_z(r')\rangle + \text{constant} \tag{6}$$

where $\delta\rho_z(r)$ is the charge fluctuation.
We find [16]

$$S_{zz}(q) = \frac{1}{\rho V}\int d^3r \int d^3r' \left\{1 + i\mathbf{q}\cdot\mathbf{r} - (\mathbf{q}\cdot\mathbf{r})^2 + \ldots\right\} \langle \delta\rho_z(\mathbf{r}')\delta\rho_z(\mathbf{r}'+\mathbf{r})\rangle \tag{7}$$

The first two terms vanish because of electroneutrality. Then remains

$$S_{zz}(q) = -\frac{q^2}{\rho V}\int d^3r \int d^3r'(\mathbf{q}\cdot\mathbf{r})^2 \langle \delta\rho_z(\mathbf{r}')\delta\rho_z(\mathbf{r}'+\mathbf{r})\rangle = \frac{2\,q^2}{\kappa^2} \tag{8}$$

These equations express the Stillinger-Lovett sum rules and define the quantity κ^2 independently of any model.
Later on, we shall also consider the case of concentration profiles [16], i.e. frozen structures. Here

$$\langle \rho_z(r) \rangle \neq 0 \tag{9}$$

but electroneutrality is still satisfied.

$$\int d^3r \langle \rho_z(r) \rangle = 0 \tag{10}$$

The sum rules remain valid, but the structure functions are modified.

C) In reality, the charges are embedded in molecular structures. There is a competition between charge and molecular structure. In some cases it is easy to separate these contributions.
We define $S_{cc}(q)$, the structure function resulting from a scattering experiment at zero average contrast.

$$\rho S_{cc}(q) = \rho_A S_{AA}(q) + \rho_B S_{BB}(q) - \sqrt{\rho_A \rho_B} S_{AB}(q) \tag{11}$$

where

$$\sqrt{\rho_A \rho_B} S_{AB}(q) = \frac{1}{V} \int d^3r \int d^3r' e^{iq,(r-r')} \langle \rho_A(r) \rho_B(r') \rangle \tag{12}$$

are the partial structure functions, associated to the species A, B.
We now assume that A and B contain respectively $+$ and $-$ charges. In some cases, there is a simple relation between $S_{cc}(q)$ and $S_{zz}(q)$. If the charges are located at the center of identical spherical molecules, then

$$S_{cc}(q) = f(q) \cdot S_{zz}(q) \tag{13}$$

where $f(q)$ is the sphere form factor. If the system is a polyelectrolyte with flexible polyions, then in the Random Phase Approximation we have at low q

$$S_{cc}(q) = \frac{q^2 \{Nh(q) + 1\}}{q^2 + \frac{\kappa^2}{2} \{Nh(q) + 1\}} \simeq S_{zz}(q) \tag{14}$$

where $h(q)$ is the normalized form function of the polyion and N the degree of polymerization. Here we recover the result (8). However the RPA result cannot be trusted and the generalization of equation (13) or (14) is doubtful. The competition between charge and molecular fluctuations is the crux of our problem.

3 The Charge-Charge Structure in Electrolyte Solutions

The distribution of charges in electrolyte solutions is described in real space by pair correlation functions and in reciprocal space, by partial structure functions.

The charge-charge structure function is a combination of the partial structure functions

$$S_{zz}(q) = S_{++}(q) + S_{--}(q) - S_{+-}(q) \tag{15}$$

The information contained in $S_{zz}(q)$ and in its elementary parts should be identical. However the correlations appear in a different combination and in some sense, $S_{zz}(q)$ reveals other properties.

3.1 The sum rules

The sum rules in the limit $q \to 0$ illustrate our point. The partial structure functions $S_{ij}(q)$ are all related in the limit $q \to 0$, to the osmotic compressibility χ_{os}. Where does this quantity appear in the charge-charge structure function? There are two approaches to answer this question.

We first consider the second order matrices $\hat{H}(q)$ and $\hat{C}(q)$, whose elements are respectively the Fourier transformation of the total and the direct partial correlation functions. The closure relation writes [17]

$$\left(1+\hat{H}(q)\right)\left(1-\hat{C}(q)\right)=1 \tag{16}$$

If we identify $C_{+-}(r)$ with the Coulomb potential $-\beta U_{+-}(r)$ and if we expand about $q=0$, we obtain to second order

$$S_{zz}(q)=q^2/(\kappa^2/2) \tag{17}$$

where $\kappa^2 = l_B\rho$. Here l_B is the Bjerrum length.

To fourth order [18],[19]

$$S_{zz}(q)=\frac{2q^2}{\kappa^2}\cdot\frac{1}{1+(q^2/\kappa^2)\rho\chi_{os}\beta^{-1}\det(\hat{I}-\hat{D}(0))} \tag{18}$$

where

$$\hat{D}_{AB}(q)=\hat{C}_{AB}(q)+\frac{4\pi l_B\sqrt{\rho_A\rho_B}}{q^2} \tag{19}$$

Expression (18) indicates that the osmotic compressibility controls here the structure at finite q rather than in the thermodynamic limit $q \to 0$. This effect was pointed out by Giaquinta et al. [18]. These authors give an interesting interpretation, based on the fact that charge density and mass density are "distinct fluctuation variables". There are therefore two contributions to the charge current, one from the electric field E and the other from the electrochemical potential μ_z. In presence of an external charge density, $\rho_e(q)$, the charge concentration in the solution writes

$$\rho_z(q)=-\rho_e(q)\left(1+\frac{q^2}{\kappa_s^2}\right)^{-1} \tag{20}$$

where

$$\kappa_s^2=4\pi e^2\frac{\partial\mu_z}{\partial\rho_z} \tag{21}$$

We recover equation (18) after introduction of the dielectric and charge response function. We note further that in the frame of the Ornstein-Zernike theory, κ^2 in (17) remains proportional to ρ even beyond the range of validity [20] of the Debye-Hückel theory.

3.2 The charge structure and the correlation hole effect

The ion concentration $\rho_{\pm}(r)$ and the charge concentration $\rho_z(r)$ have a characteristic structure in solution. Around a given charge, there is for instance a depletion of like charges and an enhancement of opposite charges. The partial structure functions $S_{++}(q)$ and $S_{--}(q)$ give a good account of this structure. However, the most direct evidence for the effects of the Coulomb interaction is the charge-charge structure function. At low q, the function $S_{zz}(q)$ is characterized by a single parameter, the inverse screening length κ^{-1}, see equations (8) and (17). It is of interest to note that a scattering experiment carried under zero average contrast conditions for a solute made of neutral particles, the result $S_{cc}(q)$ (which for charged particles is $S_{zz}(q)$) writes

$$S_{cc}(q) = f(q) \times 1 \tag{22}$$

where $f(q)$ is the form factor of the solute molecules.

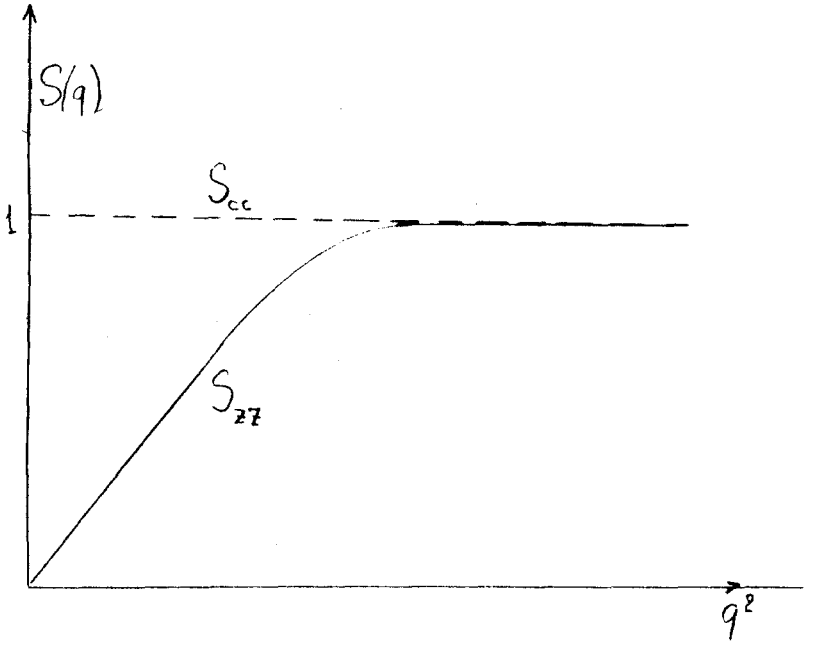

Fig. 1. Schematic display of the charge-charge structure function $S_{zz}(q)$ in electrolyte solution and the concentration structure function $S_{cc}(q)$ for two neutral solutes in a solvent. The correlation hole effect is important. An applied electric field at the Debye-Falkenhagen frequency would considerably reduce this effect.

The difference is striking (see Figure 1) and points out the correlation hole effect. The usual method to observe the screening effect consists in interpreting osmotic pressure data as a function of solute concentration ρ. A signature of the screening structure is the variation of the osmotic coefficient proportional

to $\sqrt{\rho}$. Similar behaviours are found in the variation of the electric conductivity and the macroscopic dielectric constant with ρ. These results are well unterstood, but they do not provide a real structural evidence, as given for instance by a wave vector dependence of the correlation functions. Therefore, the display of $S_{zz}(q)$, derived from an experiment (Fig. 2), gives a better representation of the screening structure. The solute concentration ρ ($\rho = 1.5 \times 10^{-4}\text{Å}^{-3}$ and $3 \times 10^{-4}\text{Å}^{-3}$) is very high compared to the domain of application of the Debye-Hückel theory ($\rho^{1/3}\kappa^{-1} \gg 1$). Nevertheless, as noted earlier, $\kappa^2 \propto \rho$.

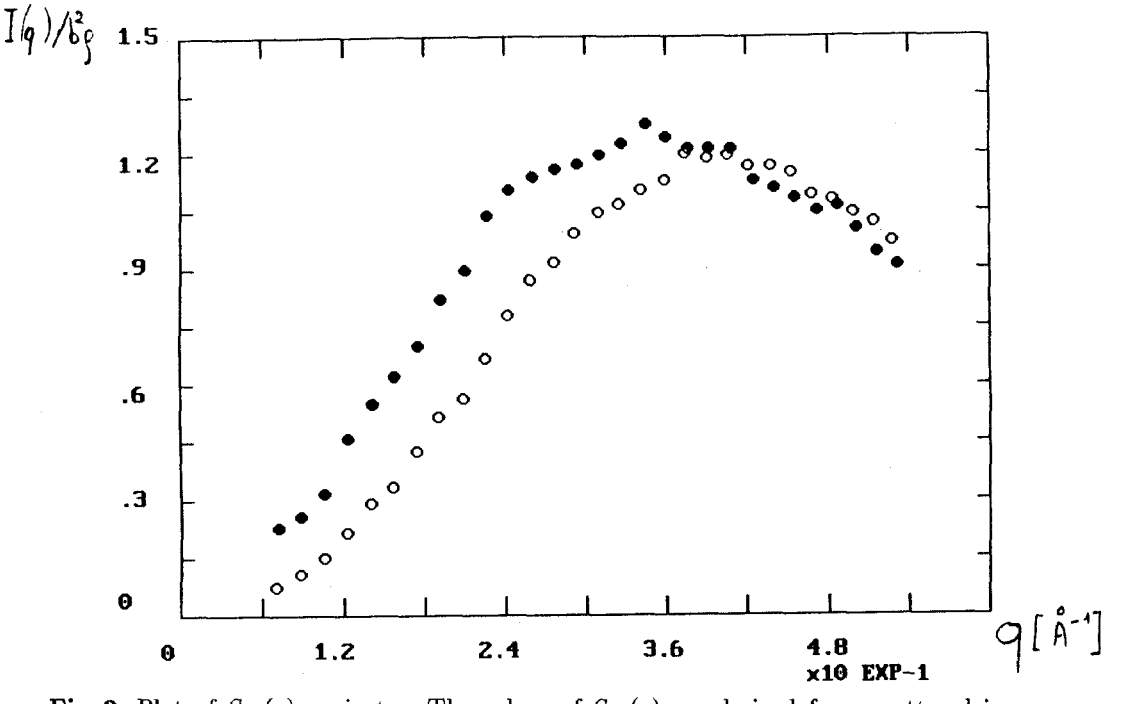

Fig. 2. Plot of $S_{zz}(q)$ against q. The values of $S_{zz}(q)$ are derived from scattered intensities $I(q) = \rho b^2 f(q) S_{zz}(q)$, where ρ is the concentration, b the contrast length at zero average contrast ($b = b_+ = b_-$) and $f(q)$ the molecular function. a) $\rho = 0.25$M; b) $\rho = 0.5$M. The cation is the triethylphenylammonium ion, the anion is deuterated tetraphenylborate, and the solvent is a mixture of hydrogenated and deuterated dimethylformamide. The characteristic lengths derived from the data are respectively $\kappa^{-1} = 4.1$Å at 0.25 M and $\kappa^{-1} = 2.8$Å at 0.5 M. These values scale like $\rho^{-1/2}$. Measurements made at lower q values, but beyond the resolution of the spectrometers, could give different values.

3.3 The neutral copolymer model

The charge distribution is a very characteristic distribution. We ask if there exists a neutral molecular model which reproduces the main properties of electrolyte structures. In Figure 1, we noted that the structure of interacting but electrically neutral particles is very different from that of charged particles.

On the other hand, the case of copolymer chains is very instructive, because it provides structures similar to (18).

A copolymer is made of two chemical species A, B which polymerize according to some chemical structures (for instance random sequency or A,B blocs, etc.). The chain follows a random walk and the A,B monomers are distributed in space depending on the chemical structure. At zero average contrast, the copolymer form function obeys some rules which have a formal ressemblance to those proposed by Stillinger and Lovett: In a large volume, the concentration ρ_A and ρ_B are strictly equal, but locally the difference may fluctuate.

We first consider the case of A,B diblocs. The A monomers and the B monomers form clouds which are separated by an average square distance $R_{AB}^2 = 5R_G^2$, where R_G is the radius of gyration of the entire chain. The form function at zero average contrast reads

$$N\,h(q) = \frac{N}{4}(h_{AA}(q) + h_{BB} - 2\,h_{AB}(q)) \tag{23}$$

where N is the degree of polymerization of one strand and $h_{AB}(q)$ are normalized partial form functions. Expanding about $q = 0$

$$Nh(q) = \frac{q^2}{3}\left(\frac{6NR_{AB}^2}{5}\right), \qquad qR_G \ll 1 \tag{24}$$

The slope increases steeply with the number N and the model is therefore unrealistic from the point of view of electrolytes. The number of particles within a volume R_{AB}^3 is $N \gg 1$. In the case of electrolytes the product $\kappa^{-3}\rho$ is a great number only in the high dilution (the Debye-Hückel) limit. In our situation $\kappa^{-3}\rho \approx 10^{-2}$, a very small number.

The alternating copolymer A,B,A,B, etc. is a more interesting case

$$Nh(q) = \frac{q^2}{3}l^2 \tag{25}$$

where l^2 is the mean square monomer size.

If we replace l by ξ, the "blob" correlation length, then we note that $\xi \propto \rho^{-1/2}$ in the mean field approach, and $\xi \propto \rho^{-3/4}$ in the scaling approach. The latter is more realistic, because the coupling constant in the polymer problem is large. This suggests that in some circumstances we may find other relationships than $\kappa^{-1} \propto \rho^{1/2}$ in the electrolyte problem.

For a random copolymer

$$N\,h(q) = 1/4 \tag{26}$$

The sum rule (17) is here violated; this reflects the annealed disorder of composition along the chain.

In summary, we have not found the molecular object which could totally reproduce the electrolyte structure. However, the comparison suggests possible alternations of the concentration dependence of the screening length.

3.4 The charge dielectric structure function. Coulomb unmixing and formation of mesomorph structures.

For the case of point charges, it is convenient to introduce the dielectric structure function $\varepsilon(q)$, which is the response [20] to an applied longitudinal field

$$\frac{1}{\varepsilon(q)} = 1 + \frac{\delta\rho_z(q)}{\delta\rho_{ext}(q)} \tag{27}$$

This function is directly related to the charge-charge structure function[20]

$$\frac{1}{\varepsilon(q)} = 1 - \frac{4\pi l_B \rho}{q^2} S_{zz}(q) \tag{28}$$

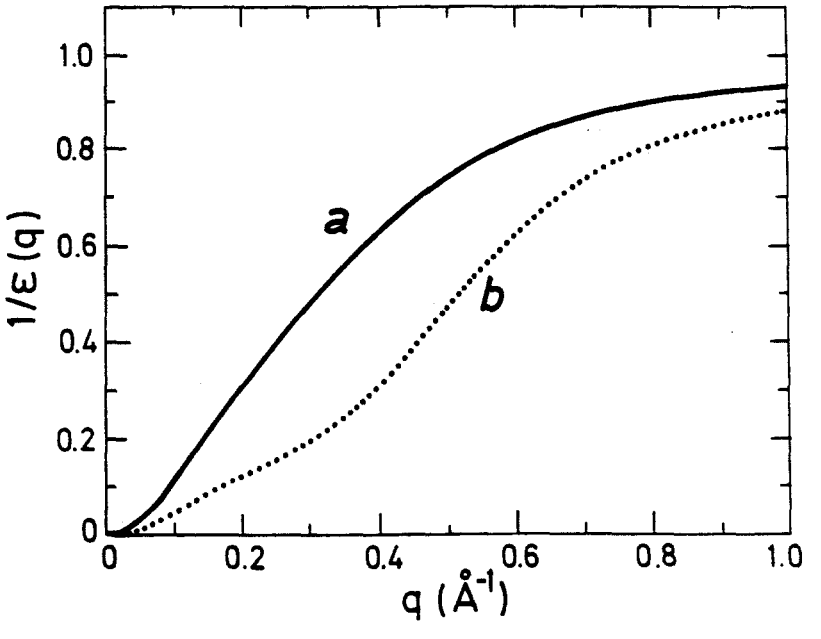

Fig. 3. Plot of $1/\varepsilon(q)$ derived from Figure 2 and relation (21). If the solvent effect is to renormalize the macroscopic dielectric constant, then $\varepsilon(q)$ is the charge dielectric structure function.

Charge screening controls the behaviour of $\varepsilon(q)$ at low q/κ values. In the range $q/\kappa > 1$, the function $1/\varepsilon(q)$ is sensitive to the formation of mesomorph structures. They occur when the second term in (28) is greater than one, i.e. when the coupling constant and the charge fluctuations are important. Such an analysis is fruitful for instance in the study of molten salts.

When the charges are embedded in a solvent we face a complex problem: The dielectric response also depends on the solvent and on the solute-solvent interactions. In a first approximation, we can argue that the (neutral) solvent is

characterized by a macroscopic dielectric constant ε_0, which is simply a renormalized quantity in the sense that the Coulomb interactions of charges at distance r remain of the form $e^2/(\varepsilon_0\, r)$. If this is true, the presence of a solvent only modifies the Bjerrum length l_B in eq. (28).

$$l_B = \frac{e^2}{\varepsilon_0\, kT} \tag{29}$$

This hypothesis is consistent with the predictions of Debye and Falkenhagen [3]. These authors calculated the effect of added salt on ε_0 and find that the existence of a screened solute structure only produces a positive shift. For KCl in water the result is

$$\Delta\varepsilon_0 = 3.10 \times 10^{-10}\sqrt{\rho} \tag{30}$$

where ρ is given in cm^{-3} units. If we interpret our data (Figure 2) in these terms, we find indeed a macroscopic dielectric constant ε_0, whose value is very close to the solvent constant ($\varepsilon_0 = 32$).

This view is however an oversimplification. In fact, the response depends on the range of interaction between solvent molecules. In particular, if there exists a polar interaction, the fluid has a longitudinal dielectric structure [21] by itself: $1/\varepsilon_L(q)$. With Parrinello and Tosi [13] we can generalize equation (28) to

$$\frac{1}{\{\varepsilon(q)/\varepsilon_L(q)\}} = 1 - \left(\frac{l_B c}{\varepsilon_L(q)/\varepsilon_0}\right)\frac{1}{q^2}\, S_{zz}(q) \tag{31}$$

However, it is necessary to know $\varepsilon_L(q)$ in order to derive $1/\varepsilon(q)$ against q, assuming $\varepsilon_L(q) \equiv \varepsilon_0$ and using the $S_{zz}(q)$ data.

3.5 Collective motion and dynamic structure function.

The Coulomb long-range interaction induces collective motion in the thermal agitation of charges. If undamped, these motions take the form of oscillations at the plasmon frequency. If damped, as in solutions, these motions are characterized by a finite relaxation time at $q \to 0$, namely $\tau = 1/(\kappa^2 D)$ where D is the diffusion coefficient. The dispersion relation $\tau(q)$ associated to the relaxation mechanism is of great interest. We discuss some characteristic features to be observed in the measurement of the dynamical structure functions.

Let us consider the ion distribution around an excess charge in a dilute solution. The charges of opposite sign form a cloud with spatial distribution $\frac{1}{r}\exp(-\kappa r)$. If the excess charge is removed at time $t = 0$, the cloud profile relaxes according to the law

$$\frac{1}{r}\,\exp(-\kappa r)\frac{1}{\sqrt{\pi}}\int_{\sqrt{\Theta}-r\kappa/2\sqrt{\Theta}}^{\infty} \exp\left(-y^2\right) dy \tag{32}$$

where $\Theta = -t/\tau$ is the reduced time and $\tau = (\kappa^2 D)^{-1}$ is the relaxation time.

For the like charges, the depletion cloud follows a similar evolution (only the sign of the deviation to uniformity is changed). These results can be used

directly in the analysis of thermal fluctuations. Namely, the dynamical charge-charge structure function has the following expression:

$$S_{zz}(q,t) = S_{zz}(q)\exp(-t/\tau(q)) \tag{33}$$

where

$$1/\tau(q) = D\,(\kappa^2 + q^2) \tag{34}$$

The observation of $\tau(q)$ has not yet been carried out. However, the measurement of the dynamical form function of the model copolymer has already been performed by Borsali et al. [8]. Here

$$h(q,t) = h(q,0)\exp(-t/\tau(q)) \tag{35}$$

where

$$1/\tau(q) = D\left\{\frac{6}{R^2} + \frac{2}{4}q^2\right\} \tag{36}$$

The dispersion relation (36) obtained experimentally by Borsali et al. [8], is plotted in Figure 4. In the case of electrolytes, we expect a stronger effect, i.e. the quantity $1/(q^2\tau(q))$ will be two orders of magnitude higher.

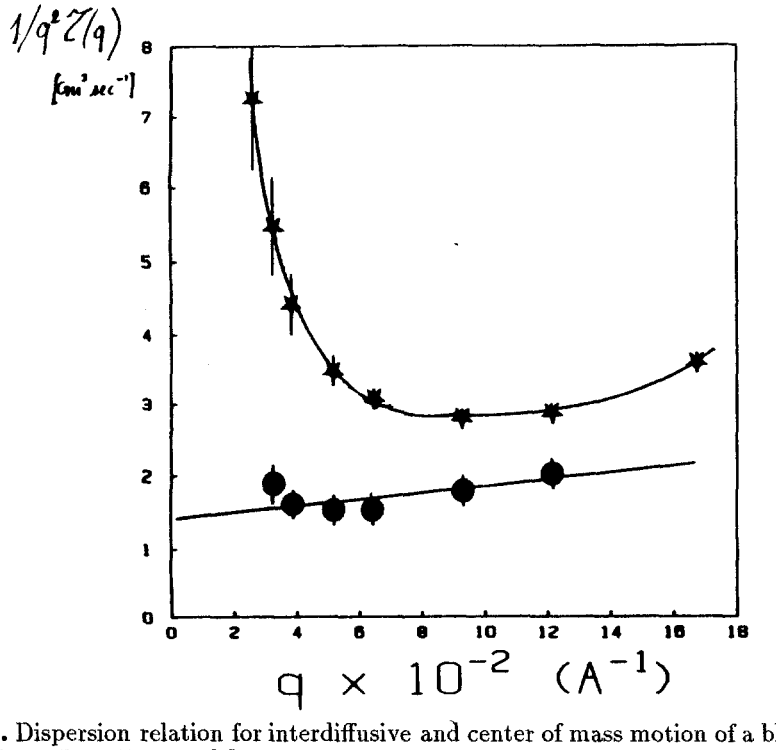

Fig. 4. Dispersion relation for interdiffusive and center of mass motion of a bloc copolymer. From Borsali et al. [8]. We expect a larger gap in the case of electrolytes.

This leads us to the main object of our investigation, namely the relation between $S_{zz}(q,t)$ and the dynamical dielectric response $\varepsilon(q,\omega)$. The results will be given in a forthcoming paper.

Also of interest are the predictions concerning effects of an applied electric field at the Debye-Falkenhagen frequency [3]. This would considerably reduce the correlation hole (Figures 1 and 2) and the gap between interdiffusion and centre-of-mass dispersion relations (Figure 4).

4 The Case of Polyelectrolytes

Polyelectrolytes are made of polyions and counterions and are characterized by an important dissymmetry in size and charge. It is possible to study polyelectrolytes by considering separately the polyion structure and the cloud of counterions adjusting quasi instantaneously to the polyions, as in the Born-Oppenheimer approximation. The study of the polyion configuration reveals indeed many significant behaviours. The variation of viscosity versus concentration is a good example.

However, a renewed interest is found in the study of the interdependence between polyion- and counterion-structures. There are well-known feedback mechanisms. For instance, the thermal agitation of counterions determines the osmotic pressure, but polyions contribute as well. There are other interesting predictions, in particular those related to attractive forces between polyions due to fluctuations of counterions and Coulomb interactions [14]. The charge-charge structure function should reveal the correlation effects between polyions and counterions and many of them result from nonlinear variation with the electric field. The relation between the measured structure function $S_{cc}(q)$ and the charge-charge structure function $S_{zz}(q)$ is here less obvious than in the case of simple electrolytes. The dissymmetry introduces a cross correlation between number and concentration fluctuations. Here we have simply identified $S_{cc}(q)$ and $S_{zz}(q)$, ignoring the linear memory in polyions (see equation (14)).

We compare two experimental results obtained at a monomer concentration of 0.2 Mol/l (i.e. $\approx 10^{-4}$ Å^{-3}) respectively on DNA rods [22] and Polystyrene sulfonate coils [23]. In both cases the counterion is tetramethylammonium (see Figures 5 and 6). We first note that the charge-charge structure functions $S_{zz}(q)$ are an order of magnitude greater in polyelectrolytes than in electrolytes (c.f. Figure 2). We attribute the difference to the confinement of a large fraction of the counterions in the vicinity of the polyion. This confinement, which is related to the strong Coulomb coupling, creates a charge structure. A decomposition of the charge-charge structure function was recently proposed [16]

$$S_{zz}(q) = \bar{S}_{zz}(q) + \tilde{S}_{zz}(q) \tag{37}$$

Here, the first term comes from the frozen structure and the second from the correlation in fluctuations. A calculation of $\bar{S}_{zz}(q)$ was made for the rod geometry, using the cell model and the Poisson-Boltzmann equation of the one particle density. We expect that the contribution of $\bar{S}_{zz}(q)$ is less important in

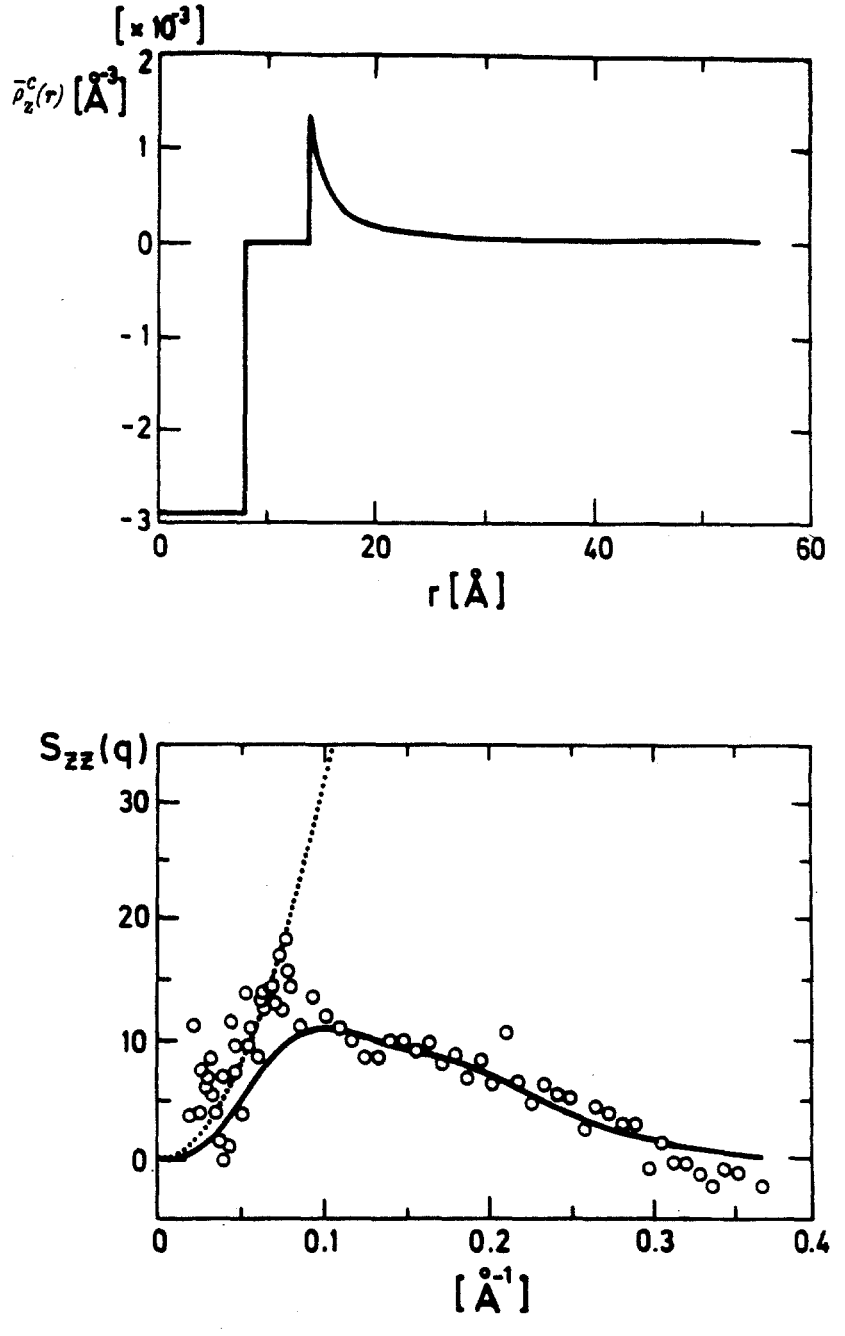

Fig. 5. Top: The charge concentration profile in the cell enclosing a polymer rod (DNA). Bottom: The observed charge-charge structure function $S_{zz}(q)$ is resolved in two components: $\bar{S}_{zz}(q)$ derived from the concentration profile and $\tilde{S}_{zz}(q)$ derived from correlation in concentration fluctuation (from J.R.C. van der Maarel et al. [16]).

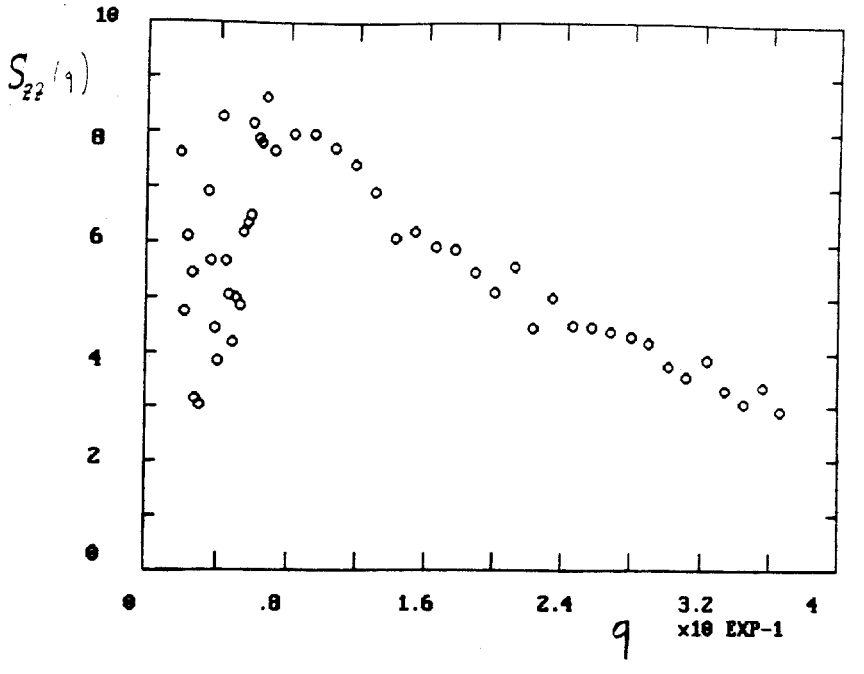

Fig. 6. The charge-charge structure function $S_{zz}(q)$ measured in Polystyrene sulfonates (from J.P. Cotton [23] et al.). As in Figures 2 and 5 $S_{zz}(q)$ is a pure number. Note the difference of magnitude between electrolytes and polyelectrolytes.

the case of the Polystyrene sulfonate coils, because of coil shape fluctuations at distances greater than the persistence length l_p. We need to evaluate $\tilde{S}_{zz}(q)$ from the two-particles density. We have not yet found an analytical expression which accounts for the interaction between charges. An interesting prediction for this effect is the lowering of the total energy of the system, inducing attractive forces between polyions. We expect a corresponding increase in the Debye-Falkenhagen relaxation time.

5 Conclusion

We have derived, from neutron scattering experiments, the structure function $S_{cc}(q)$ associated with interdiffusion of negatively and positively ionized molecules. Our aim was to determine the charge-charge structure function $S_{zz}(q)$ from $S_{cc}(q)$.

The experiments were carried out at concentrations ρ far beyond the range of validity of the Debye-Hückel theory. In the case of 1:1 electrolytes in solution, we have analyzed the important correlation hole displayed by $S_{zz}(q)$. The correlation length κ^{-1}, in the window of observation, is small ($\rho\,\kappa^{-3} \ll 1$) and scales as $\rho^{-1/2}$. A charge dielectric function $\varepsilon(q)$ was derived from $S_{zz}(q)$. Its interpretation depends on the solvent contribution to the premitivity. The latter either renormalizes the permitivity, or it introduces a longitudinal dielectric structure. Sor far, we have not found a way to deconvolute the two effects.

When the molecular structure becomes important as in the case of polyelectrolytes, the relation between mass and charge fluctuations is less explicit, and this is the point of interest.

We have compared the charge-charge structure function for DNA rods and polystyrene sulfonate coils. We note that the charge fluctuations are more important than in electrolytes. We have identified, in the case of DNA rods, the contribution of frozen and fluctuation terms. We need a physical evidence of the lowering of the energy due to the interaction of fluctuating counterions [14]. This could be a shift of the Debye-Falkenhagen relaxation time, with respect to an equivalent electrolyte solution.

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