Electrolyte and polyelectrolyte solutions: limitations of scaling laws, osmotic compressibility and thermoelectric power

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The role of counterions in polyelectrolyte solutions is considered. It is demonstrated that the naive application of scaling laws may lead to incorrect results for such physical quantities as osmotic compressibility, neutron scattering, and thermoelectric power.

INTRODUCTION

Scaling concepts have led to an increased understanding of the physical properties of polymer solutions[1]. In this approach, measured quantities such as osmotic pressure, neutron scattering structure factor, dynamic structure factor, intrinsic viscosity, etc., are expressed as asymptotic power laws in a few parameters, such as the degree of polymerization (N), the concentration of monomeric units (c), and the temperature relative to the Θ temperature

$$\tau = (T - \Theta)/T$$

Small angle neutron scattering, X-ray scattering, and light scattering have provided detailed evidence bearing on the validity of scaling laws[2–4]. However, the situation is less clear for polyelectrolytes (charged polymer chains). In very dilute solution, and in the absence of salt, it is generally agreed that polyelectrolytes are extended by the Coulomb repulsions to form a stiff configuration with a radius that scales as the degree of polymerization (N)[5,6]. The addition of salt provides Debye screening of the Coulomb interaction, so that the chains behave as neutral polymers with excluded volume[7]. At higher concentrations, in the semidilute regime where the chains overlap (but the volume fraction of the sample occupied by the polymer remains small), the situation is more complex. In the presence of salt, the system still behaves like a neutral polymer in a good solvent, and the conformational properties may be described by scaling laws[8–10]. In the absence of salt, theories have been proposed by de Gennes *et al.*[11] and Odijk[12]. Both theories distinguish two concentration regimes:

(1) low densities, where the chains are extended and exhibit both orientational and translational order reminiscent of the colloidal crystals[13];

(2) high densities, where the solution is isotropic and scaling laws are applicable.

The delineation of these regimes and the properties of the solution depend on one characteristic length in the de Gennes model[11] and on two lengths in the Odijk model[12]. There are several differences between neutral and charged polymers which explain why polyelectrolytes are less understood than neutral polymer solutions:

(i) the long-range Coulomb interaction is nonlocal, and it is not clear that a scaling analysis is appropriate; this could lead to a Wigner crystal[13] and nematic-like liquid crystalline order;

(ii) polyelectrolyte solutions are globally neutral and thus must be treated as, at least, three component systems: polymer, solvent and counterions;

(iii) in scattering experiments, the signal is much reduced (relative to neutral polymer solutions) by the lower osmotic compressibilities generated by the large Coulomb interactions.

The present paper emphasizes the role of the counterions and demonstrates that some physical properties, e.g. thermoelectric power and osmotic compressibility, are not properly described by simple scaling laws. These effects will be considered in simple electrolytic solutions, and these ideas will be extended to low ionic strength polyelectrolyte solutions.

SIMPLE ELECTROLYTE SOLUTIONS

Some physical properties of a dilute electrolyte solution of positive ions (concentration c_1 and charge $z_1 e$) and negative ions (concentration c_2 and charge $z_2 e$) dissolved in a solvent of dielectric constant ϵ will be considered. In a neutral solution, it is useful to define a total concentration of charge of one sign, c, with $c = z_1 c_1 = |z_2| c_2$.

The free energy of an electrolytic solution[14,15], F, can be expressed conveniently as a sum of three terms,

$$F = F_0 + F_1 + F_2 \qquad (1)$$

where F_0 is the translational free energy associated with the ions (entropy of mixing),

$$F_0/T \cong \sum_{i=1,2} c_i \ln c_i \qquad (2)$$

where throughout the paper units will be used in which the Boltzmann constant (k_B) is unity. The term F_1 represents the mean field interaction energy between the charges, which are assumed to be uniformly distributed. If the electrostatic

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forces between two charges were short range and could be described by a second virial coefficient v, the mean field free energy density would be

$$F_1/T = \frac{1}{2}v(z_1c_1)^2 + \frac{1}{2}v(z_2c_2)^2 + vz_1z_2c_1c_2$$

$$= \frac{1}{2}v(z_1c_1 + z_2c_2)^2 \tag{3}$$

While the bare Coulomb interaction is indeed long range, the Debye–Hückel screening[14] by the ions themselves leads to an effective screened Coulomb energy between two unit charges

$$V(r)/T = (\ell/r)e^{-\kappa r} \tag{4}$$

where ℓ is the Bjerrum length

$$\ell = e^2/\epsilon T \tag{5}$$

and κ^{-1} is the Debye–Hückel screening length

$$\kappa^2 = 4\pi\ell(z_1^2c_1 + z_2^2c_2) \tag{6}$$

For $\kappa^{-1} \gg \ell$, which is the regime of interest for dilute solutions, the second virial coefficient, v, derived from the Yukawa potential is

$$v \cong 4\pi\ell\kappa^{-2} \tag{7}$$

Combining relations (7) and (3), the mean field energy can be obtained:

$$F_1/\mathrm{T} = (2\pi\ell\kappa^{-2})(z_1c_1 + z_2c_2)^2 \tag{8}$$

For a neutral solution ($z_1c_1 + z_2c_2 = 0$), this term vanishes and is generally dropped in the electrolyte literature. However, in the case of osmotic compressibility, which is related to the second derivatives of the free energy density with respect to the concentrations, this term contributes. As the osmotic compressibility is the effective coupling constant in scattering experiments (neutron, X-ray or light) F_1 must be retained.

The final term is the free energy F_2, which represents the corrections to the previous mean field assumption of uniform charge density. This energy arises from the polarization of its surrounding by a given charge. This polarization energy u_i, which is the change in self-energy caused by the medium is[14]

$$u_i = z_i \lim_{r\to 0}[V(r) - z_i(\ell/r)T] = -z_i^2\kappa\ell T \tag{9}$$

The total polarization energy per unit volume is then

$$u = \frac{1}{2}\sum_i c_iu_i = -\frac{1}{8\pi}\kappa^3T \tag{10}$$

where the factor one-half is to avoid double counting. Using the thermodynamic relation

$$u = -T^2\frac{\partial(F_2/T)}{\partial T}$$

$$F_2/T = -(1/12\pi)\kappa^3 \tag{11}$$

which is the standard result[14]. The total osmotic pressure π is then

$$\pi/T = \sum_i c_i\frac{\partial F}{\partial c_i} - F = \sum_i c_i - (\kappa^3/24\pi)$$

$$= c(z_1^{-1} + |z_2|^{-1}) - \kappa^3/24\pi \tag{12}$$

and is independent of F_1. The total osmotic compressibility χ_0 is given by

$$\chi_0^{-1} = \sum_{i,j} c_ic_j\frac{\partial^2F}{\partial c_i\partial c_j}$$

$$= Tc(z_1^{-1} + |z_2|^{-1}) - (T\kappa^3/16\pi) \tag{13}$$

The compressibility is the response to a uniform pressure, so that local charge neutrality is respected and the result (13) is again independent of the mean field contribution to the free energy F_1.

Another quantity that may be of interest is the thermoelectric power which arises when a temperature difference δT is imposed across a conducting volume. In a dilute solution the heat is conducted by the solvent and leads to a uniform temperature gradient. Ions are attracted to the low temperature side, but the resulting concentration gradient is balanced by the osmotic pressure. If both types of ions have equal and opposite charges ($z_1 + z_2 = 0$), the concentration profiles are identical and local neutrality is preserved. On the other hand,for a less symmetrical situation ($z_1 + z_2 \neq 0$), the osmotic forces are different, leading to a nonlocal neutrality. This charge separation generates an opposing macroscopic electric field, which is the thermoelectric effect.

The thermoelectric power S is defined by $S = (\delta\phi/\delta T)$ where $\delta\phi$ is the potential difference appearing across the sample in response to the temperature difference δT. The equilibrium of the solution is maintained by requiring that the chemical potential for the ith species including the macroscopic potential $\phi(x)$ remains spatially constant,

$$\mu_i + z_ie\phi(x) = \text{constant} \tag{14}$$

where

$$\mu_i = \frac{\partial F}{\partial c_i}$$

Differentiating relation (14) yields a set of linear equations for the potential difference $\delta\phi$ and the concentration contrasts δc_i in terms of the temperature difference δT

$$ez_i\delta\phi + \frac{\partial^2F}{\partial c_i\partial T}\delta T + \sum_j \chi_{ij}^{-1}\delta c_j = 0 \tag{15}$$

where

$$\chi_{ij}^{-1} = \frac{\partial^2F}{\partial c_i\partial c_j} \tag{16}$$

Solving the set (15) with charge neutrality

$$\sum_i z_i \delta c_i = 0$$

yields

$$eS = \frac{\frac{\partial \mu_1}{\partial T}(z_2\chi_{21}^{-1} - z_1\chi_{11}^{-1}) - \frac{\partial \mu_2}{\partial T}(z_2\chi_{11}^{-1} - z_1\chi_{12}^{-1})}{z_1^2\chi_{22}^{-1} + z_2^2\chi_{11}^{-1} - 2z_1z_2\chi_{12}^{-1}} \qquad (17)$$

The structure of equation (17) clearly demonstrates that, once more, the mean field terms F_1 do not contribute to the thermopower:

(1) they do not contribute to the chemical potentials because only first derivatives with respect to the concentrations are involved;

(2) in the susceptibility terms, there is a detailed cancellation.

The physical reason is that the temperature gradient is 'democratic' and treats all ions similarly. This will break down subsequently when scattering experiments are considered. Evaluating S, in terms of the free energy given by relations (1), (2), (11), gives

$$eS = \frac{-\ln(|z_2|/z_1) + (\pi\ell^2 c/\kappa)(z_2^2\ln z_1 - z_1^2\ln|z_2|) + (\kappa\ell/4)(z_2^2 - z_1^2)}{(z_2 - z_1) - \pi z_1 z_2 (z_1 - z_2)^2 (c\ell^2/\kappa)}$$

which in the low density limit reduces to

$$eS = -\ln(|z_2|/z_1)(z_1 + |z_2|)^{-1} \qquad (19)$$

If the thermopower can be measured in very dilute solutions, this could prove to be a good method to determine the charge on colloidal particles, such as the polystyrene spheres forming colloidal crystals[13]. Alexander and Pincus[16] have proposed for such colloidal particles that there is a counterion adsorption renormalizing the charge per particle. The resulting effective charge Ze would lead to a thermopower

$$eS \simeq (\ln Z)/Z \qquad (20)$$

Scattering of photons, X-rays or neutrons

The two types of ions are considered to have, in general, different scattering amplitudes (α_i; $i = 1,2$). Introducing the susceptibility matrix

$$\chi_{ij} = (\chi^{-1})_{ij}^{-1} \qquad (21)$$

the forward scattering intensity $I(0)$ is

$$I(0) = \sum_{i,j} \alpha_i \chi_{ij} \alpha_j \qquad (22)$$

To simplify the resulting expressions, two assumptions are made:

(i) there is a large contrast in scattering amplitude between the two species such as would occur with X-ray scattering from heavy metal salt solutions; in particular, $\alpha_2 = 0$;

(ii) The polarization term in the free energy, which is proportional to $c^{3/2}$ and is small in dilute solutions, is neglected.

The matrix χ^{-1} is then

$$\chi_{ij}^{-1} = c_i^{-1}\delta_{ij} + (4\pi\ell/\kappa^2)z_i z_j \qquad (23)$$

which may be easily inverted to give the compressibility matrix

$$\chi_{ij} = [(c_1c_2)^{-1} + (4\pi\ell/\kappa^2)(z_2^2 c_1^{-1} + z_2^2 c_2^{-1})]^{-1}$$
$$\{\delta_{ij}[c_i^{-1} + (8\pi\ell/\kappa^2)z_i^2] - (4\pi\ell/\kappa^2)z_i z_j\}$$

The resulting scattered intensity is then

$$I(0) = (\alpha^2/2)(c/z_1)(z_1 - 2z_2)(z_1 - z_2)^{-1} \qquad (25)$$

The contribution of the mean field terms is not small, but is comparable to the perfect gas result ($I = \alpha^2 c/z_1$).

In summary, the mean field terms have been included in the free energy of an electrolyte solution, and it has been shown that they do not contribute to the global properties of the solution, but are important for properties involving only one constituent. In the following section, these ideas will be applied to polyelectrolyte solutions.

POLYELECTROLYTE SOLUTIONS

For a polyelectrolyte solution, each chain has N monomeric units, each of which carries a charge ($-e$). The concentration of monomeric units is c. There is a concentration c' of small monovalent ($+e$) neutralizing counterions. The coupling constant for this problem is ℓ/a, where ℓ is the Bjerrum length (equation (5)), and a is the characteristic dimension of the statistical unit. The effective ratio ℓ/a is constrained to be less than approximately one; if the bare ratio exceeds unity, counterions condense on the chain[17] to renormalize the effective charge in order to pin $\ell \approx a$. Following de Gennes *et al.*[11], it is assumed that at sufficiently high concentration there is an isotropic phase. Restricting our attention to this regime, two characteristic lengths for the polymer solution are introduced, after Odijk[12]: the chains overlap and form a transient network of mesh size ξ. As for neutral polymer chains[1,2], a blob analysis may be used such that on a distance scale exceeding ξ (the blob size), the chains are Gaussian. Within a blob, there are two types of behaviour that depend on on the concentration dependent electric persistence length b[12]. For $\xi > r > b$, the chains exhibit excluded volume behaviour. For $r < b$, the system behaves like rigid rods with a pair correlation function $g(r)$ given by

$$g(r) = c^{-1}\langle c(0)c(r)\rangle = (ar^2)^{-1} \qquad (26)$$

For $\xi > r > b$, the typical excluded volume behaviour is

$$g(r) = b^{-2/3}ar^{4/3} \qquad (27)$$

and for $r > \xi$, $g(r) \to c$. This yields a relation between b and ξ,

$$\xi = b^{-1/2}(ca)^{-3/4} \qquad (28)$$

Free energy of a polyelectrolyte solution

The first important difference between polyelectrolytes and simple electrolytes is that the screening is only provided by the counterions; the polyelectrolyte chains are large objects that cannot be polarized by a single counterion. Thus, the counterions experience a uniform negative background arising from the polymers. A monomeric unit also experiences a uniform negative background arising from other polymer chains, but a local negative field determined by $g(r)$, and counterion effects determined by the Debye–Hückel screening length κ^{-1}

$$\kappa^2 = 4\pi \ell c' \tag{29}$$

As with simple electrolytes, the free energy is expressed as a sum of three terms, F_0, arising from the translational entropy,

$$F_0/T = (c/N)\ln(c/N) + c'\ln c' \cong c'\ln c' \tag{30}$$

the mean field term analogous to relation (8) is

$$F_1/T = (2\pi\ell/\kappa^2)(c - c')^2 \tag{31}$$

The polarization contribution to the free energy (F_2) associated with the monomers has two principal terms: (1) the interaction between monomers and the polarization cloud of counterions similar to equation (11), which yields

$$F_2^{(a)}T^{-1} = -(2/3)c\kappa\ell \tag{32}$$

(2) the interactions between monomers within a screening radius on a given chain[8,10]

$$F_2^{(b)}/T \cong -c(\ell/a)\ln\kappa a \tag{33}$$

For $\kappa a \ll 1$, the energy is dominated by $F_2^{(b)}$, which yields a total free energy density

$$F/T \simeq c'\ln c' + (2\pi\ell/\kappa^2)(c - c')^2 - c(\ell/a)\ln\kappa a \tag{34}$$

which is valid for weak coupling $\ell \ll a$. The first terms neglected[8,11] in equation (34) are of order $c^{3/2}$. The osmotic pressure of the solution derived from F is then given by

$$\pi = \lim_{c' \to c}\left[c\frac{\partial F}{\partial c} + c'\frac{\partial F}{\partial c'} - F\right] \cong T(1 - \ell/2\mathrm{a}) \tag{35}$$

which is in substantial agreement with de Gennes *et al.*[11].

For polyelectrolytes, a measurement of the thermoelectric power may provide a useful tool to assess the validity of scaling laws. Using relations (17) and (34),

$$eS \cong -(\ell/2a)[3 + \ln(ca^3)]\,[1 - (\ell/2a)]^{-1} \tag{36}$$

This expression is valid for weak coupling ($\ell/a \ll 1$), but should give the correct order of magnitude for strong coupling ($\ell/a = 1$). The first scaling corrections to equation (36), which derive from terms that vary as $c^{3/2}$, in the free energy, which contributes terms of under $c^{1/2}$.

Neutron scattering

Neutron scattering experiments with polyelectrolytes are more difficult than for neutral polymer solutions, because of the lower compressibility of the polyelectrolyte systems. Nevertheless, preliminary results by Williams *et al.*[17] indicate interesting structure similar to that predicted by de Gennes *et al.*[11].

The inverse compressibility matrix is given by the second derivatives of the free energy density,

$$\chi \ \chi^{-1} = c^{-1}\begin{bmatrix} 1 & -[1 + (\ell/2a)] \\ -[1 + (\ell/2a)] & 2 + (\ell/2a) \end{bmatrix} \tag{37}$$

The compressibility matrix itself is then

$$\chi = c[1 - (\ell/2a) - (\ell^2/4a)]^{-1}\begin{bmatrix} 2 + (\ell/2a) & 1 + (\ell/2a) \\ 1 + (\ell/2a) & 1 \end{bmatrix}$$

Assuming that only the polyions scatter neutrons, the forward scattering intensity is[11]

$$I = \alpha^2 c[2 + (\ell/2a)]/[1 - (\ell/2a) - (\ell^2/4a^2)] \tag{39}$$

where α is the scattering length per monomeric unit. The intensity is proportional to the concentration c, as previously predicted[10,11].

In the description of polyelectrolyte conformations, it is assumed that, for short distances ($r < b$), the polyions behave as rods of length b and thus for wave vectors $\mathrm{q} > b^{-1}$ the scattered intensity is[11]

$$I(\mathrm{q}) = \alpha^2(c/qa) \tag{40}$$

Since $\kappa \gg b^{-1}$, equation (40) may be used to give

$$I(\kappa) \simeq \alpha^2(c/\kappa) \approx (\alpha^2/2\pi^{1/2})(c/\ell a^2)^{1/2} \tag{41}$$

By comparison with the forward scattering intensity, (39), it is noted that

$$I(0)/I(\kappa) \approx \kappa a \ll 1 \tag{41}$$

As the intensity becomes small at large wave vectors, this implies a maximum[11,17] at some wave vector q^* in the vicinity of κa.

CONCLUSION

The role of counterions in various physical properties of polyelectrolyte solutions has been discussed. In particular, counterion effects seriously modify scaling arguments that have been so useful in neutral polymer solutions. Scaling ideas do appear to provide correct results in so far as characteristic lengths are concerned. However, for properties such as osmotic pressure, thermoelectric power, and neutron scattering, counterion coupling is dominant and naive scaling arguments would give incorrect results.

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