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Cooperative diffusion in weakly charged polyelectrolyte solutions

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We study the dynamics of concentration fluctuations of a weakly charged polyelectrolyte solution in the limit where they are controlled by hydrodynamic interactions. We find three relaxation modes: a plasmon mode corresponding to the fast relaxation of charge fluctuations; a diffusive mode involving mainly the motion of the small ions (salt and counterions) to restore the "Donnan equilibrium," and a slower cooperative diffusion mode corresponding to the breathing motion of the polyelectrolyte chains and ions. In the limit where the electrostatic effects are dominant, at zero wave vector, the cooperative diffusion constant has a nonmonotonic variation with the monomer concentration. Contrary to what happens in neutral polymer solutions, in the limit of low ionic strength, it decreases with the monomer concentration in agreement with recent experimental observations of Schosseler *et al.* on gels. The cooperative diffusion constant as a function of wave vector shows a minimum for a wave vector corresponding approximately to the peak in the structure factor.

Weakly charged polyelectrolyte solutions and gels exhibit remarkable macroscopic properties. For example, the swelling degree of polyelectrolyte networks can be particularly high and may be controlled by the ionic strength.¹⁻³ One can even induce interesting phase transitions in solutions and gels by adding an appropriate amount of salt or by modifying the charge of the polyelectrolytes through the pH or by ion complexation.⁴⁻⁷ In this context, recent results obtained by small angle neutron or x-ray scattering and by quasielastic light scattering are very important as these techniques probe the system structure and fluctuations at mesoscopic scales,⁸ the organization at such scales may be responsible for the original features of the macroscopic behavior.

Electrostatic interactions produce dramatic effects even for weakly charged chains.⁹ For instance, the compatibility of chemically different polymers dissolved in a good polar solvent is greatly enhanced when a small amount of electric charges is present on one type of chains.¹⁰ This is mainly due to the presence of the counterions. First, electroneutrality has to be respected on large scales so that the counterions cannot be macroscopically separated from the polyelectrolyte chains; second, the counterions are much more numerous than the polyelectrolyte chains and it is more difficult to confine them in a limited volume. Therefore the competition between entropic effects and the macroscopic electroneutrality constraint favors mixing of otherwise incompatible chains.

The case of the dissolution of a polymer in a poor (polar) solvent is rather similar; the dissolution is favored by the presence of some charges on the chains. However, although a macroscopic phase separation can be prevented, segregation can occur at mesoscopic scales inducing the formation of intermolecular aggregates or mesophases.^{11,12}

A particularly intriguing situation occurs near the θ condition, i.e., when the solvent is not a very good one for the

backbone monomers of the equivalent neutral chains. It has been shown recently that even though there may be no permanent mesoscopic segregation, the concentration fluctuation spectrum in charged systems is very different from that of neutral ones; some finite-wavelength monomer concentration fluctuations are greatly enhanced.^{11,12} The characteristic length scale of these fluctuations depends on the charge density and salt concentration and is of the order of the period of the mesophase that would eventually appear at a lower temperature.

The aim of this paper is to study the dynamics of monomer concentration fluctuations in order to give a more quantitative basis for the interpretation of recent quasielastic light scattering experiments.⁸⁻¹⁵ We also discuss the dynamical fluctuations of charge density and salt concentration. We treat, as independent variables, the three concentrations (polymer, counterions, and salt) and we do not consider only monomers interacting through an effective potential screened by the counterions and the salt; we thus implicitly take into account electrohydrodynamic couplings and counterion polarization effects.

Consider a semidilute solution of weakly charged polyelectrolytes with a polymerization index N and a fraction of charged monomers f . The average concentration of monomers in the solution is denoted by ϕ . The macroscopic electroneutrality implies that the overall charge density ρ vanishes. Thus in the presence of a dissociated salt with concentration n we have

$$\rho = e(f\phi + n - \varphi_i) = 0, \quad (1)$$

where φ_i denotes the counterion concentration (for simplicity, the counterions of the polyion and of the salt molecules are assumed to be identical and monovalent).

Scattering experiments probe the fluctuations of the local concentrations $\delta\phi(\mathbf{r}, t)$, $\delta n(\mathbf{r}, t)$, and $\delta\varphi_i(\mathbf{r}, t)$. These

fluctuations are coupled mainly because of the electrostatic interactions: Locally electroneutrality can be violated, but this creates an electric field and costs some energy. Here we analyze systems close to equilibrium and use the linear response theory to describe the restoring forces. These forces induce displacements of the molecules and energy dissipation because of the solvent viscosity η . Hydrodynamic interactions due to backflow effects are taken into account through the Oseen tensor, i.e., by treating monomers, counterions, and salt ions as particles moving in a continuous viscous medium.¹⁶ The relaxation of concentration fluctuations follows then a Langevin-like equation¹⁷

$$\frac{\partial}{\partial t} \mathbf{c}(\mathbf{k}, t) = -\Gamma(\mathbf{k}) \mathbf{c}(\mathbf{k}, t) + \mathbf{R}(\mathbf{k}, t), \quad (2)$$

where $\mathbf{R}(\mathbf{k}, t)$ denotes a Gaussian white noise and $\mathbf{c}(\mathbf{k}, t) = \{\delta\varphi(\mathbf{k}, t), \delta n(\mathbf{k}, t), \delta\varphi_i(\mathbf{k}, t)\}$ is the Fourier transform of the vector describing local concentration fluctuations. The relaxation matrix $\Gamma(\mathbf{k})$ is given by a Kubo relation¹⁷

$$\Gamma(\mathbf{k}) = k_B T \int d\mathbf{q} / (2\pi)^3 \mathbf{S}(\mathbf{k} + \mathbf{q}) \times \frac{k^2 - (\mathbf{k} \cdot \mathbf{q} / q)^2}{\eta q^2} \mathbf{S}^{-1}(\mathbf{k}), \quad (3)$$

where $\mathbf{S}(\mathbf{k})$ is the structure factor matrix at a wave vector \mathbf{k} ; its elements are the equilibrium correlation functions $S_{\alpha\beta}(\mathbf{k}) = \langle c_\alpha(\mathbf{k}) c_\beta(-\mathbf{k}) \rangle$ ($\alpha, \beta = 1, 2, 3$); the elements of the inverse matrix $\mathbf{S}^{-1}(\mathbf{k})$ are defined as the second derivatives of the free energy of the solution with respect to the appropriate concentrations.

As explored in Refs. 11 and 12 for a semidilute solution, the free energy change induced by concentration fluctuations can be approximated by the sum of three contributions. The first one comes from the monomer–monomer excluded volume interactions characterized by second and third virial coefficients v and w^2 , respectively,

$$\Delta F_1 / k_B T = \frac{1}{2} \sum_{\mathbf{k}} \delta\varphi(\mathbf{k}) \delta\varphi(-\mathbf{k}) \left(v + w^2 \varphi + \frac{k^2 a^2}{12\varphi} \right). \quad (4)$$

Here the last term describes standard concentration gradient contributions; a denotes the statistical element length.

The second contribution arises from the translational entropy of the counterions and salt ions

$$\Delta F_2 / k_B T = \frac{1}{2} \sum_{\mathbf{k}} \delta\varphi_i(\mathbf{k}) \delta\varphi_i(-\mathbf{k}) / \varphi_i + \frac{1}{2} \sum_{\mathbf{k}} \delta n(\mathbf{k}) \delta n(-\mathbf{k}) / n, \quad (5)$$

whereas the last contributions describes the electrostatic coupling energy

$$\Delta F_3 / k_B T = \frac{1}{2} \sum_{\mathbf{k}} \frac{4\pi l}{k^2} \rho(\mathbf{k}) \rho(-\mathbf{k}) \quad (6)$$

with $l = e^2 / 4\pi\epsilon k_B T$ being the Bjerrum length and $\rho(\mathbf{k})$ the Fourier transform of the local charge density. Within the

linear response approximation, Eqs. (3)–(6) describe completely the decay rate matrix $\Gamma(\mathbf{k})$.

Clearly for each wave vector \mathbf{k} there are three relaxation modes. Their characteristic decay rates are the eigenvalues of the matrix $\Gamma(\mathbf{k})$. In order to simplify the calculations, it is useful at this point to discuss the physics of the different possible relaxation modes and their characteristic time scales. For the long wavelength fluctuations discussed in the present note, the three eigenmodes have very different characteristic relaxation times and correspond to very distinct processes.

The strongest restoring forces are the electrostatic forces, therefore electroneutrality is quickly restored by a collective displacement of the most mobile species corresponding to a plasmon mode.¹⁸ As for usual simple electrolytes its characteristic frequency is

$$\nu_{pl}(k=0) \cong \frac{k_B T}{6\pi\eta b} \kappa^{-2}, \quad (7)$$

where κ is the inverse Debye–Hückel screening length of the small ions $\kappa^2 = 4\pi l(2n + f\varphi)$ and b denotes their size [a molecular cutoff in Eq. (3)]. In a first approximation, the chains do not participate in this relaxation mode.

After this fast relaxation step, the remaining restoring forces are of entropic origin. They tend to equilibrate the electrochemical potential of each species in the whole volume. In this sense these are diffusionlike processes. It is important to keep in mind that the diffusive motion of strands of polymer are much slower than that of small ions because of backflow effects. Therefore the second step involves essentially the counterions and salt mutual repartition, governed by a characteristic diffusion time

$$\tau_{\text{Donnan}}(k) = \frac{6\pi\eta b}{k_B T} \frac{1}{k^2}. \quad (8)$$

It corresponds to the establishment of Donnan equilibrium¹⁹ on spatial scales of the order of $1/k$. Note that this time is comparable to the plasmon mode relaxation time only when k/κ is of order 1.

On time scales larger than these two times, the relaxation of the monomer concentration is governed by the effective osmotic compressibility. During this relaxation, electroneutrality and Donnan equilibrium are preserved; the polymer moves with an appropriate amount of counterions and salt. The corresponding decay rate is approximately equal to $\Gamma_{11}(k)$. The corresponding diffusion coefficient is

$$D(k) = \Gamma_{11}(k) / k^2 = \frac{k_B T}{4\pi^2 \eta k^2} \int d\mathbf{q} h(k; \mathbf{q}) \frac{S(\mathbf{q})}{S(\mathbf{k})}, \quad (9)$$

where $h(k; \mathbf{q}) = q^2 [(q^2 + k^2/2kq) \log|k + q/k - q| - 1]$ and

$$S(k) = S_{11}(k) = \frac{k^2 + \kappa^2}{d\kappa^2 + d'k^2 + (k^2 + \kappa^2)k^2 a^2 / 12\varphi} \quad (10)$$

with $d = v + w^2\varphi$, and $d = d' + 4\pi l f^2 / \kappa^2$.

Note that in the absence of charges ($f = 0, n = 0$), Eqs.

(9) and (10) give the standard Kawasaki-Ferrell result for neutral concentrated solutions.¹⁷

The diffusion constant (9) can be calculated analytically but does not lead to a form easy to discuss. We show here the plot of $D(k)$ for some typical values of the molecular parameters on Figs. 1 and 2. The most characteristic feature is the presence of a minimum for relatively small salt contents. It obviously corresponds to the peak at q^* of the static structure factor $S_{11}(q)$. Fluctuations with wavelengths comparable to $2\pi/q^*$ are energetically favored, and therefore the restoring forces are weak and their relaxation is slow. At higher ionic strength, the osmotic compressibility of the system increases and the long wavelength fluctuations become more favorable as electrostatic interactions are screened out. Eventually the diffusion coefficient $D(k)$ is a linearly increasing function of k , as for polymer solutions of neutral Gaussian chains [$D(k) = k_B T k / 16\eta$].

A minimum in the diffusion coefficient has been observed for highly charged polyelectrolytes.¹⁶⁻²⁰ We are not aware of similar results for the situations considered here.

It is instructive, to discuss the long wavelength limit $D(k \rightarrow 0)$:

$$D(k \rightarrow 0) = \frac{k_B T}{6\pi\eta} \alpha^2 / \kappa (1 + \kappa^2 / \alpha^2) \times [d'/d + 2\kappa^2 / \alpha^2 + \kappa^4 / \alpha^4]^{-1/2}, \quad (11)$$

where $\alpha^4 = [d/(d-d')](q^{*2} + \kappa^2)^2$, and as explained in Ref. 7, $(q^{*2} + \kappa^2)^2 = (48\pi f^2 \varphi / a^2)$.

The interesting situation arises when the electrostatic effects dominate the excluded volume interactions, i.e., when $f^2 4\pi l / \kappa^2 \gg d'$. Then Eq. (11) reduces to

$$D(k \rightarrow 0) = \frac{k_B T}{6\pi\eta} \alpha^3 / \kappa^2 (1 + \kappa^2 / \alpha^2) (2 + \kappa^2 / \alpha^2)^{-1/2}, \quad (12)$$

where the length $1/\alpha = [a^2 / 48\pi f^2 \varphi]^{1/4}$ describes the screening of electrostatic interactions by the polyions. The variation of D with f , φ , and n is relatively complex, but in a

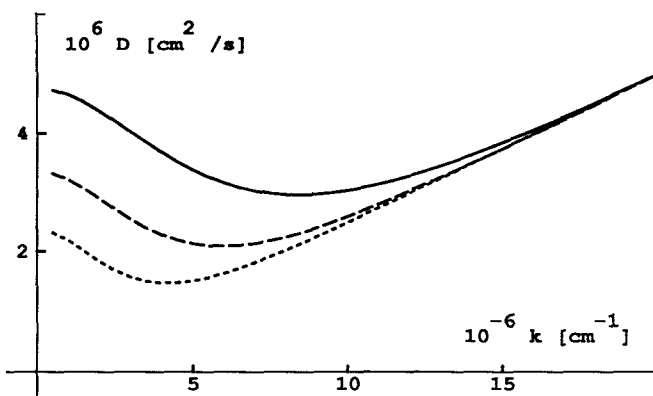


FIG. 1. Variation of the cooperative diffusion constant [Eq. (9)] as a function of the wave vector k for different values of the charge fraction in the absence of external salt: $f = 0.025$ (dashed line), $f = 0.05$ (broken line), and $f = 0.1$ (full line). The parameters used are $a = 1 = 7 \text{ \AA}$, $\eta = 10^{-2} \text{ P}$, $D' = 0$, $\varphi = 0.7 \text{ M}$.

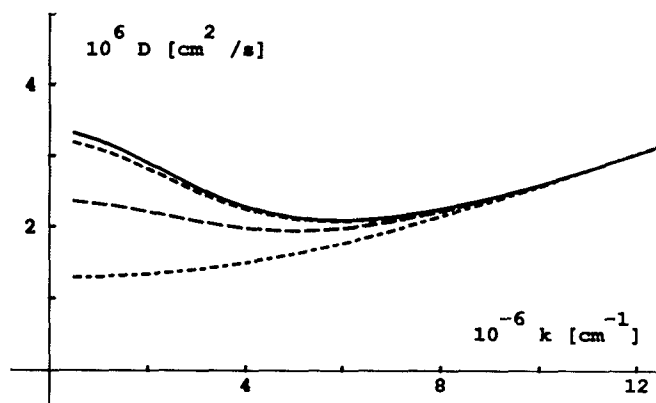


FIG. 2. Variation of the cooperative diffusion constant [Eq. (9)] as a function of the wave vector k for different values of the salt concentration when $f = 0.05$: $n = 0$ (full line), $n = 10^{-3} \text{ M}$ (dashed line), $n = 10^{-2} \text{ M}$ (broken line), $n = 510^{-2} \text{ M}$ (dashed-dot line). The same parameters as in Fig. 1 are used.

first approximation one can consider that $[1 + \kappa^2 / \alpha^2] / [2 + \kappa^2 / \alpha^2]^{1/2}$ is weakly varying and that $D(k \rightarrow 0)$ varies as

$$D(k \rightarrow 0) \sim \frac{f^{3/2} \varphi^{3/4}}{f\varphi + 2n}. \quad (13)$$

We note that as anticipated above the cooperative mode is slower than the Donnan mode, as long as $f^{1/2} \varphi^{-1/4} a^{-3/4} < 1$ (considering that $a \cong l \cong b$), or equivalently $f^{1/2} (a/\xi)^{-1/4} < 1$, where $\xi = a^{-2} \varphi^{-1}$ is the correlation length in the absence of excluded volume and charge effects.

A striking feature of expression (13) is the nonmonotonic dependence of the diffusion coefficient D on the monomer concentration φ , at fixed charge fraction f and salt concentration n . This might explain the experimentally observed unusual variation of the cooperative diffusion constant as a function of concentration for polyelectrolyte gels and solutions.^{8,13-15}

In order to have a more rigorous treatment, we have explicitly calculated the eigenvalues of the relaxation matrix $\Gamma(k)$ in two limits, for any wave vector k in the absence of salt and for long wavelengths ($k = 0$) in the presence of salt. In both cases, for small wave vectors k , the results confirm the more qualitative analysis: The three relaxation modes are the plasmon mode with a relaxation frequency $\nu_{pl}(k) \cong (k_B T / 6\pi\eta b) (\kappa^2 + k^2)$, the Donnan diffusion given by Eq. (8) and the cooperative diffusion which is exactly given by Eq. (11). However, in the very vicinity of the mesophase separation transition, or for large wave vectors, the time scales of the three modes are not well separated and the qualitative analysis breaks down. For example, the complete calculation shows that the diffusion constant at zero wave vector does not diverge on the spinodal line of the mesophase transition as Eq. (11) would suggest, but rather reaches a finite value of order $k_B T / 6\pi\eta b$. In the presence of salt, one should be aware that the time scales of the three relaxation modes are not well separated for high k value

($k > \kappa$). Therefore Eq. (9) may not describe precisely the polymer concentration fluctuation dynamics and the plots of Figs. 1 and 2 should be considered only as an indication of trends.

In conclusion, we have determined the relaxation modes of a weakly charged polyelectrolyte solution. Three modes are expected, a plasmon mode, a fast diffusive Donnan mode, and a slow cooperative diffusion mode. At zero wave vector, when the electrostatics dominates over the excluded volume effects, the cooperative diffusion constant should exhibit a nonmonotonic variation with the monomer concentration φ . In particular, it decreases with φ at low ionic strength in agreement with recent quasielastic light scattering experiments.¹⁵ As a function of the wave vector k , $D(k)$ is expected to show a minimum for a value of k of the order of the value q^* of the peak in the structure factor; this could possibly be observed in neutron spin echo experiments. Finally, let us recall that we expect these results to be relevant only for weakly charged polyelectrolytes ($f \ll 1$) in relatively marginal solvents ($|\nu| < 1$) so that the polymer chains remain locally Gaussian.

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- ¹P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1953).
- ²T. Tanaka, *Sci. Am.* **244**, 124 (1981).
- ³T. Tanaka, *Phys. A* **140**, 261 (1986), and references therein.
- ⁴T. Tanaka, S. T. Sun, Y. Hirokawa, S. Katayama, J. Kucera, Y. Hirose, and T. Amiya, *Nature (London)* **235**, 796 (1987).
- ⁵I. Richo and T. Tanaka, *Macromolecules* **18**, 83 (1986).
- ⁶E. Raphael and J. F. Joanny, *Europhys. Lett.* **13**, 623 (1990).
- ⁷L. Leibler and E. Pezron, in *Space Time Organization in Macromolecular Fluids*, edited by F. Tanaka, M. Doi, and T. Ohta (Springer, Berlin, 1989).
- ⁸F. Schosseler, F. Ilmain, and S. J. Candau, *Macromolecules* **24**, 225 (1991).
- ⁹F. Schosseler, P. Mallo, C. Cretenot, and S. J. Candau, *J. Dispersion Sci. Technol.* **8**, 321 (1986).
- ¹⁰M. B. Perreau, I. Iliopoulos, and R. Audebert, *Polymer* **30**, 2112 (1989).
- ¹¹V. Borue and I. Erukhimovich, *Macromolecules* **21**, 3240 (1988).
- ¹²J. F. Joanny and L. Leibler, *J. Phys. (Paris)* **51**, 547 (1990).
- ¹³F. Ilmain and S. J. Candau, *Makromol. Chem. Macromol. Symp.* **30**, 119 (1989).
- ¹⁴F. Ilmain and S. J. Candau, *Prog. Coll. Polym. Sci.* **79**, 172 (1989).
- ¹⁵Refs. 8, 13, and 14 concern weakly charged gels, but similar results have been obtained recently for solutions by F. Schosseler, A. Moussaid, J. P. Munch, S. J. Candau (unpublished). We are indebted to F. Schosseler and S. J. Candau for communicating and discussing these results prior to publication.
- ¹⁶J. Hayter, G. Jannink, F. Brochard-Wyart, and P. G. de Gennes, *J. Phys. Lett. (France)* **41**, L451 (1980).
- ¹⁷M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University, Oxford, 1986), Chap. 5.
- ¹⁸B. J. Berne and R. Pecora, in *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 9.
- ¹⁹F. Donnan, *Z. Phys. Chem. A* **168**, 369 (1934); F. Donnan and E. Guggenheim, *ibid.* **122**, 346 (1932).
- ²⁰M. Drifford and J. P. Dalbiez, *J. Phys. Lett. (France)* **46**, L311 (1980).