

On the Charge Structure Function of Rodlike Polyelectrolytes.

J. R. C. VAN DER MAAREL(*), M. MANDEL(*) and G. JANNINK(*)(**)

(*) *Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories Leiden University - P.O.Box 9502, 2300 RA Leiden, The Netherlands*

(**) *Laboratoire Léon Brillouin, CEN de Saclay - 91191 Gif-sur-Yvette Cedex, France*

(received 22 April 1992; accepted in final form 5 October 1992)

PACS. 61.12 – Neutron determination of structures.

PACS. 87.15 – Molecular biophysics.

PACS. 36.20 – Macromolecules and polymer molecules.

Abstract. – The charge structure function of a rodlike polyelectrolyte within an electroneutral coaxial volume can be decomposed into two parts. A first contribution is given by fluctuations. The other is related to the existence of concentration profiles, formed by counterions about the polyion. Using this simple cell model, it is possible to identify these contributions separately in different wave vector ranges, as illustrated by recent small-angle neutron scattering. We discuss the implications of this decomposition, particularly with regard to the Poisson-Boltzmann approximation.

Introduction. – The charge structure of aqueous polyelectrolyte solutions has two notable features. At a small-distance scale, it is characterized by strong time-independent inhomogeneities which stem from the charge separation at the polyion-water interface. On the other hand, the overall structure is disordered and its organization is determined by fluctuations. This effect is perhaps less conspicuous, but nevertheless fundamental.

The local inhomogeneities in the structure can be best represented by the one-particle density function. Such a function has been successfully calculated, for instance, in the framework of the cell model and the Poisson-Boltzmann equation [1]. Its main result is the counterion distribution about the cylindrical polyion.

The correlations revealing the global organization of aqueous polyelectrolyte solutions are represented by two-particle densities. Although the latter play an essential role in the determination of the structure, little has been achieved in this domain. Calculations in the random phase approximation and predictions made on the basis of scaling have been found inadequate. The main failure is the fact that these theories are unable to predict the local counterion charge distribution about the highly charged polyion.

Only a highly nonlinear theory will be able to handle the problem satisfactorily. One may, in a first approximation, combine the results obtained separately in the framework of the cell model and the two-particle theory. In this manner, attractive forces between polyions have been predicted to occur [2,3]. Another approach is to begin with the structure of simple

electrolyte solutions and subsequently to introduce a dissymmetry in molecular weight and charge between anions and cations. In the case of 1:1 electrolytes, the charge structure is described in terms of the screening effect: in the vicinity of a charge we find a depletion of like charges and an enhancement of unlike charges. However, the test charge itself is also part of the screening cloud. In the case of polyelectrolytes, there is an accumulation of counterions about the polyion. Due to the huge difference in molecular mass, a stationary-counterion concentration profile will be found in the polyion fixed coordinate system.

Our concern can then be formulated with the ideas expressed in ref. [4] on the structure of absorbed-polymer layers. Here the authors were able to separate the contributions of the average concentration profile and of the concentration fluctuations to the scattered intensity by adsorbed polymers. Their analysis indicates a contribution of fluctuations which becomes more important as the wave vector q increases. In our problem, the counterions accumulate about the polyion, characterized by an average concentration profile and concentration fluctuations. It is not *a priori* obvious to find out in which part of the wave vector interval the fluctuation contribution is more important. We focus here on the small- q limit.

We propose to gain some insight in this problem by examining a very simple model of polyelectrolyte solutions, together with the results of recent scattering experiments [5].

The charge structure function and its modelization. – We consider an aqueous solution of volume V containing ν polyions, each bearing N negative charges. The polyion charge is compensated by a total $N\nu$ positively charged counterions. The local charge carrier concentrations are denoted by $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$. The average concentration is given by $\bar{\rho}_+ = \bar{\rho}_- = \bar{\rho} = N\nu/V$. The local charge concentration is written

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

Neutrality requires that on the average the charge is zero:

$$(1/V) \int_V d\mathbf{r} \rho_z(\mathbf{r}) = \langle \rho_z(\mathbf{r}) \rangle_V = \bar{\rho}_z = 0. \quad (2)$$

The charge structure function is the quantity

$$S_{zz}(q) = \frac{1}{\bar{\rho}V} \int_V d\mathbf{r} \int_V d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] \langle \rho_z(\mathbf{r}) \rho_z(\mathbf{r}') \rangle \quad (3)$$

and q is the wave vector. It is important to note that $S_{zz}(q)$ reflects exclusively solute composition fluctuations, there is no contribution of the solvent-solute concentration fluctuations.

We now consider the simplest possible model of the charge structure function. For this we use the cell model [1], in which the volume V is partitioned into ν cylindrical volumes:

$$V_c = V/\nu = \pi r_{\text{cell}}^2 L, \quad (4)$$

with L the length of the rod and r_{cell} the cell radius. The polyion is positioned on the average along the cell axis, but it is allowed to fluctuate about this position (including rod deformation). The main assumption is that the cell remains electroneutral.

The decomposition of the solution into electroneutral cells is clearly an approximation. However, in many situations, *e.g.* in case of DNA fragments, the linear charge density on the polyion is so high that most counterions are confined to the immediate vicinity of the polyion. The counterion concentration at the cell boundary is much lower than the average

concentration (see ref. [5], fig. 9). Moreover, the interactions between different cell volumes can be made arbitrarily small by performing experiments at low concentration.

In the cell model, the counterion concentration $\rho_+(\mathbf{r})$ can be divided into two contributions:

$$\rho_+(\mathbf{r}) = \bar{\rho}_+^c(\mathbf{r}) + \delta\rho_+(\mathbf{r}), \quad (5)$$

where $\bar{\rho}_+^c(\mathbf{r})$ is the average concentration profile and $\delta\rho_+(\mathbf{r})$ the fluctuation. Within the cell $\bar{\rho}_+^c \neq \rho_+$. The average concentration profile accounts for the accumulation of counterions around the charged rod. An analytic expression for this function is derived from the Poisson-Boltzmann equation [1]. This concentration profile is uniform along the rod axis and cylindrically symmetric. Inserting eq. (5) into (1), one obtains

$$\rho_z(\mathbf{r}) = \bar{\rho}_z^c(\mathbf{r}) + \delta\rho_z(\mathbf{r}). \quad (6)$$

In eq. (6), only the counterion contribution to the charge fluctuation $\delta\rho_z(\mathbf{r})$ has been included. If desired, the contribution due to polyion fluctuations can be included too. The calculated function $\bar{\rho}_z^c(\mathbf{r})$ for a 0.1 mole/l TMA-DNA solution is plotted in ref. [5], fig. 9 as a function of the distance r away from the polyon axis.

The charge structure function in the cell is now defined as (see eq. (3))

$${}^cS_{zz}(q) = \frac{1}{\rho V_c} \int_{V_c} d\mathbf{r} \int_{V_c} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] \langle \rho_z(\mathbf{r}) \rho_z(\mathbf{r}') \rangle_{V_c}. \quad (7)$$

Due to the fact that the charge density can be divided into an average and a fluctuation contribution, the charge structure function can also be considered as the sum of two contributions:

$${}^cS_{zz}(q) = {}^c\bar{S}_{zz}(q) + {}^c\tilde{S}_{zz}(q). \quad (8)$$

The contribution due to the average concentration profile is given by

$${}^c\bar{S}_{zz}(q) = \frac{1}{\rho V_c} \left\langle \left| \int_{V_c} d\mathbf{r} \exp[i\mathbf{q} \cdot \mathbf{r}] \bar{\rho}_z^c(\mathbf{r}) \right|^2 \right\rangle_{V_c}. \quad (9)$$

The contribution due to counterion fluctuations reads

$${}^c\tilde{S}_{zz}(q) = \frac{1}{\rho V_c} \int_{V_c} d\mathbf{r} \int_{V_c} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')] \langle \delta\rho_z(\mathbf{r}) \delta\rho_z(\mathbf{r}') \rangle_{V_c}. \quad (10)$$

Equations (7)-(10) are the object of the present discussion, as in ref. [4]. We note that, although the integral in eq. (9) is limited to the cell, the structure function is meaningful at all q , if interference effects between different cell volumes are negligible. In fig. 1, the charge structure function due to the average counterion distribution ${}^c\bar{S}_{zz}(q)$ is displayed *vs.* the square of the wave vector q . This result is derived from a calculation using the analytic form of the concentration profile within the cell and averaging over all cell orientations with respect to the momentum vector \mathbf{q} [5].

The long-wavelength limit of the charge structure function, identification of average and fluctuation contributions. – The $q \rightarrow 0$ limit is of interest, because in this limit it is possible to reveal essential differences between the contributions due to the average profile and the term due to fluctuations: ${}^c\bar{S}_{zz}(q)$ and ${}^c\tilde{S}_{zz}(q)$, respectively.

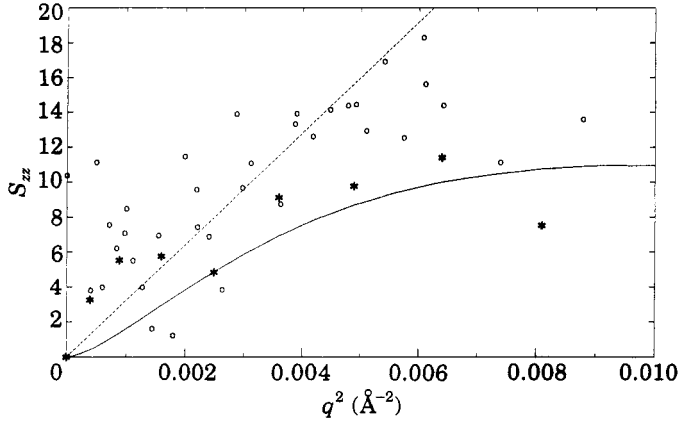


Fig. 1. – Charge structure function $S_{zz}(q)$ against q^2 : \circ values obtained in the scattering experiment on rodlike DNA particles (average length 500 Å) at a concentration of 0.1 mole P/1 [5]; * values derived from the partial structure functions for charged spherical micelles at the same charge carrier concentration [6]; — ${}^c\bar{S}_{zz}(q)$ calculated using the radial average density profile derived from the Poisson-Boltzmann equation in cylindrical geometry [5]; --- parabolic interpolation of the experimental results with $2q^2/\kappa^2$ and $\kappa^{-1} = 4$ nm.

For the contribution due to the average profile, we expand eq. (9) in terms of \mathbf{q} :

$${}^c\bar{S}_{zz}(q) = \frac{1}{\bar{\varphi}V_c} \left\langle \left| \int_{V_c} d\mathbf{r} \left[1 + i\mathbf{q} \cdot \mathbf{r} - \frac{1}{2}(\mathbf{q} \cdot \mathbf{r})^2 \dots \right] \bar{\varphi}_z^c(\mathbf{r}) \right|^2 \right\rangle_{V_c}. \quad (11)$$

In the integral, the term independent of \mathbf{q} vanishes due to electroneutrality of the cell volume. The term proportional to \mathbf{q} vanishes due to the cylindrical symmetry of the average-charge-density profile. Accordingly, to lowest order in q , eq. (11) reads

$${}^c\bar{S}_{zz}(q) = \frac{1}{\bar{\varphi}V_c} \left\langle \left| \int_{V_c} d\mathbf{r} (\hat{\mathbf{q}} \cdot \mathbf{r})^2 \bar{\varphi}_z^c(\mathbf{r}) \right|^2 \right\rangle_{V_c}, \quad (12)$$

with $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}| = \mathbf{q}/q$. The average concentration profile does not contribute a q^2 term in the charge structure function.

For the contribution due to counterion fluctuations the result is different. Expanding eq. (10) in powers of q , one obtains

$${}^c\bar{S}_{zz}(q) = \frac{1}{\bar{\varphi}V_c} \int_{V_c} d\mathbf{r} \int_{V_c} d\mathbf{r}' \left[1 + i\mathbf{q} \cdot \mathbf{r}' - \frac{1}{2}(\mathbf{q} \cdot \mathbf{r}')^2 \dots \right] \langle \hat{\varphi}_z(\mathbf{r}) \hat{\varphi}_z(\mathbf{r} - \mathbf{r}') \rangle_{V_c}. \quad (13)$$

Again, the term independent of \mathbf{q} vanishes due to electroneutrality. Accordingly, to lowest order in q , eq. (13) reads

$${}^c\bar{S}_{zz}(q) = -\frac{1}{\bar{\varphi}V_c} q^2/2 \int_{V_c} d\mathbf{r} \int_{V_c} d\mathbf{r}' (\hat{\mathbf{q}} \cdot \mathbf{r}')^2 \langle \hat{\varphi}_z(\mathbf{r}) \hat{\varphi}_z(\mathbf{r} - \mathbf{r}') \rangle_{V_c}. \quad (14)$$

We define

$$2/\kappa_c^2 = \frac{-1}{2\epsilon V_c} \int_{V_c} d\mathbf{r} \int_{V_c} d\mathbf{r}' (\hat{\mathbf{q}} \cdot \mathbf{r}')^2 \langle \partial_{\phi_z}(\mathbf{r}) \partial_{\phi_z}(\mathbf{r} - \mathbf{r}') \rangle_{V_c}, \quad (15)$$

and as a result

$${}^c\tilde{S}_{zz}(q) = 2q^2/\kappa_c^2. \quad (16)$$

The quantity κ_c^{-2} is necessarily positive because the scattered intensity in eq. (16) is a square amplitude, and is also finite. Relation (15) then expresses the charge screening due to charge fluctuations within the cell. However, κ_c^{-2} accounts only partially for the real screening effect.

We note that it is necessary to introduce fluctuations with respect to the average profiles and/or to take into account the system as a whole, if we wish to satisfy the Stillinger-Lovett sum rules.

Generalization and discussion. – To generalize our results we have to include correlations between different cell volumes. These intercell contributions will include both average two-particle distributions (*i.e.* counterion-counterion, polyion-polyion, and polyion-counterion) and fluctuation terms. Accordingly, we expect $S_{zz}(q)$ to be different from ${}^cS_{zz}(q)$. However, this difference will not be as dramatic as in case of the partial structure functions. This is due to a partial cancellation of intercell effects in the long-wavelength limit [5]. Because of electroneutrality, both S_{zz} and ${}^cS_{zz}$ tend to zero for $q \rightarrow 0$.

Expanding S_{zz} about $q \rightarrow 0$,

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

we now obtain a characteristic macroscopic screening length κ^{-1} , which in solutions of simple electrolytes accounts for overall screening [7, 8]. It is then appropriate to compare the charge structure function $S_{zz}(q)$ derived from a scattering experiment (at zero average contrast [9]) and ${}^c\tilde{S}_{zz}(q)$ derived from a calculation (see fig. 1). Although the cell parameters have been adjusted to obtain the best fit at sufficiently high q values, there remains a difference at small q . We argue that this difference is partly due to the contribution of the charge fluctuations: ${}^c\tilde{S}_{zz}(q)$. If we fit the small- q range of the experimentally observed charge structure function with a parabola, we find $\kappa^{-1} = (4 \pm 1) \text{ nm}$. On the other hand, the characteristic decay distance of the counterion profile within the cell can be obtained from the solution of the Poisson-Boltzmann equation and amounts to 2.4 nm.

We have shown that it is necessary to introduce fluctuations, or, equivalently, correlations between charges at different positions to satisfy the Stillinger-Lovett sum rules. In principle, it is possible to set up a system of coupled equations between the one- and two-particle density correlation functions [3]. The introduction of the pair correlation changes the Poisson-Boltzmann approximation in two ways:

i) It improves the average counterion density profile with respect to the polyion. In cylindrical symmetry, however, it does not generate a q^2 -dependence in ${}^cS_{zz}$.

ii) The cell model may be extended to include interactions between two polyions.

Our contention is that small ion charge fluctuations as revealed in $\tilde{S}_{zz}(q)$ may give rise to attractive forces. This has been calculated for two charged parallel plates immersed in an electrolyte solution [3]. Analogously, attractive interactions have been predicted to occur

between two parallel rods in a cell model, arising from condensed counterion fluctuations [2].

Of course, the fluctuating charge density should also include fluctuations in the polyion structure. They also contribute to $^cS_{zz}$ and attractive forces between polyions. However, this is not expected to perturb the cylindrical symmetry of the average-charge-density profile around each polyion.

* * *

We have benefitted from discussions with P. G. DE GENNES, L. AUVRAY, J. F. JOANNY and M. KUIL.

REFERENCES

- [1] KATCHALSKY A., *J. Pure Appl. Chem.*, **26** (1971) 327.
- [2] OOSAWA F., *Polyelectrolytes* (Marcel Dekker, New York, N.Y.) 1971.
- [3] KJELLANDER R. and MARCELJA S., *Chem. Scripta*, **25** (1985) 112.
- [4] AUVRAY L. and DE GENNES P. G., *Europhys. Lett.*, **2** (1986) 647.
- [5] VAN DER MAAREL J. R. C., GROOT L. C. A., MANDEL M., JESSE W., JANNINK G. and RODRIGUEZ V., *J. Phys. II*, **2** (1992) 109.
- [6] DERIAN P. J., BELLONI L. and DRIFFORD M., *Europhys. Lett.*, **7** (1988) 243.
- [7] CAILLOL J. M., LEVESQUE D. and WEIS J. J., *J. Chem. Phys.*, **91** (1989) 5544.
- [8] HANSEN J.-P. and McDONALD I. R., *The Theory of Simple Liquids* (Academic Press, New York, N.Y.) 1986.
- [9] JANNINK G. and VAN DER MAAREL J. R. C., *Biophys. Chem.*, **41** (1991) 15.