Eur. Phys. J. B **3**, 277–279 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Rapid Note

Cooperative diffusion in weakly charged polyelectrolyte gels

Y. Shiwa[a]

Division of Natural Sciences, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received: 30 January 1998 / Revised: 4 May 1998 / Accepted: 6 May 1998

Abstract. A general expression for the cooperative diffusion constant of weakly charged gels is derived as a function of the thermodynamic parameters such as polyelectrolyte concentration, salt concentration, ionic strength, and the degree of crosslinking. In the low concentration range it decreases with the monomer concentration.

PACS. 82.70.Gg Gels and sols – 36.20.-r Macromolecules and polymer molecules – 05.60.+w Transport processes: theory

For weakly charged chains, the ionizable groups are well separated on the chain and, contrary to the highly charged case (with counter-ion condensation), a small variation of the ionization degree modifies strongly the properties of the system [1]. At the same time, the introduction of crosslinking results in a large effect in the diverse physical properties [2]. As a consequence, the additional effects induced by the presence of crosslinks in the gels should be taken into account in the study of weakly charged polyelectrolyte gels.

Quite recently this difficult problem of weakly charged polymer gels has received a renewed theoretical attention [3,4]. Since the static aspects of the scattering experiment are reasonably consistent with the theoretical predictions, we can now attempt to understand the dynamical properties of charged gels. In this paper, the cooperative diffusion constant is calculated.

We assume that the light scattering from gels can be written as the sum of contributions from (thermal) concentration fluctuations of the network and contributions from frozen-in (static) inhomogeneities. Only the former is assumed to be relevant in treating the dynamics, and we define the cooperative diffusion coefficient D_c with the dynamic component of the normalized intermediate scattering function $f_N(\mathbf{q},t)$ by

$$\lim_{q\to 0} f_N(\mathbf{q},t) = \exp(-q^2 D_c t). \tag{1}$$

Thus the effect of crosslink fluctuations on the relaxation of thermal concentration fluctuations is not taken into consideration, while the statistical information about elasticity of the deformed networks due to the crosslink is contained in our result.

The cooperative diffusion coefficient can be written as [5]

$$D_c = s_D M/\rho_0. \tag{2}$$

Here s_D is the sedimentation coefficient per monomer unit of the network, and M is the longitudinal osmotic modulus given by

$$M = \rho_0 \frac{\partial \Pi}{\partial \rho_0}, \tag{3}$$

where Π is the osmotic pressure and ρ_0 is the monomer number density. The sedimentation coefficient is related to the density correlation function $S(\mathbf{r})$ through [6,7]

$$s_D = \frac{1}{\zeta_0}\Big[1 + \frac{\zeta_0}{3\eta_s} Tr \int d\mathbf{r} T(\mathbf{r}) S(\mathbf{r})\Big], \tag{4}$$

where ζ_0 is the (bare) segment friction coefficient between the polymer network and the solvent, η_s being the solvent viscosity. The Oseen tensor $\eta_s^{-1} T(\mathbf{r})$ represents hydrodynamic interations between monomers and is defined by

$$T(\mathbf{r}) = \int_{\mathbf{q}} (I - \mathbf{q}\mathbf{q}/q^2) q^{-2} \exp(-i\mathbf{q}\cdot\mathbf{r}),$$

with $\int_{\mathbf{q}} = (2\pi)^{-3} \int d^3q$, I being the unit tensor. In the formula (4) the hydrodynamic screening effect is simply ignored as a first approximation. It follows that

$$s_D = \frac{1}{\zeta_0}\Big[1 + \frac{\zeta_0}{3\pi^2 \eta_s} \int_0^\infty dk S_F(k)\Big], \tag{5}$$

where $S_F(k)$ is the Fourier transform of $S(\mathbf{r})$. At this juncture we argue that as long as we consider the semidilute

---

[a] e-mail: `shiway@hiei.kit.ac.jp`

region (in which polymer volume fraction $\phi \ll 1$), we may neglect the first term in the square brackets in equation (5) as compared with the second term. This is because, as we can see shortly below, it turns out that the second term behaves as ϕ^{-2} for $\phi \ll 1$ in accord with the scaling theory [5].

The structure factor $S_F(q)$ of the thermal fluctuations of concentration for the weakly charged gels in a Θ or poor solvent was calculated in reference [4] at the level of the Debye-Hückel theory[1]. It is given by the expression

$$S_F(q) = \left(\frac{r_0}{a}\right)^2 \left(x^2 + t_g + \frac{1}{x^2+s}\right)^{-1}. \tag{6}$$

Here a is the length of the monomer unit, and r_0 is a characteristic length scale in a (saltless) polyelectrolyte solution and is given by $(a/r_0)^2 = f\sqrt{12\phi\hat{l}_B}$; f is the fraction of charged monomers (*i.e.*, the degree of ionization), and $\hat{l}_B$ is the reduced Bjerrum length given by $\hat{l}_B = e^2/(a\epsilon_s k_B T)$ where e is the elementary charge, ϵ_s the dielectric constant of the solvent, k_BT being the thermal energy. The reduced wavevector x is defined by $x = r_0 q$, and s is a reduced ionic strength defined by $s = r_0^2\kappa^2$ where κ^{-1} is the usual Debye-Hückel screening length: $\kappa^2 = a^{-2}\hat{l}_B(f\phi + 2\phi_s)$, ϕ_s being the salt volume fraction. Similarly, t_g is the reduced temperature variable of the gel given by

$$t_g = 6\left(\frac{r_0}{a}\right)^2 \left[2\phi(1-2\chi+\phi) + \frac{1}{N}\left(B + \left(\frac{\phi_0}{\phi}\right)^{2/3}\right)\right]. \tag{7}$$

The first term in the square brackets on the rhs of equation (7) is the usual virial terms of polymer solutions (and thus χ being the Flory interaction parameter), and the second term represents the elastic contributions of the deformed gels; N is the average number of chain monomers between neighboring crosslinks, ϕ_0 the polymer volume fraction at the relaxed state, B being a positive constant.

In passing we may remark that in charged gels two types of phase separations are possible as a result of the interplay between elastic and electrostatic effects. On the one hand the scattering intensity $S_F(q=0)$ diverges on the boundary where $1 + st_g = 0$ (at which the longitudinal modulus vanishes). The gel then becomes unstable against a macroscopic separation (bulk spinodal phase separation). On the other hand, when the condition $t_g = s - 2$ is satisfied, the divergence takes place at a finite $q = q^*$. This corresponds to a microphase separation with a domain periodicity $2\pi/q^*$, q^* being given by $q^* = \sqrt{r_0^{-2} - \kappa^2}$.

Combining equations (2, 3, 5, 6) with the relation $\partial\Pi/\partial\rho_0 = k_BTS_F^{-1}(0)$, we then arrive at the explicit expression for the cooperative diffusion constant. Defining the hydrodynamic radius R_H by the relationship $D_c = k_BT/(6\pi\eta_s R_H)$, we find

$$R_H^{-1} = r_0^{-1}\frac{\alpha(s,t_g)\beta(s,t_g)}{s[\alpha(s,t_g)+\beta(s,t_g)+t_g]^{1/2}} \tag{8}$$

with $\alpha(x,y) = \sqrt{1+xy}$, $\beta(x,y) = x + \sqrt{1+xy}$. This is the main result of this paper. As a function of the variables t_g and s, it has the same functional form as the cooperative diffusion constant of polyelectrolyte solutions. The only difference is that for gels the temperature variable t_g contains the effect of crosslinking. Naturally, the $N \to \infty$ limit of the above result (8) reproduces the known expression for the polyelectrolyte solutions [8].

Since the result (8) is a function of a rather large number of parameters, an extensive analysis of the parameter space will be discussed elsewhere. Here we list several noticeable features of our result: (1) General features of D_c for gels and solutions are very close as already found in references [9,10]. It is worth adding that the theoretical prediction of reference [8] for solutions was checked quantitatively by Moussaid *et al.* [11]. The measured values are systematically lower than the theoretical ones by a factor of about 5. Beside this numerical factor these authors reported the qualitative disagreement between experimental results and theory. However, in view of the other experimental results [9,10], it seems we need further experiments to resolve the latter discrepancy. (2) The variation of D_c as a function of temperature and the influence of added salt are consistent with the available experimental data [10,12,13]. (3) We predict that D_c shows a critical slowing-down as in critical fluids [14] near the macrophase separation transition, while in the vicinity of the microphase separation D_c should exhibit a critical speeding-up. (This difference can be understood as follows. That $D_c \to 0$ as one approaches the macrophase separation point is the usual consequence of the broken symmetry due to the long-range order with $q = 0$. On the other hand, upon approaching the microphase separation transition, the fluctuations with $q = q^* \neq 0$ dominate and soften. Hence the time scale of diffusion modes, *i.e.*, $1/D_cq^2, q \to 0$, becomes well separated from that of those critical modes so that one obtains $D_cq^2 \gg 1$). (4) The variation of D_c with the crosslinking degree is in accord with the recent experimental observation [15]. (5) Unusual nonmonotonic dependence of D_c on the monomer concentration in the presence of electrostatic forces.

As an example, the last point is illustrated in Figure 1; in particular, a strikingly similar feature to the experimentally observed variation [12,16] of D_c with the degree of ionization is to be noticed in Figure 1a. The lower concentration of free counterions implies the strong repulsive electrostatic forces. Since the friction coefficient increases with polymer concentration for swollen chains, the diffusion coefficient decreases when the polymer concentration increases (Fig. 1b). The increase of D_c upon increasing f, which is in agreement with the experimental trends [16],

---

[1] Use of this rough approximation might be questioned on the grounds that a supposedly more rigorous expression of S_F is presented in reference [3]. However, as described in detail in reference [4], there is some disagreement between these theories about the qualitative features of the structure factor. Thus in this paper we shall use equation (6) since it enables one to carry through the calculation analytically giving a qualitative behavior of D_c in agreement with experiment.

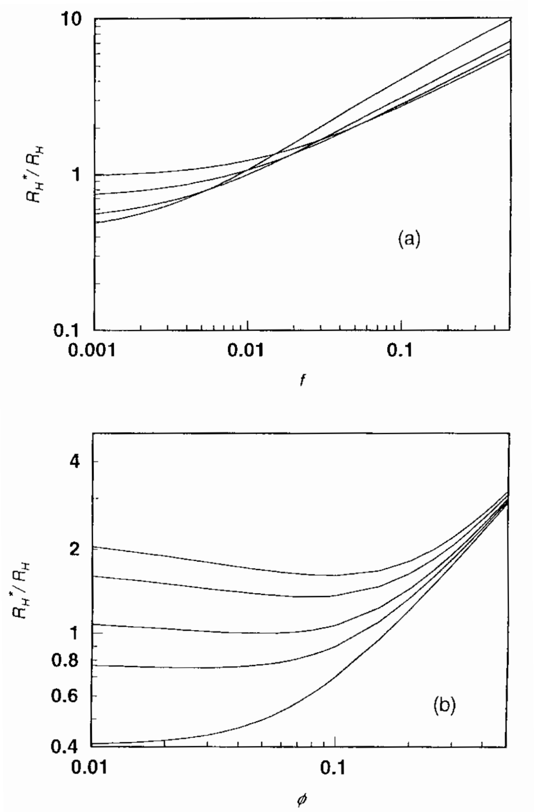

Fig. 1. (a) Log-log plots of the normalized inverse hydrodynamic radius $R_H^{-1} \equiv 6\pi\eta_s D_c/k_BT$ *versus* the ionization degree f for different polymer volume fractions: $\phi = 0.01$, 0.05, 0.1, 0.15 from the right-hand top to bottom. R_H^* is the value of R_H for $f = 0.01$ and $\phi = 0.05$. (b) Log-log plots of the normalized R_H^{-1} *versus* polymer volume fraction ϕ for different ionization degrees: $f = 0$, 0.005, 0.01, 0.02, 0.03 from the lowest to the uppermost. We have set $\phi = \phi_0$ (corresponding to the reactor batch gels) and used $a = 8.12$ Å, $\hat{l}_B = 10.8$, representative values of the experiment of reference [17]. The other parameters used are $N = 100$, $B = 0$, $\chi = 0.5$ and $\phi_s = 0$.

is due to the increase of the osmotic pressure associated with the free counterions. For larger values of ϕ, the relative increase of D_c *versus* f is reduced upon increasing ϕ. This is due to the increase of ionic strength resulting in a more efficient screening, whereupon one observes a behavior tending towards that of a neutral gel.

Finally I would like to thank M. Shibayama for informative conversations.

References

1. For a recent review, see J.L. Barrat, J.F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).
2. See, for instance, J. Bastide, S.J. Candau, In *Physical Properties of Polymeric Gels*, edited by J.P. Cohen-Addad (Wiley, Chichester, 1996) p. 143.
3. Y. Rabin, S. Panyukov, Macromol. **30**, 301 (1997).
4. Y. Shiwa, Euro. Phys. J. B **1**, 345 (1998).
5. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
6. Y. Oono, P.R. Baldwin, Phys. Rev. A **33**, 3391 (1986).
7. Y. Oono, AIP Conf. Proc. **137**, 187 (1985).
8. A.A. Ajdari, L. Leibler, J.F. Joanny, J. Chem. Phys. **95**, 4580 (1991).
9. A. Moussaid, J.P. Munch, F. Schosseler, S.J. Candau, J. Phys. II France **1**, 637 (1991).
10. F. Schosseler, A. Moussaid, J.P. Munch, S.J. Candau, J. Phys. II France **1**, 1197 (1991).
11. A. Moussaid, F. Schosseler, J.P. Munch, S.J. Candau, ACS Symp. Series **548**, 287 (1994).
12. F. Schosseler, F. Ilmain, S.J. Candau, Macromol. **24**, 225 (1991).
13. M. Shibayama, Y. Fujikawa, S. Nomura, Macromol. **29**, 6535 (1996).
14. T. Tanaka, Phys. Rev. **17**, 763 (1978); S. Candau, J.P. Munch, G. Hild, J. Phys. France **41**, 1031 (1980).
15. M. Shibayama, T. Norisuye, S. Nomura, Macromol. **29**, 8746 (1996).
16. F. Ilmain, S.J. Candau, Makromol. Chem., Macromol. Symp. **30**, 119 (1989).
17. M. Shibayama, T. Tanaka, C.C. Han, J. Chem. Phys. **97**, 6842 (1992).