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Effect of Counterion Valence and Polymer Charge Density on the Pair Potential of Two Polyions

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ABSTRACT: A theory of attractive forces between identical highly charged polyions in a 1:1 supporting electrolyte, generated by the interaction of the layers of condensed counterions, is extended to a Z:Z' electrolyte and to rodlike polymer segments of any charge density. If the combined charge density of a polyion pair does not exceed the charge density critical for counterion condensation, then there is no attraction. But an attraction arises if the combined charge density does exceed the condensation threshold, even if the individual polymer charge densities lie below the critical value. The intensity of the attraction at a fixed ionic strength decreases with higher values of counterion valence. The effect of increased ionic strength is to decrease both the range and the intensity of the attractive force.

Introduction

In a previous paper we analyzed the pair potential of two polyionic chains in parallel orientation.[1] For a limiting-law theory of the long-range ionic effects on the pair potential, it suffices to model each polyion as a linear lattice of point charges with uniform spacing. We restricted attention to monovalent counterions and to lattice charge spacings corresponding to polymer charge densities above the critical threshold for condensation of counterions. Under these circumstances we found a pair potential that is repulsive when the separation distance between polymers is on the order of a Debye length. The pair potential is again repulsive at small distances, well within a Debye length. But the potential is attactive in an intermediate range of separation distances within a Debye length.

An ingredient of the theory is an internal partition function for the condensed counterions.[2,3] In the attractive range of distances the partition function increases strongly with approach of the polyions (i.e., the free energy of the condensed counterions decreases), providing the underlying reason for the attraction. Interpreting the partition function as the volume of the condensation region, we were able to show that the condensed layers not only expand but merge into a commonly held condensate enveloping both polymers, much like a covalent bond.[1] The greatly enhanced translational entropy of the counterions in the expanded common condensation layer becomes the primary driving force for the attraction. A qualitatively equivalent interpretation is that the electric field between the polymers becomes flat as the fields of the approaching polymers overlap, allowing the condensed counterions to diffuse freely into the space between polymers.

The theory can be viewed in the light of current information from experiments. Direct visualization of the appearance of polyion clusters in 1:1 salt at the same polymer concentration at which static and dynamic light scattering anomalies occur[4] has perhaps removed lingering doubt about the interpretation of the latter. The polymer concentrations needed for cluster formation are lower than the range expected for manifestation of crowding effects, so it is difficult to avoid the conclusion that the clusters are stabilized by attractive interactions among identically charged polymers.[4] That the stabilizing attraction is ionic in origin is strongly suggested by existing data.[5]

Although polymer clusters in most experiments would appear to consist of many individual polymers, fluorescence labeling methods in solutions of poly(L-lysine) with univalent counterions are most readily interpreted as indicating the presence of segment pairs.[6] Close contact within the pair can be ruled out by the range of labels used. Separation between constituent segments is measured instead at about 30−60 Å, which is about the same as our rough estimate of where the minimum in the theoretical polymer−polymer potential is located.[1]

Our previous report was restricted to polymers of high charge density, higher than the condensation threshold, and the attractive interaction was found to be a consequence of the behavior of the condensed counterions. By progressive titration of a weak polyacid, Sedlak *et al.* have found, however, that the slow diffusion mode indicative of clusters can be observed at low polymer charge densities as well as high.[7] When two or more polymers of given charge density approach, they form an assembly with an effectively higher charge density, possibly high enough to produce condensation of counterions. In this paper we ask and answer the question of whether such an effect may be strong enough to generate an attractive interaction.

Drifford and Dalbiez have developed an empirical rule implying that at fixed ionic strength of supporting electrolyte the polymer concentration required for observation of the slow diffusion mode by their procedures increases in proportion to the valence of the counterion in the electrolyte.[8] Ferrari and Bloomfield have observed that the amplitude of the slow diffusion signal for CaDNA is substantially less than for NaDNA.[9] We therefore extend our previous calculations for 1:1 electrolyte to the general Z:Z' salt. We do not consider here the more difficult mixed-salt problem of polymer compaction and cluster formation induced by titrating multivalent ions into a solution with 1:1 supporting electrolyte.[10]

Still another aspect of polyion clustering is its dependence on ionic strength. DNA clustering is more readily found in low concentrations of NaCl than high,[4] the amplitude of the slow diffusion mode in poly(styrenesulfonate) solutions decreases as salt is increased,[11] and, indeed, the observed onset of clustering has typically

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been probed by lowering the salt concentration.[6] This trend is counterintuitive if one assumes that the electrostatic interactions among polymers are purely repulsive, since if the observed attraction is not of electrostatic origin, then addition of salt should weaken the electrostatic repulsion and thus strengthen the net attraction. Therefore we examine the ionic strength dependence predicted by our theory.

The attractive interaction of our analysis should be distinguished from the thermalized residue of ionic crystal formation that seems to underlie several other theories and simulations of attractive forces,[12,13] and that has not produced attraction with univalent counterions,[12,13] except perhaps at extreme ionic strengths and/or polymer charge densities.[14−17] It is entirely possible that different mechanisms of counterion-induced attraction are simultaneously present, with different ones dominating in various conditions.

Theory

Two polyions are before us, immersed in a solvent of dielectric constant D that contains the concentration (molarity) c_s of electrolyte $A_{\nu}B_{\nu'}$. The valence of the cation A is Z, and the absolute value of the valence of the anion B is Z', so that $\nu Z = \nu' Z'$. The solvent with electrolyte has a Debye screening length $1/\kappa$, where

$$\kappa^2 = a^2 c_s \tag{1}$$

$$a^2 = 4\pi \times 10^{-3}\, L_{A\nu} l_B Z Z'(\nu + \nu') \tag{2}$$

l_B is the Bjerrum length

$$l_B = q^2/Dk_BT \tag{3}$$

(q is the unit electrostatic charge, k_B is Boltzmann's constant, and T is the temperature) and $L_{A\nu}$ is Avogadro's number.

Each polyion is represented by a linear lattice of P negative charges $-q$ with spacing b. Length effects are neglected, implying that the linear charge arrays are much longer than the Debye screening length. The counterions are the electrolyte ions of species A of charge Zq. The dimensionless polymer charge density ξ is defined as usual as the ratio l_B/b. We recall the existence of a critical charge density $\xi = 1/Z$ marking the onset of counterion condensation.[2,3] We will consider three regimes of charge densities. *Weakly charged polymers* are defined to have $\xi < 1/(2Z)$. *Highly charged polymers* have $\xi > 1/Z$. We define *moderately charged polymers* as those with ξ in the range $1/(2Z) < \xi < 1/Z$. Polymers in the latter regime have the property that a pair of them have a combined charge density 2ξ above the condensation threshold ($2\xi > 1/Z$), even though their individual charge densities are below the threshold ($\xi < 1/Z$).

The two polyions are taken in parallel orientation, where their electrostatic interaction is strongest, and the separation distance is denoted by r (we used the less conventional symbol ρ in our previous paper[1]). We recall the involvement of four ranges of separations between the polymers.[1] The first, $r = \infty$, represents the isolated noninteracting polymers and serves as our reference state. Then there is the range of distant separations, where r is on the order of $1/\kappa$. The theory is an approximation valid to leading order terms in electrolyte concentration. The meaning of "r is on the order of $1/\kappa$" is that when we allow κ to become small, the product κr is held at a constant value. By assigning different constant values to this product, we get a range of distant values for r at a fixed small value of κ.

We produce a close range of polymer separations with specification that r remain constant when κ is allowed to become small. By assigning different constant values to r, we get a range of separations. These separations are "close", in the sense that they are much less than $1/\kappa$ (r is held fixed as κ becomes small, and $1/\kappa$ becomes large).

Finally, an intermediate range of separations is defined by the formula

$$\kappa r = (\kappa r_0)^{1-x} \tag{4}$$

In this formula r_0 is a fixed distance, and the parameter x is greater than 0 but less than 1. By assigning different values to x, we produce a range of separations r for some fixed small value of κ. In eq 4, $r = r_0$ when $x = 0$. Thus $x = 0$ corresponds to a close separation r, according to the definition of "close" in the preceding paragraph. When $x = 1$, κr also equals 1. It follows from our definition of "far" distances that $x = 1$ corresponds to a far distance. Values of x between 0 and 1 therefore correspond to a range of distances that bridges close and distant separations. This range is "intermediate" in the precise sense, as easily checked from eq 4, that when $\kappa \to 0$, and hence $1/\kappa \to \infty$, we have $r \to \infty$ but $\kappa r \to 0$. In words, r becomes large when κ is allowed to become small but remains much less than the screening length $1/\kappa$. According to our definitions, then, r is larger than a close separation but smaller than a distant separation.

In each of these ranges of separation distances between polyions, we calculate the free energy of the system $G(r)$. Then the free energy difference $\Delta G(r) \equiv G(r) - G(\infty)$ is formed. This quantity equals the work required to bring the polymers to separation distance r from infinite separation; it is the polyion−polyion potential of mean force. We represent the free energy by g, where $g = G/2Pk_BT$, that is, free energy per polyion charge ($2P$ charges for the two polyions) in units of k_BT.

We recall that the free energy in our limiting-law theory comes from two sources.[1,2] There is a Debye−Huckel screened Coulomb potential between each pair of polymer charges, summed over all pairs, including pairs within the same polymer and pairs with one charge on one polymer and the other charge on the other polymer. To account for the possibility of counterion condensation, each polymer charge is taken as reduced by a factor $1 - Z\theta$, where θ is the fractional number of condensed counterions (the total number of counterions condensed on the two polymers is $2P\theta$). The condensation of counterions is not assumed; it is simply recognized as a possibility. In fact, a conclusion of the free energy minimization is that there are no condensed counterions below a threshold polymer charge density.

The second source of θ-dependent free energy is the transfer of counterions from bulk to the condensed layer (if there turns out to be no condensed layer, this contribution vanishes). A term of the form $\theta \ln(\theta/Q\nu c_s)$ is written for the transfer free energy. The partition function Q has only recently been introduced into our theory.[2,3] It replaces, as an important physical generalization, the volume V of the condensed layer.[1] Formally, however, it amounts only to a notational change from V to Q. Not counting the reference state, we have to consider nine cases; weakly, moderately, and highly charged polymers are each studied at distant, intermediate, and close separations. Our methods have been fully developed and applied,[1,2] and we concentrate here on the results.

(a) The reference State at Infinite Separation. For the isolated polyions at $r = \infty$, there is a threshold polymer charge density $\xi = 1/Z$. We get

$$\theta_\infty = 0 \quad \text{if} \quad \xi < \frac{1}{Z} \tag{5}$$

that is, for weakly and moderately charged polymers, but

$$Z\theta_\infty = 1 - \frac{1}{Z\xi} \quad \text{if} \quad \xi > \frac{1}{Z} \tag{6}$$

for highly charged polymers. The condensed layer partition function for $\xi > 1/Z$ is given by

$$Q_\infty = 4\pi e L_{Av} Z' \frac{\nu + \nu'}{\nu}\left(\xi - \frac{1}{Z}\right) b^3 \quad \text{if} \quad \xi > \frac{1}{Z} \tag{7}$$

These results are of course not new.[18] Equations 5 and 6 signify the onset of counterion condensation on individual polymers at the critical charge density $\xi = 1/Z$. The right-hand side of eq 7 is the same expression as previously obtained for the volume of the condensed layer of counterions.[18] The overall condensed ion partition function may have a much more complicated structure than a mere volume, but its various contributions (including the volume as only one of them) together must satisfy eq 7.

With eqs 5–7, we have a formula for the free energy of the reference state at infinity

$$g(\infty) = -\sigma_\infty \ln(\kappa b) + \tau_\infty \tag{8}$$

where for weakly and moderately charged polymers

$$\sigma_\infty = \xi \qquad \tau_\infty = 0 \tag{9}$$

while

$$\sigma_\infty = \frac{1}{Z^2\xi} \qquad \tau_\infty = \theta_\infty \ln \frac{10^3\theta_\infty}{Q_\infty \nu c_s} \tag{10}$$

for highly charged polymers.

(b) The Potential of Mean Force. The polyion–polyion potential of mean force with reference state at infinity may be written in the compact form

$$\Delta g(r) = -\{\xi[1 - Z\theta(r)]^2 - \sigma_\infty\} \ln(\kappa b) + \xi[1 - Z\theta(r)]^2 K_0(\kappa r) + \theta(r) \ln\left[\frac{10^3\theta(r)}{Q(r)\nu c_s}\right] - \tau_\infty \tag{11}$$

where $K_0(\kappa r)$ is the zeroth-order modified Bessel function of the second kind, and it remains for us to find by energy minimization, by well-known methods,[1,2] the condensation fraction $\theta(r)$ and the condensation layer partition function $Q(r)$ as functions of polyion–polyion distance r. At close and intermediate separations, where κr is small, we make use of the asymptotic form of the Bessel function[1]

$$K_0(\kappa r) \approx -\ln\left(\frac{1}{2} e^\gamma \kappa r\right) \tag{12}$$

where γ is Euler's constant with numerical value 0.5772....

(c) Weakly Charged Polymers. Weakly charged polymers have $\xi < 1/(2Z)$. Even the combined charge density of two of them, that is, 2ξ, lies below the condensation threshold $1/Z$. We find that in all three regions of separation, *distant*, *intermediate*, and *close*, there is no counterion condensation, $\theta(r) \equiv 0$, and that the polyion–polyion potential of mean force is

$$\Delta g(r) = \xi K_0(\kappa r) \tag{13}$$

Equation 13 represents a pure screened Debye–Huckel interaction between the polyions. The Bessel function is a solution of the two-dimensional linearized Poisson–Boltzmann equation (although our method of derivation is different), and proportionality to the charge density ξ also signifies a linear result.

(d) Highly Charged Polymers. Highly charged polymers are defined to have $\xi > 1/Z$ and are therefore enveloped in a sheath of condensed counterions when isolated, described by eqs 6 and 7. The results that follow are simply the generalization to counterions of arbitrary valence of our previous results for univalent counterions.[1]

When the polyion pair is in the range of *distant* separations

$$Z\theta(r) \equiv 1 - \frac{1}{Z\xi} \tag{14}$$

$$Q(r) = Q_\infty \exp[-2K_0(\kappa r)] \tag{15}$$

$$\Delta g(r) = \frac{1}{Z^2\xi}(2Z\xi - 1)K_0(\kappa r) \tag{16}$$

Note that the condensation fraction in eq 16 is the same as for the isolated polyions, eq 6. As the polyions approach from infinity to distances on the order of the Debye length, there is no change in the number of condensed counterions. The partition function for the condensed layer is modified, however, becoming dependent on r. In eq 11, Q_∞ is the condensed layer partition function of the isolated polyions, given by eq 7 (the Bessel function in eq 15 tends to zero as r becomes infinite with κ fixed). The physical meaning is that the structure of the condensed layers is perturbed by interaction of the polyions, even at separations too large for their mutual penetration (in the range of distant separations, r on the order of $1/\kappa$, only the diffuse Debye–Huckel clouds penetrate).

The behavior of the polyion–polyion potential of mean force is important to understand. The coefficient of the Bessel function in eq 16 is not linear in ξ, so eq 16 is not a linear result of the Debye–Huckel type. The condensed counterions reduce the electrostatic repulsion between the polyions, with counterions of higher valence being most efficient in this regard. The reduction of the repulsive interaction, however, is not nearly as strong as one would expect if the only effect of the condensed counterions were to reduce the net charge density of the polyions. The mutual polarization of condensed layers also plays a role.

If the highly charged polyions are *closely* separated at distances much less than a Debye length, our results are as follows

$$Z\theta(r) \equiv 1 - \frac{1}{2Z\xi} \tag{17}$$

$$Q(r) = \frac{1}{4}e^{\gamma}\frac{2Z\xi - 1}{Z\xi - 1}\frac{r}{b}Q_{\infty} \tag{18}$$

$$\Delta g(r) = -\frac{1}{4Z^2\xi}\ln\left[e^2\kappa^2 b^2\left(\frac{1}{2}e^{\gamma}\frac{r}{b}\right)^{4Z\xi-1}\right] \tag{19}$$

Equation 17 signifies that at close distances the two polyions with individual charge densities ξ “cooperate” to condense the same number of counterions as a single polyion of twice the charge density. Equation 19 shows that the potential of mean force at these distances reflects an unscreened ln r potential, as the two polyions are well within the Debye screening length. There is a salt dependence of $\Delta g(r)$, however, originating from the additional number of counterions condensed from bulk solution and the additional screening of the doubly charged polymer pair considered as a unit.

At *intermediate separations*, where the Debye clouds are incompletely penetrated

$$Z\theta(r) = 1 - \frac{1}{Z\xi[2 - x(r)]} \tag{20}$$

where the function $x(r)$ is defined implicitly by eq 4

$$Q(r) = Q_{\infty}\left(\frac{1}{2}e^{\gamma}\right)^{2/(2-x)}\frac{1}{2 - x} \times \frac{Z(2 - x)\xi - 1}{Z\xi - 1}\left(\frac{r_0}{b}\right)^{2(1-x)/(2-x)} \tag{21}$$

where r_0 is the fixed boundary between close and intermediate polyion−polyion separations and

$$\Delta g(r) = -\frac{1 - x}{(2 - x)Z^2\xi}[1 + \ln(\kappa b)] - \frac{2(2 - x)Z\xi - 1}{(2 - x)^2Z^2\xi}\ln\left[\frac{1}{2}e^{\gamma}\left(\frac{r_0}{b}\right)^{1-x}\right] \tag{22}$$

Equation 20 shows that the condensation fraction increases as the polyions approach (i.e., as x goes from 1 to 0), bridging the values of θ in the distant and close regions. Equations 21 and 22 indicate a nontrivial dependence on separation r, through the function $x(r)$, of both the structure of the condensed layers and the polyion−polyion potential of mean force.

(e) Moderately Charged Polymers. Recall that moderately charged polymers are defined as those with ξ in the range $1/(2Z) < \xi < 1/Z$. Since the ξ-value of a moderately charge polymer is less than the condensation threshold $1/Z$, there are no condensed counterions in the reference state of infinite separation between two polymers. In the range of *distant separations*, just as for weakly charged polymers, we find $\theta = 0$ and

$$\Delta g(r) = \xi K_0(\kappa r) \tag{23}$$

For *close separations*, the situation is different. The two polyions are found to cooperate as a unit to condense counterions, and since a pair of moderately charged polymers has an effective charge density 2ξ in excess of the threshold $1/Z$, the result is a nonzero number of condensed counterions given by the same formula, eq 17, as for closely separated highly charged polymers. Similarly, the partition function of the condensed layer is given by the same formula, eq 18, as for closely separated highly charged polymers. The potential of mean force is not the same as for closely separated highly charged polymers, because the free energy in the reference state at infinity is different

$$\Delta g(r) = -\frac{1}{Z}\left(1 - \frac{1}{2Z\xi}\right) + \frac{2Z^2\xi^2 - 4Z\xi + 1}{2Z^2\xi}\ln(\kappa b) - \frac{1}{Z}\left(1 - \frac{1}{4Z\xi}\right)\ln\left(\frac{1}{2}e^{\gamma}\frac{r}{b}\right) \tag{24}$$

This expression agrees with eq 19 at the charge density $\xi = 1/Z$ common to moderately and highly charged polymers. It also agrees at $\xi = 1/2Z$ with eq 13 for weakly charged polymers, if the asymptotic form of $K_0(\kappa r)$, valid at close separations, is used.

In the range of *intermediate separations r*, there is a critical distance r_{crit} for moderately charged polymers, corresponding *via* eq 4 to a critical value of x

$$x_{\text{crit}} = 2 - \frac{1}{Z\xi} \tag{25}$$

Note that $0 < x_{\text{crit}} < 1$ for moderately charged polymers. For $r > r_{\text{crit}}$ ($x > x_{\text{crit}}$), there are no condensed counterions, $\theta = 0$, and the potential of mean force is the linear result, eq 23. In other words, the behavior of moderately charged polymers at distant separations is maintained into the range of intermediate separations up to the distance r_{crit}. At $r = r_{\text{crit}}$, the combined charge density of the two polymers becomes sufficient for counterion condensation to set in, and for $r < r_{\text{crit}}$ in the intermediate range, the formula for the condensed fraction is the same as eq 20 for highly charged polymers in the intermediate range. Likewise, the partition function for the condensed layer when $r < r_{\text{crit}}$ is the same as eq 21 for highly charged polymers (note in eq 21 that Q vanishes at $x = x_{\text{crit}}$). The unwieldy formula for$\Delta g(r)$ for moderately charged polymers in the intermediate range of distances when $r < r_{\text{crit}}$ is not displayed here. It can be obtained by substituting eqs 20 and 21 into the general formula, eq 11, using eqs 9 and 12.

Numerical Examples

In constructing numerically generated curves of the polyion−polyion potential, we have to consider that each is composed of three separate branches, corresponding to distant, intermediate, and close separations. The constraints we choose are that the distant region lies beyond $r = \kappa^{-1}$, the intermediate region is between distance r_0 and κ^{-1}, and the close range is $r \leq r_0$. In accord with our definitions, r_0 must be substantially less than κ^{-1}, but it must also be well removed from the polymer. We then adjust r_0 until a curve of reasonably smooth appearance is obtained.

Figure 1 compares the pair potential of mean force for weakly and moderately charged polymers in 1:1 electrolyte. The former is repulsive over the whole range of separations, but a shallow local minimum emerges for the moderate charge density. When two moderately charged polymers approach, there is a critical distance marking the onset of counterion condensation. Figure 2 illustrates the abrupt emergence of a condensed fraction for the moderately charged polymers, and Figure 3 shows the behavior of the partition function of the condensed layer, which rises from a zero value at the threshold separation distance to attain very high values with further approach of the polyions. The decreasing free energy of the condensed layer with approach of the polyions is the primary reason for their attraction.

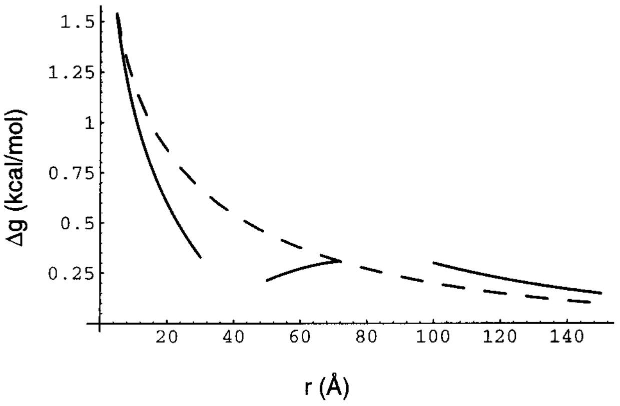

Figure 1. Comparison of polyion−polyion potential of mean force (kcal/mol of charged groups on the two polymers) for weakly and moderately charged polymers: dashed curve, $\xi = 0.5$ (weak); solid curve, $\xi = 0.75$ (moderate). For both curves: 1−1 electrolyte concentration 0.001 M ($\kappa^{-1} = 96$ Å); $r_0 = 40$ Å.

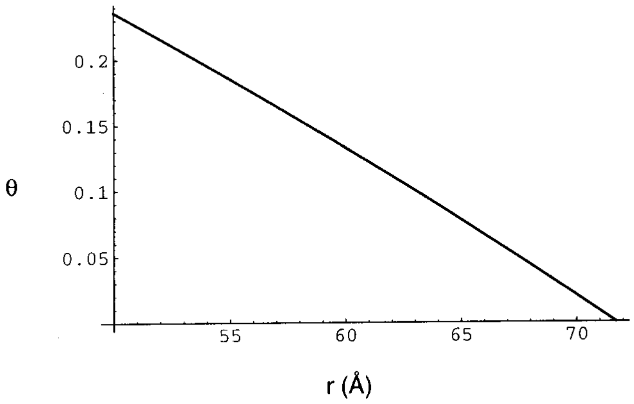

Figure 2. Emergence of a fraction of condensed counterions on approach of two moderately charged polymers ($\xi = 0.75$). Other parameters are as in Figure 1.

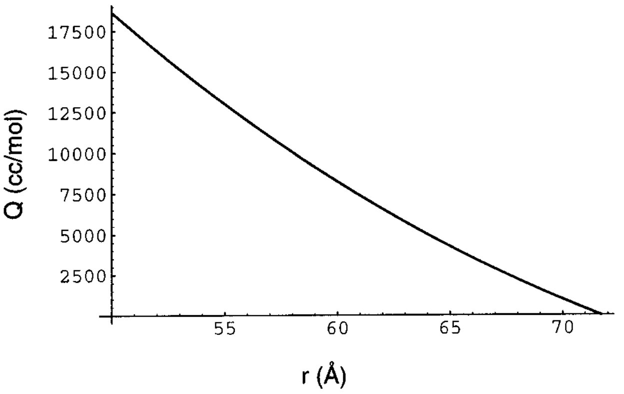

Figure 3. Partition function of the condensed layer on moderately charged polymers ($\xi = 0.75$). Other parameters are as in Figure 1.

In Figure 4 we compare the results for highly negatively charged polymers at a common ionic strength set by 1:1, 2:1, and 3:1 electrolyte. Both the repulsive part of the polyion−polyion potential at distant separations and the depth of the potential minimum are attenuated when the valence of the counterion is increased, although the range of the attraction does not seem to change much. Comparison of the 1:1 curve in Figure 4 with Figure 1 shows that the attraction between highly charged polymers is much stronger than between moderately charged polymers.

Figure 5 shows what happens when the ionic strength of 1:1 electrolyte is increased. All electrostatic effects are weakened. Both the repulsive (not shown) and attractive components of the pair potential are less, and the range of the attraction is decreased. Sedlak[11] has demonstrated that clustering persists at quite high ionic strengths, and the theory does produce an attractive well at ionic strengths in excess of what we show in Figure 5, but the accuracy of our essentially dilute-solution calculations are then expected to deteriorate.

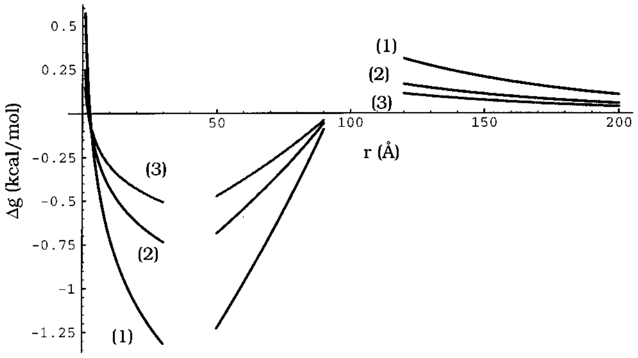

Figure 4. Potential of mean force for two highly charged polyanions ($\xi = 4.2$) in Z:1 electrolye: curve 1, $Z = 1$; curve 2, $Z = 2$; curve 3, $Z = 3$. The common ionic strength is 0.001 M ($\kappa^{-1} = 96$ Å); $r_0 = 40$ Å.

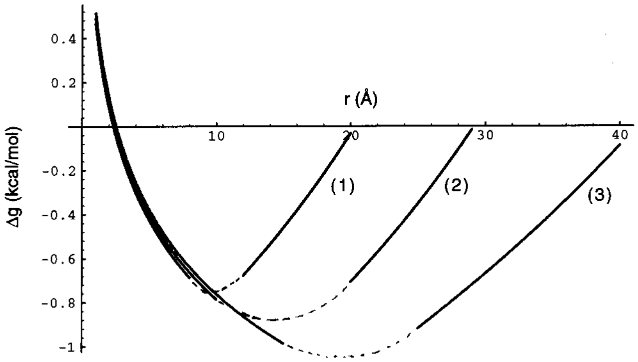

Figure 5. Dependence of the polyion−polyion potential of mean force on the ionic strength I of 1:1 electrolyte. $\xi = 4.2$. Key: curve 1, $I = 0.02$, $r_0 = 10$ Å; curve 2, $I = 0.01$ M, $r_0 = 15$ Å; curve 3, $I = 0.005$ M, $r_0 = 20$ Å. The dashed portions of the curves connecting the close and intermediate branches have been drawn in by hand as a visual aid; only the solid portions represent calculated values.

Discussion

We have defined a moderately charged polymer as one with charge density less than the threshold for counterion condensation but greater than half the threshold value. The combined charge density of two moderately charged polymers consequently lies above the condensation threshold. We have found that when two such polymers approach, they repel each other until a critical separation distance is reached (Figure 1). On continued approach, counterions condense on the polymer pair (Figure 2), and the strong decrease of free energy of the condensed layer, represented by the behavior of the condensation partition function in Figure 3, drives an attractive interaction.

The experimental data of Sedlak *et al.*[7] suggest attractive polyion−polyion forces for polymer charge densities below the value critical for counterion condensation, and the theory indeed discloses a local minimum in the pair potential of two moderately charged polymers. But the observation of Sedlak *et al.* extends to what we have called weakly charged polymers as well—polymers, which, even when paired, do not have a combined charge density lying above the value critical for condensation. The polymers used in the experiments are flexible, and a weakly charged flexible chain may fold in such a way as to raise its effective charge density above its nominal value. An alternate consideration may be that three or more weakly charged polymers have a combined charge density in excess of the critical value.

We saw from Figure 4 that both the repulsive and attractive components of the potential of mean force become smaller when the valence of the counterion is increased, in qualitative agreement with the light scattering measurements of Ferrari and Bloomfield,[9] who observed a decrease in the amplitude and cooperativity of the slow diffusion signal of DNA on replacement of Na^+ by Ca^{2+}, and also with the empirical rule of Drifford and Dalbiez,[8] which, in salts with higher-valent counterions, yields a higher polymer concentration required by their experiments to detect slow diffusion. We have found additionally that both the range and the depth of the attractive interaction decrease in solutions of higher ionic strength, a property of the theory consistent with the observed ionic strength dependence of polymer clustering.[4,6,9,11]

Figure 2 conveys some information quite apart from the question of clustering. It shows that some counterions may be condensed (on transiently proximate polymer segments) even when the charge density ξ is less than the threshold value for condensation on isolated segments. It is possible that NMR might be able to detect and measure this effect.

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