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DIELECTRIC BEHAVIOR OF LINEAR POLYELECTROLYTES

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The dipolar correlation function for a system of counterions diffusing on the surface of a polyelectrolyte cylinder is computed. Repulsive coulombic interactions between the counterions are taken into account. Lateral dissociation and reassociation to the cylinder is treated microscopically. Numerical calculations needed to obtain quantitative results for the long time behavior are presented. The model dependence on its parameters is interpreted with special emphasis on parameter values typical of DNA.

1. Introduction

The dielectric behavior of solutions of synthetic and natural polyelectrolytes has attracted much attention recently. A number of mechanisms for the dynamics are involved in the dielectric response and, despite a voluminous literature, their relative importance and role are still a source of controversy. Mandel [1–3] developed a model of the dielectric dispersion based on the distortion, caused by applied electric fields, of the counterion atmosphere surrounding a rodlike polyion. In order to generate a model prediction of two dispersion regions, as is often observed experimentally, Mandel supposed that the polyelectrolyte molecule is represented by a sequence of charged rodlike subunits. Fluctuation in ion distribution along each subunit is relatively facile whereas fluctuations between subunits takes place on a longer time scale. The intramolecular ion dynamics was coupled to the rotational diffusion of the molecule as a whole in order to compute the system dipolar correlation function (and hence the dielectric behavior). Dissociation and association from the rod was accounted for in a somewhat arbitrary manner by assuming that the fluctuations in the number of associated counterions causes the closed system result for the correlation function to be multiplied by an exponential in time. All model calculations of the dielectric behavior found in the literature suffer from approximate treatment of the association-dissociation kinetics. We examine this portion of the overall dynamics in more detail in the present work. Mandel does not include interactions between the counterions with the result that the predicted dielectric increment is linear in the number of associated counterions. However, it is known from experiment that the dielectric increment returns to zero as the counterion complement approaches the saturation limit [4]. Some dielectric measurements on DNA solutions were recently interpreted in terms of Mandel's model [5]. Warashina and Minakata [6–7] in a development of the Oosawa [8] theory of counterion concentration fluctuations conclude that the origin of the separated dispersion regions lies in the association-dissociation kinetics. They treat a multi-site model and introduce average dissociation and association rates for each site. The effect is to increase the relaxation rate of every relaxation mode by a constant amount. We prefer a more detailed picture of the association-dissociation kinetics and account explicitly for the dynamics of individual ions. Warashina and Minakata make certain that saturation effects operate by limiting the number of counterions in each site to zero or one. They introduce an interion potential, but it is not used (by itself) to prevent multiple occupancy of sites. Indeed when they use Boltzmann statistics to compute the dielectric increment no interactions between ions on the same site can be accommodated. This is a difficulty associated with the site model approach since the coulombic interaction energy of like ions on the same site is infinite. Warashina and Minakata avoid this conceptual difficulty by treating the ions as "loosely bound" (i.e. separated in space) in this limit. We employ a continuum picture with Boltzmann statistics. Configurations in which ions approach each other closely are assigned low probability via the equilibrium distribution function. The association-dissociation kinetics is treated by adapting the scheme of Berg and Blomberg [9]. They developed a model to explain the unexpectedly rapid association of lac repressor to the operator on DNA. The portions of their picture which we borrow are the coupled diffusion of the particle on the rod and in the bulk. In particular, particles which leave the rod at a given point are allowed to return later at some other point. This possibility is absent from previous calculations of the dielectric response.

2. The dielectric response

The molecular quantity of interest is the dipolar correlation function γ given by

$$\gamma = \langle \boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0) \rangle . \qquad (2.1)$$

$\boldsymbol{\mu}(t)$ is the system dipole moment at time t. The average is taken over the equilibrium distribution of system configurations at time 0.

The correlation function may be related to the complex dielectric permittivity ϵ^* (an experimental observable) via Laplace transformation (indicated by ~)

$$(-\tilde{\gamma})/(-\tilde{\gamma})_{\omega=0} = \int_0^\infty -\exp(-\mathrm{i}\omega t)(\mathrm{d}\gamma/\mathrm{d}t)\mathrm{d}t/\gamma(0)$$

$$= (-\mathrm{i}\omega\tilde{\gamma} + \gamma(0))/\gamma(0) \approx (\epsilon^* - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) . \qquad (2.2)$$

In general a more complicated function of ϵ^*, ϵ_0, and ϵ_∞ will be required to account for the effect of the internal field. The internal field problem was reviewed recently [10].

3. The model

3.1. Free diffusion of one particle with dissociation

We consider a rod of length L and employ cylindrical coordinates.

For this case the unnormalized dipolar correlation function is

$$\gamma = \int_0^L \mathrm{d}z' P_{\mathrm{eq}}(z') e(z' - L/2) \int_0^L \mathrm{d}z \, e(z - L/2) P(z, z', t) . \qquad (3.1)$$

$P(z, z', t)$ is the system Green's function; i.e. the (one-dimensional) probability density of finding the particle at position z at time t given position z' at time 0. The average is taken over the equilibrium distribution of z'. For a single particle diffusing freely $P_{\mathrm{eq}} = 1/L$. $P(z, z', t)$ may be computed from the kinetic scheme of Berg and Blomberg [9].

$$\partial P/\partial t = D_1 \, \partial^2 P/\partial z^2 - \lambda P$$

$$+ \lambda \int_0^L \mathrm{d}z'' \int_0^t \mathrm{d}t' F(z, z'', t - t') P(z'', z', t') , \qquad (3.2)$$

D_1 is the (one-dimensional) diffusion constant of the particle on the rod and λ is the dissociation rate from the rod. F is the flux of particles (per unit length) to the rod at position z and time $t - t'$ arising from particles which left the rod at position z'' at time t'. To find F the diffusion in bulk must be analyzed. The (three-dimensional) probability density c evolves according to

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} = \frac{1}{D_3}\frac{\partial c}{\partial t} , \qquad (3.3)$$

F is given by [9]

$$F(z, z'', t) = 2\pi b D_3 \, \partial c/\partial r|_{r=b} , \qquad (3.4)$$

b is the radius of the rod (cylinder). Note that the angular co-ordinate in cylindrical co-ordinates has been suppressed. We return to this point below. To solve this system of equations the following boundary and initial conditions are introduced [9].

$$\partial P/\partial z = 0; \quad z = 0, L; \quad P(z, z', 0) = \delta(z - z') , \qquad (3.5)$$

$$\partial c/\partial r = kc\,, \quad r = b; \quad \partial c/\partial z = 0\,, \quad z = 0, L\,;$$
$$c(z, r, 0) = \delta(z - z'')\,\delta(r - b)/2\pi b\,. \tag{3.6}$$

The boundary conditions on P prevent flow off the ends of the rod. For short rods this condition is unrealistic and could be modified. The constant k plays the role of a rate constant for association. The boundary conditions on c involving z are somewhat arbitrary but correspond to those used by Berg and Blomberg in their "closed cell" approach [9]. The solution of this set of equations is shown in Appendix II leading to an expression for the Laplace transform of γ (the B's are given by eqs. (II.6) and (II.7))

$$\tilde{\gamma}(p) = \sum_{n=0}^{\infty} B_{2n+1}(p)\,\frac{4e^2L^3}{(2n+1)^4\pi^4}\,. \tag{3.7}$$

The flow of the calculations leading to γ is as follows. The (one) particle density in bulk, c, evolves via free diffusion eq. (3.3) subject to the boundary conditions eq. (3.6). The solution to this problem is well known [11]. F is found from c using eq. (3.4) which is just Fick's first law. F is used in eq. (3.2) to find P which appears in the second integral in eq. (3.1) to compute $\mu(t)$. The integral over P_{eq} in eq. (3.1) corresponds to the brackets in eq. (2.1). The stumbling block is extraction of P from eq. (3.2). To obtain a solution in closed form we took the Laplace transform of eqs. (3.1) and (3.2) (see Appendix II).

In subsequent sections the method is the same. However, the dimensionality of the problem increases as particles are added to the rod and P and P_{eq} are influenced by particle–particle forces.

3.2. Free diffusion of independent particles

For n' particles if $\lambda = 0$ (no dissociation) $\tilde{\gamma}(p)$ is just n' times the one-particle result. The dielectric increment, as reflected in $\gamma(0)$ is also linear in n'. This feature is unacceptable as experiments demonstrate and physical insight demands that a rod-like polyelectrolyte molecule with sufficient counterions to force a uniform distribution via coulombic repulsions has a squared dipole moment of zero. The independent particle assumption is in conflict with the concept of saturation. The independent particle assumption is relieved in section 3.3. If $\lambda \neq 0$, $\tilde{\gamma}(p)$ does not follow directly from the one-particle result and it is best obtained as a special case of the interacting particle expression (below).

3.3. Forced diffusion of interacting particles

We choose to treat the diffusion in bulk as unaffected by specific particle-particle (ion-ion) forces but an interparticle (Coulombic) potential is presumed operable on the rod. The potential serves to keep the particles apart and thereby forces a decrease in the dielectric increment as the number of particles approaches the saturation limit (neutral molecule). The diffusion equations become

$$\frac{\partial P}{\partial t} = D_1 \sum_i \frac{\partial^2 P}{\partial z_i^2} + \frac{D_1}{k_{\mathrm{B}}T} \sum_i \left(P\,\frac{\partial^2 V}{\partial z_i^2} + \frac{\partial V}{\partial z_i}\,\frac{\partial P}{\partial z_i}\right)$$
$$- \lambda P + \lambda \int_0^L \ldots\ldots \int_0^L \prod_i \mathrm{d}z_i''$$
$$\times \int_0^t \mathrm{d}t'\, F(\{z_i\}, \{z_i''\}, t - t')\, P(\{z_i''\}, \{z_i'\}, t')\,, \tag{3.8}$$

$$P = P(\{z_i\}, \{z_i'\}, t)\,, \tag{3.9}$$

$$P_{\mathrm{eq}} = \exp(-V/k_{\mathrm{B}}T) \bigg/ \int_0^L \ldots\ldots \int_0^L \prod_i \mathrm{d}z_i' \exp(-V/k_{\mathrm{B}}T)\,, \tag{3.10}$$

$$\frac{\partial c}{\partial t} = D_3 \sum_i \frac{1}{r_i} \left\{ \frac{\partial}{\partial r_i}\left(r_i\,\frac{\partial c}{\partial r_i}\right) + r_i\,\frac{\partial^2 c}{\partial z_u^2} \right\}, \tag{3.11}$$

$$F = \prod_i (2\pi b D_3)\,\frac{\partial c}{\partial r_i}\bigg|_{r_i = b} \tag{3.12}$$

$$\partial P/\partial z_i = 0\,, \quad z_i = 0, L\,;$$
$$P(\{z_i\}\,\{z_i'\}, 0) = \prod_i \delta(z_i - z_i')\,. \tag{3.13}$$

$$\partial c/\partial r_i = kc\,, \quad r_i = b; \quad \partial c/\partial z_i = 0\,, \quad z_i = 0, L\,;$$
$$c(\{z_i\}, \{r_i\}, 0) = \prod_i (\delta(z_i - z_i'')\delta(r_i - b)/2\pi b)\,. \tag{3.14}$$

The solution for F may be written down immediately as it is simply a product of terms of the type found previously. This is a consequence of the free bulk diffusion assumption which leads to separation of co-ordinates in the differential equation for c. For the potential V

we choose (Debye–Hückel screening may be accomodated without much difficulty)

$$V = \sum_{j} \sum_{i<j} e^2/\epsilon |r_i - r_j| (4\pi\epsilon_0) . \qquad (3.15)$$

The potential appears in the differential equation for P thereby influencing the dynamics. The potential also appears in P_{eq} and influences strongly the calculation of γ. The presence of the potential in P_{eq} causes no insurmountable computational difficulties but the coupling of the particle co-ordinates caused by V in the differential equation for P makes analytical treatments of the dynamics intractable. Previous treatments of the dielectric behavior of systems involving diffusion over potential barriers show that the average effect of the barrier system is to slow the relaxation [12]. To avoid being forced to numerical methods at this stage we approximate $\partial^2 V/\partial z_i^2$ and $\partial V/\partial z_i$ by their values (in a Taylor's series expansion about the uniform distribution) of k' and 0 respectively. In a gross way this introduces a "restoring force" for P into eq. (3.8), prevents the evolution of P, and thereby slows the relaxation process. Although this procedure is clearly open to criticism our real reason for having V in the calculation is to have a physically reasonable P_{eq}. This procedure leads to independent particle dynamics. The analog of eq. (3.1) for the multiple particle case is

$$\gamma(t) = e^2 \int_0^L \cdots\cdots \int_0^L \prod_i \mathrm{d}z_i' \sum_i (z_i' - L/2) P_{\mathrm{eq}}(\{z_i'\})$$

$$\times \int_0^L \cdots\cdots \int_0^L \left[\prod_i \mathrm{d}z_i\right] \sum_i (z_i - L/2) \prod_i P_i \, . \qquad (3.16)$$

The solution of eqs. (3.8) to (3.16) is shown in Appendix II. An expression for γ valid for long times (small p) is

$$\gamma = \sum_{n=0}^{\infty} C_n \exp(-\lambda_n t) = \sum_{n=0} \frac{-4e^2 L^2 R_n}{(2n+1)^2 \pi^2}$$

$$\times \exp \left\{ -2D_{\mathrm{R}} t - (2n+1)^2 \pi^2 D_1 t/L^2 + k' D_1 t/k_{\mathrm{B}} T \right.$$

$$-(n'-1)\lambda \left(1 - bk \int_0^{\infty} C(u) \mathrm{d}u/u^2 \right) t \qquad (3.17)$$

$$\left. - \lambda \left(1 - bk \int_0^{\infty} C(u) \mathrm{d}u/(u^2 + (2n+1)^2 \pi^2/L^2)\right) t \right\} .$$

Note that $2D_{\mathrm{R}}$ has been added to each relaxation rate λ_n. This accounts for the coupling of rotational diffusion of the molecule as a whole to the counterion dynamics. The coupling here is a (very straightforward) special case of a general formalism [16].

4. Discussion

4.1. *Qualitative features of the model*

As is often seen in dielectric relaxation, the principal modes (largest amplitudes) of relaxation have the longest relaxation times. For $V = 0$ (independent particles) $R_m = -2n'/\pi^2 m^2$ and the amplitudes in eq. (3.17) go as $1/(2n+1)^4$. Only the first term has appreciable amplitude. In general ($V \neq 0$) the independent particles result for R_m is approached as n' goes to one. As n' increases the R_m grow at first and then decrease to zero as the particles tend to the uniform distribution for which the dipole moment is zero. This saturation effect is caused exclusively by the potential and does not require artificial restrictions on the allowed particle co-ordinates. Values of R_m as a function of m and n' are shown in table 1.

For the principal mode ($m = 1$) R_1 falls increasingly short of the independent particles result. This is a result of the interactions which force the particles apart. The effect is noticeable even for $n' = 2$. The other R_m become larger (in magnitude) than the independent particle result before decreasing. As the mode index increases (fixed n') the R_m decrease but not nearly as rapidly as the $1/m^2$ dependence of the independent particle model. The feature tends to increase the importance of the higher modes and generate a (discrete) distribution of relaxation times which will be reflected in a broadening of the dielectric absorption. For a softer potential the effect will be more pronounced. The calculation of R_m requires a value ofr L. We set $L = 5.1 \times 10^{-8}$ m. Although we do not have a calculation of R_1 (228) (the condensation model prediction for the equilibrium number of counterions on a DNA rod of the dimensions selected) it is clearly in the region where the dielectric increment decreases with increasing n'. For a site model (site occupancy 0 or 1) with no counterion repulsions the maximum in the dielectric increment occurs for the half occupied rod ($n' = 150$ here). The maximum

Table 1
Integrals over the equilibrium distribution, eq. (II.13)

n'	$-2n'/\pi^2$	R_1	$-2n'/9\pi^2$	R_3	$-2n'/25\pi^2$	R_5	$-2n'/49\pi^2$	R_7
2	−0.405	−0.376	−0.045	−0.050	−0.016	−0.020	−0.008	−0.011
3	−0.608	−0.530	−0.068	−0.074	−0.024	−0.036	−0.012	−0.017
5	−1.013	−0.780	−0.113	−0.126	−0.041	−0.062	−0.021	−0.031
10	−2.026	−1.16	−0.225	−0.232	−0.081	−0.129	−0.041	−0.089
20	−4.052	−1.4	−0.450	−0.31	−0.162	−0.17	−0.082	–
30	−6.079	−1.6	−0.675	−0.3	−0.243	–	−0.124	–
40	−8.106	−1.6	−0.901	–	−0.324	–	−0.162	–

found here for smaller n' is a result of the presence of the repulsive potential.

With respect to the amplitudes of the dielectric response, the model makes specific predictions about the dependence on L ($L^2 R_n$) and on mode index n ($R_n/(2n+1)^2$). The L dependence of R_n is weak.

Eq. (3.17) also allows an interpretation of the various terms contributing to the relaxation rate λ_n.

There is rotational diffusion of the molecule as a whole which contributes $2D_R$. The effect of the potential on the dynamics (as we have treated it) is to subtract $k'D_1/k_BT$ (k' is positive) from the rate slowing the relaxation which takes place by diffusion of ions on the rod. Finally terms involving the dissociation-association kinetics contribute to λ_n. For one particle the terms involving λ and k reduce to

$$\lambda\left(1 - bk\int_0^\infty \frac{C(u)\,\mathrm{d}u}{u^2 + (2n+1)^2\pi^2/L^2}\right). \tag{4.1}$$

The relaxation rate is increased by the dissociation since the value of eq. (4.1) is always between 0 and λ. The rod by itself is an open system and relaxation proceeds in part by loss of particles. Some of these return as described by the second term in eq. (4.1). If $k = 0$ no particles return to the rod whereas for large k the integral equals $(bk)^{-1}$ and the coefficient of λ vanishes. This means simply that the recombination rate is so large that dissociating particles return to the chain immediately. Values of the integral term in eq. (4.1) as a function of k and n (b and L fixed at 1.3×10^{-9} m and 5.1×10^{-8} m respectively) are shown in table 2. Romberg quadrature was employed with polynomial approximations to the Bessel functions [14]. Some dependence on n is seen indicating a variation in the role of the association-dissociation kinetics with relaxation mode. As k increases the integral term tends to unity indicating a compensation of the effect of dissociation by rapid recombination. Note, however, that in the relaxation rate these terms are multiplied by λ so that if the dissociation is sufficiently rapid it may prevail even though an individual ion has a large probability of reassociating. Note that D_3 (the bulk diffusion constant) does not appear in the result. This is a result of the approximation (p small) made in eqs. (II.6) and (II.7) to give eq. (3.17). For arbitrary p, $\tilde{\gamma}$ will depend on D_3. In physical terms the cancellation of D_3 is a compensation of the decrease in relaxation rate by recombination (through F) and an increase in relaxation caused by motion (in bulk) away from the original position. The n' independent particle result is n' times the single particle expression if $\lambda = 0$ since $B_0^{-1}(p) = 1/L$. If $\lambda \neq 0$ the results differ according to the difference between (see Appendix II)

$$B_{2n+1}(p) \quad \text{and} \quad [\widetilde{B_{2n+1}^{-1}(p)}]\,[B_0^{-1}(p)L]^{n'-1}\,.$$

(−1 indicates the inverse Laplace transform).

This difference shows up in eq. (3.17) in the term contributing to λ_n which goes as $(n'-1)\lambda$. Roughly

Table 2
Values of the integral term in eq. (4.1)

k	$n = 0$	$n = 1$
10^6	0.0035	0.0021
10^7	0.0335	0.0213
10^8	0.2579	0.1791
10^9	0.7766	0.6863
10^{10}	0.9714	0.9563
10^{11}	0.9970	0.9956
10^{12}	0.9998	0.9997
10^{13}	1.0000	1.0000

speaking the contribution to the relaxation rate of the dissociation-association kinetics is proportional to n'. The physical interpretation of this is that the rate of particle loss from the rod is proportional to the number of particles. Real polyelectrolyte molecules will have a cylindrical rather than linear shape. Thus surface diffusion in the ϕ as well as z direction should be considered. For a single particle without dissociation consideration of the (separable) diffusion in the ϕ direction yields

$$\gamma = e^2 b^2 \exp(-D_1 t/b^2) + \frac{8e^2L^2}{\pi^4} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4} \exp(-(2n+1)^2\pi^2 D_1 t/L^2). \tag{4.2}$$

For typical molecular dimensions (DNA) the amplitude of the first term in eq. (4.8) is less than 1% of the amplitude of the first term in the sum. The relaxation rate of the first term is 100 times that of the first term in the sum. Thus diffusion around the cylinder introduces a small high frequency contribution. Numerical values for some of the model parameters may be estimated. For a DNA molecule with 300 phosphate groups $L = 5.1 \times 10^{-8}$ m and $b \approx 1.3 \times 10^{-9}$ m. $D_3 = 1.34 \times 10^{-9}$ m^2 s^{-1} (calculated from the sodium ion mobility in water, note that D_3 drops out of the expression for γ in eq. (3.17)). $T = 298$ K. A reasonable guess for D_1 is 10^{-11} m^2 s^{-1}. We do not have good estimates for k and λ except they are presumably $>10^7$ (SI units) as sodium-NMR in DNA solutions occurs in the rapid exchange limit [17]. Note that a term $2D_R$ has been added to the relaxation rate. This accounts for the relaxation via independent molecular rotational diffusion of the rod [16]. D_R may be computed via hydrodynamics from the known dimensions of the rod (cylinder). It is entirely possible for the terms in the relaxation rate involving D_R, D_1 and λ to be of similar magnitude. For example, we have $\pi^2 D_1/L^2 = 3.79(10)^4$ s^{-1}, the Kirkwood–Auer–Riseman [18] equation yields $2D_R = 1.98 \times 10^3$ s^{-1}, and the terms λ and k may be found using table 2 for given n' (the condensation model value is $n' = 228$ [20]).

If k' is calculated for a uniform distribution of 228 ions on a line of length 5.1×10^{-8} m with bare coulombic interaction, one finds $k'D_1/k_BT \approx 10^9$ which is unrealistically large. The separation of charges is actually much larger as they are on the surface of a cylinder and are screened to some extent. The charge separation should reduce k' by several orders of magnitude from the value calculated. The Berg and Blomberg scheme contains a function $G(z, z', t)$ which is the probability that a particle at z' in the bulk at time 0 is on the rod at position z at time t. Such particles do not contribute to the dielectric response calculated here as we are interested in correlations involving particles on the rod at time 0. The contribution to the dielectric response from the particles in the bulk is not treated here. A justification for dividing the system and analyzing part of it is given in Appendix I. Thus the G function is not part of our kinetic scheme. What G does is to maintain the equilibrium number of condensed counterions on the polyelectrolyte, replacing those which move from the rod to the bulk. For a closed system we would find $\lim_{t\to\infty} P = P_{eq}$. This is not true here, rather $\lim_{t\to\infty} P = 0$ due to the dissociation. The zero limit is due to placing the outer boundary at infinity.

4.2. *Comparison with the literature*

A brief survey of the dielectric behavior of polyelectrolytes (including DNA) has been given by Mandel [3]. For sufficiently high molecular weights two separated dispersion regions are observed [5]. The low frequency dispersion can be very large and its specific dielectric increment and (mean) relaxation time are molecular weight dependent. The parameters of the smaller high frequency dispersion are independent of molecular weight. All parameters show dependence on polyelectrolyte concentration and dependence on the type and concentration of added salt. For some polyelectrolytes (poly acids for example) the condensed counterions can be varied to the point where repulsive forces cause a decrease in the measured dielectric increment [4]. Any model of the dielectric behavior of polyelectrolyte solutions must address these observations and provide physically reasonable values for the parameters (disperson amplitudes, relaxation times) as well. Mandel's model [3] generates two dispersion regions via the presence of subunits along the rod. However, such structure has not been detected in non-dielectric experiments. In addition, the possibility of dissociation and rapid reassociation of counterions would assist particle motion between subunits and wipe out the effects of such structure. Mandel's model does not generate saturation effects since the interparticle forces are neglected.

Wada et al. [21–23] have focused on the low frequency dispersion. Wada assumes that the surface diffusion of ions on the polyelectrolyte and the association-dissociation kinetics are slow compared with rotational diffusion of the molecule. Thus $2D_R$ dominates the relaxation rate (see eq. (3.17)). Support for this picture is based on agreement between the observed mean relaxation time and values calculated from the solution viscosity and molecular dimensions (mean square radius of gyration). O'Konski suggested an extended Maxwell–Wagner mechanism [24]. Shurr [25] gave a three-dimensional model for the ion distribution with ion motion constrained to one dimension. His evaluation of the repulsive forces led to the conclusion that Oosawa's [8] estimate of the dielectric increment caused by longitudinal ion fluctuations was much too large. In addition, he found that the self field of the fluctuation forces ohmic conduction thereby reducing the relaxation time. This is reminiscent of the role of k' in our model. However, Minakata [6,7] calculated the repulsive term for Oosawa's picture and found a much smaller effect. In Minakata's model the two dispersion regions arise from the effect of the association–dissociation kinetics on the relaxation times. Our treatment of the kinetics does not cause such a division of the dielectric response. A clear candidate for the origin of a molecular weight independent fast relaxation process is surface diffusion perpendicular to the rod axis (our eq. 4.2)). Apart from small effects of coupling of the ϕ and z diffusion through the potential (which will tend to broaden the distribution along the ϕ coordinate) the relaxation of individual ions via diffusion (also dissociation-association) will be independent of the rod length. Our model and Minakata's both yield γ in the form $\Sigma_n C_n \exp(-\lambda_n t)$ and a numerical comparison is possible. A comparison of the first few terms ($\lambda = 0$) for the case of no interaction and interaction via the bare Coulomb potential is shown as a function of n' (model parameters as given above) in table 3. The λ_n are in units of D_1/L^2 and the C_n in units of e^2L^2. Our amplitudes drop off much faster with mode index than Minakata's and our relaxation rates are smaller. For no interaction our dielectric increments are slightly larger than Minakata's as his model has some saturation built in via the use of Fermi–Dirac statistics. For Coulomb interactions the predicted dielectric increments are roughly equal as might be expected since the details of the dynamics do not affect static properties. The model calculation here can be improved in several respects. The combined ϕ, z multiparticle problem should be set up with screening incorporated in the counterion repulsive potential. This latter step will have the beneficial effect of reducing the long-ranged interactions and presumably thereby improve the convergence of the numerical results. In addition, we wish to move away from the condensation hypothesis for determining the number of counterions on the rod and treat the particle fluxes onto the chain in the context of the Poisson–Boltzmann model. This requires reformulation of the bulk diffusion calculation. Encouraging results as to the likely success of this procedure were obtained recently by Anderson and Record [26] in an

Table 3
Comparison dielectric amplitudes and relaxation rates

n'	C_0	λ_0	C_1	λ_1	C_2	λ_2	ΣC_n	Model
2	0.1006	39.5	0.0252	157.9	0.0112	355	0.166	M
2	0.0831	47.8	0.0215	185.2	0.0097	409	0.13	M(C)
2	0.1643	9.9	0.0020	88.8	0.0003	247	0.1667	V
2	0.1524	9.9	0.0023	88.8	0.0003	247	0.1551	V(C)
10	0.4897	39.5	0.1224	157.9	0.0544	355	0.806	M
10	0.2419	79.9	0.0665	290.6	0.0314	616	0.40	M(C)
10	0.8213	9.9	0.0101	88.8	0.0013	247	0.8333	V
10	0.4701	9.9	0.0104	88.8	0.0021	247	0.4838	V(C)
20	0.9457	39.5	0.2365	157.9	0.1051	355	1.56	M
20	0.3176	117.6	0.0901	414.2	0.0435	858	0.51	M(C)
20	1.6426	9.9	0.0203	88.8	0.0026	247	1.6667	V
20	0.5674	9.9	0.0140	88.8	0.0028	247	0.5854	V(C)

M = Minakata model, V = present model, C = Coulomb interaction.

analysis of the low salt form of the Donnan coefficient. The calculations proposed above will be reported in subsequent work.

Appendix I

The two phase approximation

The relaxation of the ions in the bulk phase has not been considered in this derivation. Our dipole moments $e\Sigma(z_i - L/2)$ are a portion of the system dipole moment and the γ we compute describes the relaxation of only those ions on the rod at time zero (the remaining counterions are in the bulk phase). Partial treatment of the system in this manner is allowed since the ions in the bulk (at time zero) are involved in dielectric dispersion at higher frequencies (analysis of this dispersion is complicated [10]). Under the condition of separate time scales for the relaxation of ions initially on the rod and initially in bulk the system correlation function becomes the sum of terms with no cross correlations (except for internal field effects [15]). An illustration of this feature for a simple model is given by analysis of a two phase four site model. The kinetic scheme is

$$\begin{array}{ccccccccc} \mu & & -\mu & & -\mu' & & \mu' & & \\ 1 & \underset{k}{\overset{k}{\rightleftharpoons}} & 2 & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & 3 & \underset{k'}{\overset{k'}{\rightleftharpoons}} & 4 & \underset{k_1}{\overset{k_2}{\rightleftharpoons}} & 1 \end{array} , \qquad (I.1)$$

$k_1 . k_2 . k$, and k' are the rate constants and the dipole moments of the individual sites are shown. Sites one and two constitute one phase and sites three and four the other phase. Evaluation of the correlation function of the full system by the usual procedure [13] yields

$$\gamma = C_+ \exp(\lambda_+ r) + C_- \exp(\lambda_- t) , \qquad (I.2)$$

where

$$C_+ = \frac{\mu^2[-X_-] + \mu'^2[(k_1/k_2)X_+] + \mu\mu'[-X_+X_- + k_1/k_2]}{(1 + k_1/k_2)(X_+ - X_-)} , \qquad (I.3)$$

$$X_+ = (k_1 + 2k + \lambda_+)/k_2 , \qquad (I.4)$$

and λ_+ and λ_- are the roots of $(k_1 + 2k + \lambda)(k_2 + 2k' + \lambda) - k_1 k_2 = 0$. Negatively subscripted quantities are obtained by interchanging plus and minus. In general the correlation function involves the coupled response of both phases. Note in particular the presence of terms in $\mu\mu'$. However, if $k_1, k_2, k \ll k'$ (rapid relaxation in the phase containing sites three and four) we find eqs. (I.2) through (I.4) become

$$\gamma = \frac{\mu^2}{(1 + k_1/k_2)} \exp[(-k_1 - 2k)t] + \frac{(k_1/k_2)\mu'^2}{(1 + k_1/k_2)} \exp[(-2k')t] . \qquad (I.5)$$

The correlation function separates into parts involving each phase separately weighted according to the relative populations of the phases at equilibrium. The relaxation of one phase is dominated by internal motion (k') whereas the "slow" relaxation of the other phase contains a contribution from dissociation (k_1). This scheme is analogous to our model kinetics except our dissociation rate is more structured than that above and our rate is computed from the system kinetics. For the present calculation the system dipole moment at $t = 0$ is

$$\boldsymbol{\mu}(0) = \sum_{i=1}^{n} \boldsymbol{\mu}_{i\mathrm{r}}(0) + \sum_{i=1}^{n} \boldsymbol{\mu}_{i\mathrm{b}}(0) , \qquad (I.6)$$

where n is the total number of free ions and r and b refer to the rod and bulk phases respectively. $\boldsymbol{\mu}_{i\mathrm{r}}(0) = 0$ if ion i is in the bulk at $t = 0$ and $\boldsymbol{\mu}_{i\mathrm{b}}(0) = 0$ if ion i is on the rod at $t = 0$. To find the collections $\boldsymbol{\mu}_{i\mathrm{r}}(t)$ and $\boldsymbol{\mu}_{i\mathrm{b}}(t)$ the relevant kinetic scheme is solved subject to an initial condition of a fixed number of ions on the rod (n') and fixed ion positions on the rod and in the bulk. To construct the system correlation function, averages over n' and the initial positions are taken with the equilibrium distribution function. Our procedure does not average over n'; however, the rod correlation function is obtained as an explicit function of n'. Clearly the system correlation function contains four kinds of terms. We treat only one of these, viz.

$$\left\langle \sum_{i=1}^{n'} \boldsymbol{\mu}_{i\mathrm{r}}(0) \cdot \sum_{i=1}^{n} \boldsymbol{\mu}_{i\mathrm{r}}(t) \right\rangle . \qquad (I.7)$$

Note that the second sum runs over all ions in the system and $\boldsymbol{\mu}_{i\mathrm{r}}(t)$ as calculated has built into it the probability that the ion is on the rod at time t. Only n' terms need be evaluated as the others have value zero in the dot product (recall that we have assumed independent particle dynamics). For determining P_{rob} (i on rod at t) we employ Berg and Blomberg's F function for the n' ions. The G function would be needed for the remaining $n - n'$ ions, but they are not part of our calculation.

Although we would like to evaluate the rod-bulk cross correlations and the bulk-bulk term the present scheme is insufficient. Ion motion in the bulk is complicated and involves hydrodynamic coupling with solvent (which is also involved in the bulk relaxation) [10]. Our hope is that conditions such as those for the two phase-four site model (above) hold and the rod-rod term appears as an increment in the dielectric response.

A detailed comment was received from a referee to the effect that the term calculated here will be largely cancelled by the moment of the surrounding electrolyte $\Sigma_{i=1}^{n}\boldsymbol{\mu}_{ib}(t)$ which is presumed approximately equal and of opposite sign to $\Sigma_{i=1}^{n}\boldsymbol{\mu}_{ir}(t)$. If this is correct (and the matter has yet to be addressed in a detailed manner in the literature), the amplitude of the term including a cross-correlation)

$$\left\langle \sum_{i=1}^{n}\boldsymbol{\mu}_{ir}(0)\cdot\left\{\sum_{i=1}^{n}\boldsymbol{\mu}_{ir}(t)+\sum_{i=1}^{n}\boldsymbol{\mu}_{ib}(t)\right\}\right\rangle , \qquad \text{(I.8)}$$

will be much less than what we have calculated.

Since our formalism does not allow computation of $\Sigma_{i=1}^{n}\boldsymbol{\mu}_{ib}(t)$ we can neither reject nor confirm this assertion. Our feeling is that the fact that large dielectric increments are observed for (low salt) polyelectrolyte solutions suggests that the cancellation does not occur and that the model result, eq. (I.5), relates to the polyelectrolyte case.

Appendix II

Mathematical details

II.1. Free diffusion of one particle with dissociation

The solution of eqs. (3.3) and (3.6) is found in the literature [11]. Eq. (3.4) yields F as

$$F(z,z'',t) = \sum_{m=0}^{\infty} Z_m \cos\frac{m\pi z}{L}\cos\frac{m\pi z''}{L}$$
$$\times \exp(-m^2\pi^2 D_3 t/L^2)\int_0^{\infty} C(u)\exp(-D_3u^2t)\,\mathrm{d}u , \qquad \text{(II.1)}$$

$$Z_0 = bD_3k/L , \quad Z_m = bD_3k2/L , \quad m \neq 0 . \qquad \text{(II.2)}$$

$$C(u) = (4u/\pi^2b^2)/\{[uJ_1(ub) + kJ_0(ub)]^2$$
$$+ [uY_1(ub) + kY_0(ub)]^2\} . \qquad \text{(II.3)}$$

The J's and Y's are Bessel functions of the first and second kind respectively. The expression for F may be inserted into eq. (3.2) and the result Laplace transformed to eliminate the time derivative and the convolution integral. This yields an expression for $\tilde{P}(z,z',p)$ which suffices to calculate $\tilde{\gamma}(p)$ and hence ϵ^* ($p = \mathrm{i}\omega$). We find

$$0 = \delta(z-z') - p\tilde{P}(z,z',p)$$
$$+ D_1\frac{\mathrm{d}^2\tilde{p}(z,z',p)}{\mathrm{d}z^2} - \lambda\tilde{P}(z,z',p)$$
$$+ \lambda\int_0^L \mathrm{d}z''\tilde{P}(z'',z',p)\sum_{m=0}^{\infty} Z_m\cos\frac{m\pi z}{L}\cos\frac{m\pi z''}{L}$$
$$\times\int_0^{\infty}\frac{C(u)\,\mathrm{d}u}{p + D_3u^2 + m^2\pi^2D_3/L^2} . \qquad \text{(II.4)}$$

$\tilde{P}$ is found via the ansatz

$$\tilde{P}(z,z',p) = B_0(p) + \sum_{m=1}^{\infty} B_m(p)\cos\frac{m\pi z}{L}\cos\frac{m\pi z'}{L} . \qquad \text{(II.5)}$$

The coefficients B_m are found using the projection operator

$$B_0(p) = (1/L)/\left[p + \lambda - \lambda bD_3k\int_0^{\infty}\frac{C(u)\,\mathrm{d}u}{p+D_3u^2}\right], \qquad \text{(II.6)}$$

$$B_m(p) = (2/L)/\left[p + \lambda + m^2\pi^2D_1/L^2\right.$$
$$\left. - \lambda bD_3k\int_0^{\infty}\frac{C(u)\,\mathrm{d}u}{p + D_3u^2 + m^2\pi^2D_3/L^2}\right] . \qquad \text{(II.7)}$$

Performing the integrations in eq. (3.1) yields

$$\tilde{\gamma}(p) = \sum_{n=0}^{\infty} B_{2n+1}(p)\frac{4e^2L^3}{(2n+1)^4\pi^4} . \qquad \text{(II.8)}$$

II.2. Forced diffusion of interacting particles

The presence of V in eq. (3.8) prevents analytic treatment of the kinetic scheme. We replace $\partial^2 V/\partial z_i^2$

and $\partial V/\partial z_i$ by their values (in a Taylor's series expansion about the uniform distribution) of k' and 0 respectively. The rationale for this is that fluctuations which differ markedly from the uniform distribution carry little weight in P_{eq} which is used to compute γ. The fact that the dynamics of large fluctuations is incorrect will therefore not affect the final result. It is easy to establish via numerical estimates that P_{eq} becomes small within the range of $\{z_i\}$ for which V is approximated accurately by a Taylor's series truncated at quadratic terms and with no cross terms. However, it appears that $k'/k_{\mathrm{B}}T$ is comparable or even larger than π^2/L^2 and the forcing terms in the one dimensional diffusion could dominate ion motion on the rod. Clearly the role of V on the dynamics deserves detailed investigation. For the present we carry k' along in the formalism. We have

$$P = \prod_i P_i(z_i, z_i', t)\,, \tag{II.9}$$

$$\widetilde{P}_i(z_i, z_i') = B_0(p) + \sum_{m=1}^{\infty} B_m(p) \cos\frac{m\pi z_i}{L} \cos\frac{m\pi z_i'}{L}\,, \tag{II.10}$$

$$B_0(p) = (1/L)/\left[p + \lambda - \frac{k'D_1}{k_{\mathrm{B}}T} - \lambda b D_3 k \int_0^\infty \frac{C(u)\,\mathrm{d}u}{p + D_3 u^2}\right]. \tag{II.11}$$

$$B_m(p) = (2/L)/\left[p + \lambda + m^2\pi^2 D_1/L^2 - \frac{k'D_1}{k_{\mathrm{B}}T} - \lambda b D_3 k \int_0^\infty \frac{C(u)\,\mathrm{d}u}{p + D_3u^2 + m^2\pi^2 D_3/L^2}\right]. \tag{II.12}$$

To obtain $\widetilde{P}$ the inverse Laplace transform of $\widetilde{P}_i$ is required. However, the integrations over $\{z_i\}$ may be performed and this calculation shows that only odd values of m contribute to $\widetilde{\gamma}$.

The integrations over $\{z_i\}$ are trivial and are the same as in the one particle calculation. The integrals over $\{z_i'\}$ are of the form

$$LR_m = \int_0^L \cdots\!\int_0^L \left(\prod_i \mathrm{d}z_i'\right) \exp\left[\sum_i \sum_{j<i} \frac{-B}{|z_i' - z_j'|}\right] \times \sum_i (z_i' - L/2) \sum_i \cos(m\pi z_i'/L) \times \left\{\int_0^L \cdots\!\int_0^L \left(\prod_i \mathrm{d}z_i'\right) \exp\left[\sum_i \sum_{j<i} \frac{-B}{|z_i' - z_j'|}\right]\right\}^{-1}. \tag{II.13}$$

These integrals were evaluated by Monte Carlo methods on a Harris/7 computer. (A variable change makes the limits 0 to 1.) The time required for computation grows rapidly with the multiplicity of the integral (number of particles n') and with the mode index m ($m = 1, 3, 5, 7$). For the bare Coulomb potential employed here departure from the independent particle result ($B = 0$) occurs for even a few particles. Thus the calculation is very sensitive to the assumed form of the potential. The calculations shown here represent a strong interaction bound in that screening of the counterions is ignored and the vector separation of the particles $|\boldsymbol{r}_i' - \boldsymbol{r}_j'|$ is replaced by the axial distance $|z_i' - z_j'|$. This will be correct for particles separated by large distances but overestimates the interaction for closely spaced particles. The Monte Carlo calculations become very time consuming in the region where $R_1(n')$ goes through a maximum (vicinity $n' = 50$) (an analytical calculation proves that $\lim_{n'\to\infty} R_m(n') = 0$ as anticipated by physical insight). Uniform random sampling of the configuration space was employed. A Metropolis–Monte Carlo procedure gave no advantage [19]. About 10^6 samplings of the integrand were taken for each n' using a total of 100 hours CPU for the entire problem. Finally we require the inverse Laplace transform of $\widetilde{P}_i$ so that the time dependence of P may be found. If the p dependence in the integral term in eq. (II.12) is overlooked, the denominator of $B_m(p)$ is of the form $p + 1/\tau$ (τ a relaxation time, $1/\tau$ a relaxation rate) with

$$1/\tau \approx \lambda + m^2\pi^2 D_1/L^2 - k'D_1/k_{\mathrm{B}}T - \lambda b D_3 k \int_0^\infty \frac{C(u)\,\mathrm{d}u}{D_3u^2 + m^2\pi^2 D_3/L^2}\,. \tag{II.14}$$

For small p (long times) we use the approximate forms of eqs. (II.11) and (II.12) to form the required products $[B_{2n+1}^{-1}(p)]\,[B_0^{-1}(p)L]^{n'-1}$ and the combined result is as shown as eq. (3.17).

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