Long-Range Attraction in Polyelectrolyte Solutions

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ABSTRACT: The recently discovered attractive force between hydrophobic surfaces is incorporated in a theory of polyelectrolyte solutions. Its influence on the second and third virial coefficients is estimated. Binary collisions between two polyions are virtually unaffected by attractive forces of long range whereas the impact on the third virial coefficient is enormous. The theoretical coefficients are compatible with those determined for solutions of rodlike xanthan by Kawakami and Norisuye. When the third virial coefficient is negative, the solution may become unstable. This instability appears to explain the onset of aggregation of DNA. The long-range attraction is strong enough to enforce stability of a hexagonal phase at low ionic strength. The predicted spacings agree with those found for tobacco mosaic virus by Millman et al.

Introduction

Despite intense research during the past four decades, many phenomena witnessed in polyelectrolyte solutions remain unexplained. It often seems as if the screened Coulomb interaction on its own is unable to offer a rationalization for the experimental data. For instance, there is evidence that long-lived entanglements among intrinsically flexible polyions influence the light scattered by such a solution to a substantial degree.¹ More concretely, there seem to be long-range attractive forces operative in solutions of rigid or slightly flexible polyions. Gels of tobacco mosaic virus whose positional order is hexagonal are stable against dilution at fairly low ionic strengths.^{2,3} The virus particles often aggregate under similar conditions.⁴ At low salt, Van der Waals forces are too weak to overcome the screened Coulomb repulsion between the charged rods which are enhanced by slight undulations, although an undulation theory is almost quantitative at high ionic strengths.⁵ Double-stranded, rodlike DNA in a semidilute solution also exhibits a peculiar aggregational phenomenon at high salt concentration.⁶ Recent scattering experiments on rodlike xanthan show strong anomalies in the third virial coefficient as I point out at the end of this paper in a comparison of the present theory with the data by Kawakami and Norisuye.⁷

On the other hand, a newly discovered attraction between hydrophobic surfaces has been studied by colloid scientists.⁸⁻¹² It is asserted to be weak but of long range; its origin is unclear at present though it appears to be quite insensitive to the chemical nature of the surface.¹² In particular, it does not seem to depend on its polarity.¹² Christenson et al.¹² have been able to summarize a range of experimental data for the force F exerted by perpendicularly crossed cylinders which are covered by hydrophobic molecules

$$F/a = Ae^{-s/\xi} \tag{1}$$

where a is the cylinder radius, s is the shortest distance between the hydrophobic surfaces, and ξ is a decay length of about 14 nm which is not disturbed by the monovalent electrolyte. The magnitude of the force does depend on the ionic strength.¹² For the purpose of this paper, I

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approximate it roughly by

$$A \approx c \lambda k_{\rm B} T \tag{2}$$

where T is the temperature, $k_{\rm B}$ is Boltzmann's constant, the constant $c \approx 0.008$ nm⁻³ at room temperature, and λ is the Debye screening length ($\lambda^{-2} = 8\pi Q n_{\rm s}$ with the Bjerrum length Q = 0.714 nm for H₂O at room temperature and $n_{\rm s}$ the concentration of the 1–1 electrolyte). When extrapolated to "pure" water (which if not specially treated, contains traces of ions amounting to an effective molarity of 10^{-5} – 10^{-6} M), eq 2 is still a fairly reasonable estimate for the magnitude of the attraction.¹² There is no consensus on the nature of these attractive forces. Some workers believe electrostatic forces are implicated.¹³ Others have tried to dismiss the attractive nature of the force altogether.¹⁴ By contrast, the Russian and Australian schools in colloids treat eq 1 as a well-established fact.^{15,28}

Leaving aside the debate about the validity and nature of eq 1, I here adopt the naive and probably bold hypothesis that eq 1 may be applied to the solution behavior of certain rodlike biopolymers (xanthan, DNA, tobacco mosaic virus [TMV]). It is often thought that the charges effect solubility of these macromolecules whose backbones are hydrophobic in part. However, the real justification is whether eq 1 is able to rationalize heretofore unexplained phenomena. I will argue that this is indeed the case: (1) Recent theoretical work on slender rods by Van der Schoot and Odijk¹⁶ shows that weak dispersion forces may have a significant impact on three-body interactions under conditions when binary interactions are perturbed only mildly. I here extend this analysis to electrostatic and long-range attractive forces along similar lines and investigate the virial coefficients of xanthan; (2) I formulate an approximate stability criterion to estimate the onset of aggregation in DNA; (3) Long-range attraction is incorporated in a recent analysis of the hexagonal phase^{5,17} and applied to TMV.

Interactions between Two Rodlike Polyions. Equations 1 and 2 can be rewritten in terms of the attractive interaction W_A between two fat cylinders crossed at 90°

$$W_{\rm A}/k_{\rm B}T = -c\lambda\xi a e^{-s/\xi} \qquad (\xi \ge \lambda; a \gg \xi; a \gg \lambda) \qquad (3)$$

We now wish to extrapolate eq 3 to the regime $a \ll \xi$ which often applies to polyelectrolyte solutions. Such an extension necessarily involves additional suppositions.

Scenario 1. Equation 3 contains the combination $a\xi$ which may be regarded as the geometrical "area of

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Figure 1. Two skewed polyions.

interaction"¹⁶ for two crossed cylinders in the limit $a \gg \xi$. For $a \ll \xi$, this area is independent of a and scales as ξ^2 if one assumes a polyion perturbs the surrounding water over a distance of order ξ by its mere presence. Furthermore, it is conceivable that the influence of the electric double layer on the attraction is altered by the fact that a is no longer much greater than ξ so this might introduce a power law λ^m with $m \neq 1$. For cylinders skewed at an angle δ , the "area of interaction" is inversely proportional to sin δ (Figure 1). Therefore, one possible extension of eq 3 reads

$$W_{\rm A}/k_{\rm B}T = -\frac{He^{-x/\xi}}{\sin\delta} \qquad (\delta \ge p^{-1}) \tag{4}$$

with

$$H = H_1 \approx h\lambda^m (a+\xi)\xi^{-m-1} \exp(2a/\xi) \tag{5}$$

where $p \equiv L/\xi \gg 1$, $x \equiv 2a + s$ is the distance between the polyion centerlines and I have introduced a dimensionless coupling constant $h \equiv c\xi^3 \approx 20$ for convenience.³⁰

Scenario 2. Equation 3 is a screened form (albeit of attractive nature) and plausibly interpretable as a superposition of Debye-Hückel-like potentials with screening length ξ . In other words, I suppose the formal manipulations in the respective long-range attraction and electrostatic theories are identical. The theory of charged rods interacting by screened Coulomb forces has been discussed at length by various authors.^{18–21} By analogy, we then have for the coefficient of attraction for cylindrical polyions skewed at an angle δ

$$H = H_2 = \frac{\pi h a^2 \lambda^m \exp(2a/\xi)}{2\xi^{m+2} g(a/\xi)}$$
(6)

where²¹

$$g(z) \equiv z^2 e^{2z} K_1^2(z) \tag{7}$$

and K_1 is the first-order modified Bessel function of the second kind.³⁰ In the case $a \gg \xi$ and $\delta = \pi/2$, eqs 4 and 6 reduce to eq 3. At the opposite extreme, we have

$$H_2 \approx \frac{\pi h a^2 \lambda^m}{2\xi^{m+2}} \quad (a \ll \xi) \tag{8}$$

Thus, the attraction now scales as a^2 as it should, for $a^2 \sin^{-1} \delta$ signifies the "area of interaction" for thin cylinders, at least within the context of the second scenario.

Equation 4 breaks doen when the polyions are almost parallel. According to the arguments of refs 16 and 22, we



Figure 2. Interaction between two polyions that are almost parallel $(D_{\text{eff}}/L \leq \delta \leq p^{-1} \equiv \xi/L)$.

should then have

$$W_{\rm A}/k_{\rm B}T \approx -pH\left(1 - \frac{|\Delta z|}{L}\right)e^{-x|\xi}$$

(-L \le \Delta z \le L; \delta \le p^{-1} \equiv \xi/L) (9)

One of the rods is placed along the z axis of a Cartesian coordinate system; Δz is the distance between the centers of mass of the two rodlike polyions. Equation 9 represents a sticking energy proportional to the area of contact and crosses over fairly smoothly to eq 4 at $\delta \approx p^{-1}$. The total energy of interaction is now a superposition of attractive and electrostatic potentials (see Figure 2)

$$W_{\rm tot} \equiv W_{\rm el} + W_{\rm A} \tag{10}$$

where the electrostatic term $W_{\rm el}$ has been discussed in detail in ref 21.

$$W_{\rm el} \approx \frac{Ee^{-\kappa x}}{\sin \delta} \qquad (\delta \ge D_{\rm eff}/L)$$
(11)

$$W_{\rm el} \approx \frac{LE\left(1 - \frac{|\Delta z|}{L}\right)e^{-\kappa x}}{D_{\rm eff}} \qquad (-L \le \Delta z \le L; \, \delta \le D_{\rm eff}/L) \quad (12)$$

Here, E is generally a very complicated function of the polyion parameters²¹ and D_{eff} is the effective diameter^{19,20} which scales approximately as the Debye screening length $\lambda \equiv \kappa^{-1}$.

Second and Third Virial Coefficients. Precise computations of the virial coefficients are complicated in general.^{16,23} Here, I present a semiquantitative analysis focusing on the leading order terms which should be reasonable for $\xi \geq D_{\text{eff}}$. I first note that two test polyions are prevented from approaching each other closer than $D_{\rm eff}$ in view of the repulsive electrostatic force.²⁴ This argument is legitimate even when the macromolecules are enclosed in the confined orientational space $\delta \leq p^{-1} \equiv$ ξ/L . Hence, in calculating attractive contributions to the virial terms we simply let the variable x run from D_{eff} to infinity (see Figure 2). Next, we know that whenever the influence of the attractive forces becomes discernible in thermodynamic quantities, the lead terms are dominated by Boltzmann factors.¹⁶ Moreover, configurations that are almost parallel give the largest contributions to the virial coefficients.¹⁶ These caveats allow for a considerable simplification of the analysis below.

The second virial coefficient may be written as^{16,22}

$$B = B_{\rm el} + B_{\rm A} \tag{13}$$

where the electrostatic contribution is often represented

by¹⁹⁻²¹

$$B_{\rm el,o} \approx \frac{\pi}{4} L^2 D_{\rm eff} \tag{14}$$

although in practice one must include end effects²³

$$B_{\rm el} \approx B_{\rm el,o} \left(1 + \frac{4D_{\rm eff}}{L} \right)$$
 (15)

and the attractive contribution $is^{16,22}$

$$B_{\rm A} \approx -\frac{1}{32\pi^2} \int \int \int_{X > D_{\rm eff}} d\mathbf{u} \, d\mathbf{u}' \, d\Delta \mathbf{R} \phi_{\rm A} \, (\Delta \mathbf{R}, \mathbf{u}, \mathbf{u}') \quad (16)$$

where the Mayer function $\phi_A \equiv \exp(-W_A/k_BT) - 1$, u and u' are the orientational unit vectors along the two test polyions and $\Delta \mathbf{R}$ is the vector distance between their centers of mass.

The first steps in the evaluation of eq 16 are analogous to those in the calculation of the Van der Waals coefficient in refs 16 and 22. Parallel configurations are the most heavily weighted ones: eq 9 is independent of δ so the two integrations over the orientational variables in eq 16 yield $4\pi^2/p^2$. Next, I introduce polar coordinates

$$B_{\rm A} \approx \frac{1}{8p^2} \int_0^{2\pi} {\rm d}\phi \int_{-1}^1 {\rm d}\Delta z \, \int_{D_{\rm eff}}^\infty {\rm d}x \, x(1 - e^{-W_{\rm A}/k_{\rm B}T}) = -\frac{\pi L \xi^2 J}{2p^2}$$
(17)

with

$$J \equiv \int_{D_{\text{eff}}/\xi}^{\infty} dX \, X[\mu^{-1}e^{X+\mu e^{-X}} - \mu^{-1}e^{X} - 1] \qquad (\mu \equiv H/p; \, X \equiv x/\xi)$$
(18)

I eliminate the awkward exponent by setting $X \equiv \log w$

$$J = \int_{\alpha}^{\infty} \mathrm{d}w \log w [\mu^{-1} e^{\mu w^{-1}} - \mu^{-1} - w^{-1}]$$
(19)

where $\alpha \equiv \exp(D_{\text{eff}}(\xi))$ varies between fairly narrow bounds $1 < \alpha < O(e)$. The logarithm in the integrand poses difficulties but fortunately it can be eliminated quite simply by deleting it: (i) If $\mu \ll 1$, an exact series expansion of eq 19 is possible and the approximate J can then be shown to underestimate the exact J by a factor of two at most; (ii) If $\mu = O(1)$, one sets $w = \alpha + q$ noting that the leading contribution of the integral stems from the region $q = O(\alpha^2|\mu)$; the approximate J is now very close to the exact J; (iii) The case $\mu > O(10)$ is of no interest because the attraction then overwhelms the Coulomb repulsion so that the virial expansion is rendered meaningless.³¹

After the substitution $w = \mu t$, the integral

$$J \approx \int_{\alpha/\mu}^{\infty} dt [e^{t^{-1}} - t^{-1} - 1]$$
 (20)

is readily tackled by one integration by parts which circumvents potential divergences

$$J(z) = I(z) - z^{-1}e^{z} + z^{-1} + 1$$
 (21)

with $z \equiv \mu/\alpha$

$$I(z) \equiv \lim_{\epsilon \to 0} \int_{\epsilon}^{z} dy \left(\frac{e^{y} - 1}{y} \right) \equiv \sum_{n=1}^{\infty} \frac{z^{n}}{n!n}$$
(22)

$$J(z) \approx z/2 \qquad (z \ll 1) \tag{23}$$

$$J(z) \sim z^{-2} e^{z}$$
 $(z \ge 1)$ (24)

The summation in eq 22 is easily carried out numerically since z is never very large in practical applications.

It is expedient to define the relative attractive contribution to the second virial coefficient (neglecting end (25)

effects)

with

$$\alpha \equiv \exp(D_{\rm eff}/\xi) \qquad \mu \equiv LH/\xi$$

 $\eta_2 \equiv -\frac{B_{\rm A}}{B_{\rm el,o}} \approx \frac{2\xi^4 J(\mu/\alpha)}{L^3 D_{\rm eff}}$

When $\mu/\alpha \ge 1$, the physical interpretation of eq 25 is as follows: by eq 24 J contains a Boltzmann factor depending on a sticking energy $k_{\rm B}T\mu/\alpha$ for two almost parallel polyions fairly close to each other though always separated by the intervening electric double layer (Figure 2); this is partly offset by an entropy of orientational confinement equal to 5 log(ξ/L).

The analysis of the third virial coefficient proceeds by arguments advanced in ref 16.

$$C = C_{\rm el} + C_{\rm el,A} + C_{\rm A} \tag{26}$$

The purely electric term $C_{\rm el}$ is approximated by the hard-rod coefficient²⁵ but with the hard-core diameter replaced by $D_{\rm eff}$

$$C_{\rm el} \approx \frac{4D_{\rm eff}B_{\rm el,o}^2}{L} \tag{27}$$

This approximation neglects end effects. The cross term is given by 16

$$C_{\rm el,A} \approx B_{\rm A} B_{\rm el,o}$$
 (28)

The purely attractive term is assessed qualitatively as in ref 16

$$C_{\rm A} \approx B_{\rm A}^2 e^{\mu/\alpha}$$
 (29)

Therefore, the relative attractive contribution to C can be expressed as

$$\eta_3 = \frac{|C_{\rm A} + C_{\rm el,A}|}{C_{\rm el}} = \frac{L}{4D_{\rm eff}} (\eta_2^2 e^{\mu/\alpha} + \eta_2)$$
(30)

Whenever $\mu/\alpha \ge 1$, eq 30 contains *three* exponential terms $\exp(\mu/\alpha)$: three pairs of virtually parallel polyions are involved in the attraction.

Thermodynamic Stability. According to eqs 25 and 30 the influence of attractive forces on the third virial coefficient is much greater than on the second, at least in the case when the Boltzmann factor dominates. Hence, under certain conditions the third virial may be negative whereas the second remains positive. There is a distinct possibility of the solution becoming unstable. If the osmotic pressure for an isotropic solution is given by

$$\pi_{\rm p} = k_{\rm B} T \rho (1 + B \rho + C \rho^2 + ...) \tag{31}$$

where ρ is the polyelectrolyte number density, we require

$$\frac{\partial \pi_{\rm p}}{\partial \rho} > 0 \tag{32}$$

for the solution to remain stable.

Neglecting virials higher than the third, we thus have the following criterion for the onset of instability

$$\frac{2a}{L} + \frac{D_{\rm eff}\phi}{a} + \frac{3}{2} \left(\frac{D_{\rm eff}}{a}\right)^3 \phi^2 (1 - \eta_3) \approx 0$$
(33)

where $\phi \equiv \pi a^2 L \rho$ is the macromolecular volume fraction. Equation 33 represents an upper bound on *H* since most of the higher virials are expected to be negative also. The end result arising from the instability of the solution cannot be ascertained from eq 31. We need more information to investigate whether phase separation, aggregation, or gelation occurs. **Hexagonal Phase.** It is straightforward to incorporate eq 9 into a recent theory of hexagonal polyelectrolyte gels.^{5,17} The undulations of a test polyion which is stiff or semiflexible are postulated to be distributed according to a Gaussian

$$G \sim (\pi d^2)^{-1} e^{-r^2/d^2} \tag{34}$$

where d is a variational amplitude and r is the distance from an infinitesimal segment of the test polyion to its position in the perfect nonundulating hexagonal lattice. An extension of ref 5 leads to a total Helmholtz free energy per unit length of polyion and scaled by $k_{\rm B}T$

$$F_{\text{tot}} = F_{\text{tot}}(U, \mathsf{d}(U)) = \sum_{i} \tilde{F}_{i} J_{i}$$
(35)

where U is the interaxial spacing of the hexagonal lattice and the summation i is over the electrostatic (E), van der Waals (W), long-range attractive (A), and entropic interactions (S). The bare or unrenormalized interactions are given by

$$\tilde{F}_E = \frac{3(2\pi)^{1/2} \Gamma^2 e^{-\kappa U}}{Q(\kappa U)^{1/2}}$$
(36)

$$\bar{F}_{W} = -\frac{WD^{1/2}}{8.2^{1/2}(U-D)^{3/2}} \left[1 - \frac{2(U-D)}{D} \right]$$
(37)

for
$$U \leq \frac{3}{2}D$$

$$\tilde{F}_{W} = -\frac{9\pi W}{128D} \left(\frac{D}{U}\right)^{5} \left[1 + \frac{25}{16}\frac{D^{2}}{U^{2}} + \frac{31.9}{16}\frac{D^{4}}{U^{4}} + \frac{150.7}{64}\frac{D^{6}}{U^{6}}\right]$$
(38)

for
$$U > {}^{3}/{}_{2}D$$

 $\tilde{F}_{A} = -\frac{3H}{\xi} e^{-U/\xi}$
(39)

$$\tilde{F}_S = (2d)^{-2/3} P^{-1/3} \tag{40}$$

Here, P is the persistence length, W is the Hamaker constant scaled by k_BT , the bare diameter $D \equiv 2a$, and Γ is an effective charge density scaled by Q (Γ is denoted by ξ_{eff} in refs 5 and 17). The renormalizing factors are caused by undulations (see eq 34)

$$J_E = \frac{e^{1/2\kappa^2 d^2}}{1 + \frac{1}{2}\kappa d^2 U^{-1}}$$
(41)

$$J_W = -1/4(U - D)^2 d^{-2} \log \left[1 - \frac{4d^2}{(U - D)^2} \right]$$
(42)

$$J_A = e^{d^2/2\xi^2}$$
(43)

$$J_S \equiv 1 \tag{44}$$

Equations 34, 40, and 41 have been introduced in ref 17; eqs 34-38, 40-42 have been reviewed in detail in ref 5. A secondary minimum can be established by solving the following equations

$$\frac{\partial F_{\text{tot}}}{\partial d} = \frac{\partial \bar{F}_{\text{S}}}{\partial d} + \sum_{i \neq S} \tilde{F}_i \frac{\partial J_i}{\partial d} = 0$$
(45)

$$\frac{\partial F_{\text{tot}}\left(U, \mathbf{d}(U)\right)}{\partial U} = \sum_{i} \frac{\partial \tilde{F}_{i} J_{i}}{\partial U} \bigg|_{d=\text{constant}} = 0 \quad (46)$$

Application to the Virial Coefficients of Xanthan (ref 7). Recently, Kawakami and Norisuye⁷ determined

Table 1. The Ratios R_2 and R_3 for Xanthan (ref 7)

ns (M)	λ (nm)	D _{eff} (nm)	R_2	R_3	H	η_2	<i>R</i> ′3	H'
1.0	0.30	2.6	0.53	12	-	-	_	_
0.6	0.39	2.8	0.60	9	-	-	-	-
0.2	0.67	3.8	0.61	4	-	-	1	-
0.1	0.95	4.9	0.74	1.8	-	-	0.45	0.60
0.06	1.22	6.0	0.64	1.46	-	-	0.37	0.74
0.03	1.73	8.3	0.61	0.81	0.82	0.028	0.20	1.02
0.02	2.12	10.1	0.51	0.52	1.17	0.040	0.13	1.25
0.01	3.0	14.5	0.64	0.38	1.84	0.041	0.10	1.91
0.007	3.5	17.0	0.56	0.22	2.34	0.043	0.06	2.38
0.005	4.2	20.6	0.49	0.122	3.21	0.043	0.03	3.24

 A_2 and A_3 , the macroscopic second and third virial coefficients of aqueous solutions of reasonably monodisperse xanthan as a function of the concentration of added sodium chloride. Since the theory of long-range attraction is approximate and sensitive to the precise choice of input parameters, the best policy is to gauge the extent of attractive forces from the experimental data, if possible.

First, I evaluate the following ratios defined with respect to the theoretical virials as if there were no attractive forces (see eqs 15 and 27; note that end effects are included in $B_{\rm el}$ but not in $C_{\rm el}$). This procedure presupposes that the electrostatic theory for the effective diameter is in good shape¹⁹⁻²¹

$$R_2 = \frac{M^2 A_2}{N_{\rm A} B_{\rm el}} \tag{47}$$

$$R_3 = \frac{M^3 A_3}{N_A^2 C_{\rm el}} \tag{48}$$

Here, M is the xanthan molar mass and N_A is Avogrado's number. If attractive forces are indeed absent or negligible, A_2 should scale as D_{eff} and A_3 as D_{eff}^3 and both R_2 and R_3 ought to be constant and close to unity. The effective diameter D_{eff} can be computed according to ref 21 using the accurate analytical solution to the nonlinear Poisson– Boltzmann equation developed by Philip and Wooding.²⁶ The following parameters pertain to xanthan:⁷ the bare radius a = 1.1 nm, the molar mass per unit contour length $M/L \approx 2.0$ kg/mol nm, the Bjerrum length Q = 0.714 nm at room temperature, and charge spacing 0.35 nm per electron charge.

The ratio $R_2 \approx 0.6$ is constant within experimental accuracy (See Table 1). It is less than unity, but this is to be expected in view of the neglect of semiflexibility in the theory.¹⁹⁻²¹ In principle, $B_{\rm el}$ should be corrected by the factor (1 - kL/P + ...) where k is an unknown constant and P is the persistence length equal to about 120 nm for xanthan²⁷ (In ref 7, $L \approx 110$ nm). Accordingly, it is reasonable to conclude that the experimental second virial coefficient A_2 can be understood within electrostatic theory¹⁹⁻²¹ without appeal to attractive forces, provided end effects²³ are taken into account.

By contrast, the ratio R_3 decreases systematically and very strongly with decreasing salt concentration, irrespective of the large margin of error in the scattering experiments.⁷ In view of the arguments presented in ref 16, one is immediately inclined to suspect the influence of weak attractive forces: they may have a considerable impact on A_3 yet merely perturb the second virial coefficient A_2 . In the present theory of long-range attraction, the magnitude of the parameter μ/α plays a crucial role in this respect.

Now, it is well to realize that the magnitudes of the theoretical coefficients C_{el} and C_A are not known to a high degree of precision. Then, the best option appears to be

Table 2. Critical Volume Fraction ϕ_{\bullet} at Which DNA Starts to Aggregate (refs 6 and 29); η_3 is Calculated with the Help of eq 33 and H is Obtained Iteratively from eq 30.

п _в (М)	<i>I</i> ∗ (M)	λ (nm)	D _{eff} (nm)	<i>ф</i> *	η_3	H
1	1.03	0.30	2.71	0.068	2.62	0.55
0.1	0.114	0.90	5.21	0.038	1.78	0.95
0.01	0.020	2.15	10.4	0.027	1.26	1.86

to let H be an adjustable parameter and force the quantity $R_3/(1-\eta_3)$ to equal unity (the anomalously large entries for R_3 in Table 1 at the two highest salt concentrations are disregarded). The resulting H values in Table 1 are quite insensitive to either the experimental accuracy⁷ of A_3 or the prefactors in the theoretical values for B_A and C_A . In fact, setting $R'_3 \equiv R_3/4$ (rather arbitrarily) leads to new H' values very close to the original ones. The reason is that η_3 is dominated by the Boltzmann factor mentioned earlier. Note that in Table 1 the respective values of η_2 are very small so that R_2 is indeed unperturbed by the attraction. Moreover, the dependence of η_3 on the effective diameter is convoluted, yet the series of H parameters is quite reasonable. Thus, the theory is internally consistent. The exponent m in eqs 5 and 6 turns out to equal about 1.5. If the first scenario were valid (see eq 5), h_1 would equal about 19; if the second (eq 6) were true, $h_2 \approx 103$.

In the macroscopic experiments on hydrophobic surfaces, ¹² the dimensionless coupling constant h is about 20. This is in good agreement with the first scenario $(h_1 \approx 19;$ eq 5). I tentatively conclude that a xanthan molecule perturbs the surrounding water molecules up to distances of order E.

Application to DNA Aggregation. Recently, isotropic solutions of 50 nm long DNA have been investigated by light scattering and cryomicroscopy^{6,29} at concentrations higher than studied previously. The DNA was found to aggregate reversibly even though all precautions were taken to ensure purity of the samples. In order to explain this phenomenon, we would need a comprehensive formal theory of rod aggregation. In principle, there must be a relation between solution thermodynamics and aggregation but this is obscure at present. Here, I adopt a naive point of view, simply equating the onset of thermodynamic instability with the onset of aggregation, and see whether eq 33 bears on the ionic-strength dependence of DNA aggregation at the critical DNA volume fraction ϕ^* (see Table 2). The values of the DNA parameters are contour length L = 50 nm, bare diameter D = 2a = 2 nm, Bjerrum length Q = 0.714 nm, and charge spacing along the axis 0.17 nm per electron charge. In view of "uncondensed" counterions arising from the DNA itself, the ionic strength I is not n_s but $I \approx n_s + 2\phi/\pi N_A Q D^2$. The H parameters are adjusted so as to satisfy eqs 3 and 33.

In Table 2 we see that H increases with decreasing ionic strength roughly as we expect, and its magnitude is about 1.5 times larger than the respective values for xanthan (Table 1). It would seem that $h \approx 30$ according to the first scenario. It is interesting to note that the postulated longrange attraction is able to rationalize a very puzzling problem: a lower onset of DNA aggregation with decreasing ionic strength.

Application to the Hexagonal Phase of TMV. The hexagonal mesophase³ of TMV was interpreted in terms of undulation theory⁵ but without long-range attraction $(H \equiv 0; H \text{ in ref 5 is } W \text{ in this paper})$. At low ionic strengths, the van der Waals force is too small by several orders of magnitude to explain the stability of the gels. For instance, the Hamaker constant needed to rationalize

Table 3. Theoretical Values of the Spacing U, Undulations Scaled by the Debye Length κd , and the Free Energy LF_{tot} of a TMV Particle, at the Secondary Minimum

ns	λ	кd	LF_{tot}	U	U _{exp}	ΔU_{exp}
(M)	(nm)		($k_{\rm B}T$)	(nm)	(nm)	(nm) ^a
0.87	0.32	1.35	-34	19.8	22	2
0.096	1.0	0.97	-60	24.5	27	5
0.01	3.0	0.49	-83	34	35	7
0.001	9.5	0.58	-10	68	58	?

^a The experimental spacings U_{exp} of Millman et al.³ exhibit a large variation $\pm \Delta U_{exp}$; only one spacing was measured at the lowest ionic strength.

the interaxial spacing at 10^{-3} M would have to be an absurdly high $10^4 k_{\rm B} T$.

For TMV, I set the bare diameter D = 18 nm, length L = 300 nm, persistence length $P = 10^4$ nm, scaled Hamaker constant W = 0.6 and linear charge density = 14 nm^{-1} (see ref 5). Since $D > \xi$, one expects $H \approx h\lambda a\xi^{-2}$ as in eq 2. If h is set equal to about 40, the data of Millman et al.³ are compatible with the analysis of eqs 35-46 (See Table 3). The undulation enhancement is strong at 1 M despite the stiffness of TMV, as has been argued before.⁵

Concluding Remarks

I have shown that the long-range attraction given by eq 3 is able to rationalize the virial anomaly of xanthan (coupling constant $h \approx 20$), the perplexing stability of TMV gels ($h \approx 40$) and the remarkable aggregation of DNA (h ≈ 30). I point out that: (1) there has been no tampering with parameters except for the adjustment of H (or h); (2) the theories are uniformly valid with respect to the ionic strength even though the electrostatic interaction varies very strongly; (3) given the present theories and experiments, it is very difficult to see how the additional interaction one would need to postulate could be other than attractive and of long range. A value of $h \approx 20$ may be inferred from the proposal by Christenson et al.¹² which is a summary of a fair number of experiments on coated surfaces. I conclude that there is a long-range attraction which fits a diverse variety of data in aqueous solutions. Its origin, hydrophobic or otherwise, is obscure at present.

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Note added in proof: Preliminary calculations (setting h = 40) by Henk Lekkerkerker and myself show that eq 3, when suitably adapted for the interaction between two platelets, is able to "explain" the spacings of lithium and *n*-butylammonium vermiculite $clays^{32-34}$ except at very low ionic strengths ($n_{\rm s} < 0.0025$ M). It has been pointed out a number of times in the past^{33,35} that conventional van der Waals forces offer an unconvincing resolution for the swelling of vermiculite where edge interactions are thought to be unimportant.

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