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Anomalous viscosity of polyelectrolyte solutions

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The electrostatic contribution to the viscosity of dilute polyball solutions is calculated using the "two-fluid" model of colloidal liquids. A similar approach is applied to dilute and semidilute ionic solutions of rodlike polyelectrolytes, and the experimentally observed anomalous rise of the reduced viscosity with decreasing polymer concentration, the phenomenological Fuoss law, and the maximum seen at low added-salt concentration are derived.

The anomalous behavior of polyelectrolyte solutions at low salt concentrations has been well known for many years.[1-3] The main effects observed in viscometric experiments include the apparently unbounded rise of the specific viscosity (per unit polymer concentration) with dilution in the salt-free regime, its nonanalytic dependence on the polymer concentration, and the appearance of a maximum in the reduced viscosity, at small (but nonzero) salt concentrations. Although it has been suggested that the above anomalies are produced by long-range Coulomb interactions between polyions,[4] to the best of our knowledge, no theory has been able to account for these effects.[13]

In this report we discuss the consequences of a model which estimates the electrostatic contribution to the viscosity of dilute solutions of charged polyballs[5-7] and apply it to solutions of rodlike polyelectrolyes. According to the "two-fluid" model of colloidal liquids,[5] the viscosity can be written as the sum of three terms: the solvent viscosity η_0, the hydrodynamic contribution η_H which is proportional to the volume fraction of the colloidal particles (polyballs), and the viscosity of the "fluid" of these interacting polyballs, η_1. We adopt the phenomenological relationship between the latter, the shear modulus E, and the stress relaxation time τ,

$$\eta_1 = E\tau \;, \tag{1}$$

which was found to be in excellent agreement with experiments on charged polyballs.[5] Although long-range crystalline order is not present in the liquid state, one assumes that the shear modulus can be computed from the expression for the elastic energy associated with small displacements from the equilibrium location in the colloidal crystal. Since the polyball lattice is immersed in a uniform background of univalent counterions (number density C_{CI}) and salt ions (density C_S and valence Z_S), it can be shown[6] that, upon a suitable renormalization of the polymer charge Z (i.e., replacing Z by a renormalized value Z^*), the pair interaction potential between the charged polyballs can be approximated by the Debye-Hückel expression $V(r)=(Z^*e)^2e^{-\kappa r}/\epsilon_0 r$, where ϵ_0 is the dielectric constant of the solvent, e the electron charge, and κ the inverse Debye screening length given by $\kappa^2 = 4\pi l_B(Z^*C_p+2Z_s^2C_s)$, with $l_B=e^2/\epsilon_0 k_B T$ being the Bjerrum length, k_B the Boltzmann constant, and T the temperature (we have used the charge neutrality condition $C_{CI}=Z^*C_p$ to relate κ to the polyball density $C_p=1/d^3$). For a lattice with equilibrium spacing d, the shear modulus is related to $V(d)$ (in the nearest-neighbor approximation[7])

$$E \simeq (1/d^3)(\kappa d)^2 V(d) \;. \tag{2}$$

The relaxation time τ appearing in Eq. (1) can be related to the time it takes the polyball to diffuse across a lattice spacing d,

$$\tau \simeq d^2/D \;, \tag{3}$$

where $D \simeq k_B T/\eta_0 a$ is the diffusion constant of a polyball of radius a. Using the above equation and the definition of the reduced viscosity $\eta_{sp}/C_p=(\eta-\eta_0)/\eta_0 C_p$, we get

$$\begin{aligned}\eta_{sp}/C_p \simeq {} & a l_B^2 Z^{*3}(1+2Z_s^2C_s/Z^*C_p)\\ & \times \exp[-(4\pi l_B Z^* C_p^{1/3})^{1/2}\\ & \times (1+2Z_s^2C_s/Z^*C_p)^{1/2}] \;,\end{aligned} \tag{4}$$

where we have neglected the small hydrodynamic contribution η_H to the viscosity (dominant for neutral particles).

The exponential decrease of the η_{sp}/C_p with $C_p^{1/6}$ at zero salt concentration is due to the fact that the density of counterions increases as we increase the polyball concentration and, although the interpolyball separation decreases, the net effect is that the interaction between polyballs becomes increasingly screened. At finite salt concentrations we expect a transition between the regimes $C_s \ll C_p$ in which our previous arguments apply and $C_s \gg C_p$ in which the screening length becomes a function of salt concentration only (e.g., constant) and further reduction in C_p decreases the interpolyball interaction. In between, a maximum in the interparticle interaction is expected. If, on the other hand, we keep C_p constant and vary the salt concentration, we expect to observe exponential decay with $C_s^{1/2}$ at high salt concentration (with, possibly, nonmonotonic behavior at lower C_s).

The case of polyelectrolyte solutions is complicated by the fact that flexible polyions can change their conformation depending on the salt and polymer concentrations. In the following we shall assume that the stoichiometric degree of ionization (Z/N) of the polyion is of order unity and take the salt concentration to be low enough so that the polyions can be described as uniformly charged rods.[8,9] While this approximation breaks down at high polyion concentrations, the assumption that the electrostatic persistence length scales like the square of the Debye screening length[9] implies that the stretched-polymer assumption remains valid as long as the polyion concentration remains below $1/l_B^2bN^2$, where b is the monomer length and N the degree of polymerization, e.g., well into the semidilute regime (the onset of which is defined by the overlap concentration for rods, $C_p^* = 1/b^3N^3$). Thus, according to the classification of Ref. 9, our considerations pertain to the so-called, dilute-semidilute regime.

Coulomb interaction energies for various arrangements (hexagonal, β-tungsten, grain boundary) of charged rods have been calculated by de Gennes *et al.*[8] In all cases the interaction energy was found to be of the form $V = V(\kappa d)$, where $d \simeq (1/bc)^{1/2}$ is the nearest-neighbor distance between rods ($C = NC_p$ is the monomer concentration) and where κ^{-1} is the Debye screening length given by $\kappa^2 = 4\pi l_B \alpha C(1+2Z_s^2C_s/\alpha C)$, with $\alpha = Z^*/N$ being the effective degree of ionization which accounts for charge renormalization $(Z \rightarrow Z^*)$ due to counterion condensation on the polyion.[10,11] The other difference compared to the spherical polyball case is that the translational diffusion coefficient is replaced by that appropriate for a rod, $D \simeq kT\ln N/n_0bN$. Substituting into Eqs. (1)–(3) and noticing that the reduced viscosity is defined with respect to the monomeric concentration, one obtains

$$\eta_{sp}/C \simeq b^{3/2}(N/\ln N)(\kappa d)^2 V(\kappa d)/k_BTC^{1/2} . \tag{5}$$

In the limit of vanishing salt concentration $\kappa d \simeq (4\pi\alpha l_B/b)^{1/2}$ becomes independent of C [apart from possible logarithmic dependence of α on C (Ref. 6)] and one arrives at the phenomenological Fuoss law[12] for the reduced viscosity of salt-free polyelectrolyte solutions, $\eta_{sp}/C \sim 1/C^{1/2}$. Notice that the above result is universal in the sense that it does not depend on the choice of the polyion lattice. At concentrations below C_p^* (physically realizable only for short polyions), one needs to correct the interaction energies[8] for finite polyion size effects; the spherical polyball result [Eq. (4)] is approached, as expected, in the limit of pointlike polyions $(C \ll C_p^*)$.

At finite salt concentrations, the behavior is no longer universal and depends on the polyion arrangement. One obtains $\kappa d = [\gamma(l_B/b)\alpha(1+2Z_s^2C_s/\alpha C)]^{1/2}$, where $\gamma = 8\pi/\sqrt{3}$ and 3π for the hexagonal and the β-tungsten phases, respectively. Substituting the corresponding interaction energies[8] into Eq. (5) gives

$$(\eta_{sp}/C)_{\text{hexag}} \simeq (N/\ln N)[l_B\alpha(1+2Z_s^2C_s/\alpha C)]^{3/2}\exp\{-[(8\pi l_B/\sqrt{3}b)\alpha(1+2Z_s^2C_s/\alpha C)]^{1/2}\}/C^{1/2} \tag{6}$$

and

$$(\eta_{sp}/C)_{\beta} \simeq (N/\ln N)[b^2l_B\alpha(1+2Z_s^2C_s/\alpha C)]^{1/2}\exp\{-[(3\pi l_B/b)\alpha(1+2Z_s^2C_s/\alpha C)]^{1/2}\}/C^{1/2} . \tag{7}$$

Both expressions show Fuoss law behavior for $C \gg C_s$, followed by a maximum in η_{sp}/C versus C curve when $C \sim 0(C_s)$ and a rapid increase with concentration at $C \ll C_s$—*all* in qualitative agreement with existing experimental data.[1–3] In the limit of high salt concentrations, one recovers the neutral polymer behavior since both the intrapolyion and interpolyion Coulomb repulsions become small and the neglected hydrodynamic contribution to the viscosity (η_H) becomes larger than the electrostatic contribution (η_1) given by Eqs. (6) and (7). A detailed comparison with recent experimental results will be published shortly.[12] Notice that although energy considerations favor the hexagonal over the β-tungsten phase,[8] there is no experimental evidence for long-range order in polyelectrolyte solutions and, since twist deformations increase the energy of the former but not of the latter phase,[8] one might expect that entropy considerations will favor a local β-tungsten-like arrangement (roughly perpendicular nearest-neighbor rods) in the liquid state.

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