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# Undulation-enhanced electrostatic forces in hexagonal polyelectrolyte gels

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#### Abstract

A self-consistent theory is developed for the hexagonal phase of semiflexible polyelectrolytes. The electrostatic interactions analyzed in the Poisson-Bolzmann approximation, couple non-linearly to the undulations of the polyions so that the intermolecular forces may be enhanced by an order of magnitude. The theory is in good agreement with the osmotic stress measurements on DNA by Podgornik et al. It also seems to bear on unresolved discrepancies arising in stress experiments on tobacco mosaic virus and muscle thin filament.

Keywords: Polyelectrolyte gels; Undulation-enhanced electrostatic forces; Hexagonal phase theory

## 1. Introduction

The osmotic stress technique [1] allows one to monitor the intermolecular forces between hexagonally packed biopolymers as a function of their mean spacing which is measured by X-ray diffraction. The method has been applied to cylindrical gels of stiff macromolecules like tobacco mosaic virus (TMV) [2-4], muscle filaments [3,4] DNA [5-7], xanthan [8] and schizophyllan [8]. Under conditions where the electrostatic interactions may be presumed to dominate, the measured forces [2-4,6] are often an order of magnitude greater than expected on the basis of the non-linear Poisson-Bolzmann equation. This equation is certainly not exact but the effect of ion correlations [9] appears way too small to rationalize the discrepancy. Besides, it should be explained why the Poisson-Boltzmann equation sometimes does work and at other times does not.

Podgornik and Parsegian [10] argued that chain fluctuations would give rise to an enhanced decay length. They hypothesized that the semiflexible macromolecule could be modeled by a Gaussian chain enclosed in a non-fluctuating tube. Their model agrees with their data [6] on DNA provided the step length is adjusted to about 4 nm. This turns out to be close to an *a priori* estimate of the deflection length [11]. Podgornik and Parsegian's treatment goes some way toward a qualitative explanation of the enhancement of the intermolecular forces. The problem with their calculation is of course that the Gaussian step length of DNA is not 4 nm but actually about 100 nm. Furthermore, in practice [1-8], the effective tube in hexagonal biopolymer gels is of the order of the interchain spacing or perhaps even substantially less; so thin in fact that the stiff polyions undulate without folding along the long hexagonal axis (see Fig. 1). In effect, in this limit the



Fig. 1. (a) Undulating semiflexible polyions aligned along the long hexagonal z-axis, and (b) a section perpendicular to the z-axis. The points denote the intersection with the centerlines of polyion cylinders in the reference configuration, a perfect hexagonal array. Because of thermal motion the centerlines are displaced at any given moment. The origin of the (x, y)-axes is placed at the reference point of the test chain we focus attention on.

Gaussian chain model becomes completely invalid so one must resort to the wormlike chain model because scales much smaller than the persistence length are sampled in the configurational statistics. Moreover, since any one test chain experiences a fluctuating electric field exerted by its neighbours, we have to solve, in general, a formidable problem in statistical physics. Still, under certain conditions, the fluctuations may be rather small in some sense, so it becomes realistic to formulate a theory in which *all* the macromolecular fluctuations are treated self-consistently. Such a line of attack was adopted by the author in two recent studies on interacting surfaces [12,13]. In particular, the electrostatic potential in a stack of charged membranes was found to be modulated by the surface undulations in a highly non-linear fashion [13]. Here, the hexagonal gel of wormlike polyelectrolytes is investigated along similar lines in order to assess the magnitude of the undulation-enhanced electric forces.

## 2. Free energy of confinement

In principle it is possible to set up a complete self-consistent field theory of the hexagonal phase of wormlike chains in terms of a distribution function depending on both position and orientation of an infinitesimal segment of a test chain by extending refs. [14-16]. One complication is the geometry of the hexagonal lattice: another is the effect of electrostatic twist [15,17,24]. Fortunately, in the experiments [2-6] the orientational fluctuations of the chains turn out to be modest so that we may adopt a highly simplified approach. We assume the undulations are fairly weak in a manner to be quantified below (even so, they may still enhance considerably the electrostatic interaction, as we shall see). Hence, it is sensible to postulate a Gaussian distribution for the Cartesian position (x, y) of an infinitesimal segment of some particular chain we happen to focus on, defined with respect to its position in the reference configuration of the chain. The latter configuration is the one where there are no undulations, i.e. a straight rod parallel to the long hexagonal axis z.

$$G(x, y) = \pi^{-1} d^{-1} \exp\left[-(x^2 + y^2)/d^2\right] \qquad (1)$$

The coordinates x and y are defined within the plane perpendicular to the z-axis (Fig. 1). Fluctuations along the z-axis are disregarded. Because of the imposed self-consistency, eq. (1) pertains to all the chains in the array. Clearly, the variational parameter d must be much smaller than the interaxial spacing R of the hexagonal lattice otherwise the isotropic Gaussian distribution Gloses meaning. Equation (1) may be interpreted as a Boltzmann factor involving an effective harmonic potential; accordingly, we expect it to be valid in an asymptotic sense.

Equation (1) implies each wormlike chain is effectively confined within a cylindrical tube along the z-axis of approximate diameter d. If the polyion is semiflexible with a persistence length  $P(P \gg d)$ , the characteristic scale of the undulations along the z-axis is the deflection length [11]

$$\lambda = d^{2/3} P^{1/3} \tag{2}$$

The free energy per unit length of chain is given by [11,16,18]

$$\Delta F_{con} = ck_{\rm B}T/\lambda \tag{3}$$

where  $k_{\rm B}$  is Boltzmann's constant and T the absolute temperature, because  $\lambda$  is the sole relevant scale (and not P). The logarithmic factor of ref. [11] is spurious [15]; an estimate of the coefficient c is  $2^{-2/3}$  \*. Computer simulations by Dijkstra and Frenkel [19] for a worm trapped in a hard tube appear to bear out eq. (3). As d decreases the free energy of confinement is enhanced by an entropic effect: an increasing number of configurations is frozen out. In order to determine d, we next need an expression for the electrostatic repulsion which becomes smaller as d is diminished.

## 3. Electrostatic free energy

If the double layers between two neighboring chains interpenetrate, the mathematical problem of calculating the electric potential is very intricate, especially because the undulations couple strongly with the distribution of "condensed" counterions close to the polyion surfaces. If we wish to leave unperturbed the inner double layers surrounding the polyions in our array, we require that the lattice spacing R is typically larger than about  $D + 2d + 2\kappa^{-1}$  where  $\kappa^{-1}$  is the Debye screening length and D is the polyion diameter. In addition, we demand that the deflection length greatly exceeds  $\kappa^{-1}$  so a deflection segment behaves like a rod, electrostatically speaking. With these restrictions in mind, it becomes possible to make substantial headway since the electrostatic potential of interaction in the hexagonal array is determined in the main by the outer double layers of effectively rodlike sections.

It is expedient to write the far field of the electric potential  $\phi$  exerted by a cylindrical polyion beyond its inner double layer as [17]

$$\Psi(\kappa r) \sim 2\xi_{\text{eff}} K_0(\kappa r)$$

$$\sim \frac{(2\pi)^{1/2} \xi_{\text{eff}} e^{-\kappa r}}{(\kappa r)^{1/2}}$$
(4)

The dimensionless potential  $\psi \equiv q |\phi| k_B T$  felt by an elementary charge q at a distance r from the centerline of the polyion decays essentially as a zero-order modified Bessel function of the second kind when  $r \geq \frac{1}{2}D + \kappa^{-1}$ . The dimensionless charge parameter  $\xi_{eff} \equiv Qv_{eff}$  can be calculated within the nonlinear Poisson-Boltzmann approximation [20];  $Q \equiv q^2/\epsilon k_B T$  is the Bjerrum length and  $v_{eff}$  is the effective linear charge density i.e. the number of charges per unit length viewed along the polyion axis. The solvent which has a uniform permittivity  $\epsilon$ , contains excess monovalent electrolyte of concentration  $n_s$  so that the Debye length is given by  $\kappa^2 = 8\pi Qn_s$ .

Next, for stiff biopolymers the deflection length  $\lambda$  will be substantially greater than the variational parameter d (see eq. (2)). The polyions are virtually parallel to the long hexagonal axis. Then, the renormalized potential of a particular polyion i.e. the potential averaged over its undulations, at a distance s from its axis in the reference configuration is given by

$$\psi_{R}(\kappa s) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy G(x, y)$$
$$\times \psi \left( \kappa \left[ (s+y)^{2} + x^{2} \right]^{1/2} \right)$$
(5)

in view of eq. (1). Note that simple superposition applies because our concern is solely with the outer double layer, i.e. s which ultimately will be O(R), is much greater than both d and  $\kappa^{-1}$ . We now expand  $\kappa((s + y)^2 + x^2)^{1/2} = \kappa s + \kappa y$  $+ \frac{1}{2}\kappa x^2 s^{-1} + O(\kappa d^3 s^{-2})$  keeping in mind that we

<sup>\*</sup> This is obtained by a second moment condition  $\langle x^2 \rangle = \frac{1}{2}d^2$ i.e. we set  $\mu = \frac{1}{2}$  in eq. (13) of ref. [18]. Our estimate is approximate since the Helfrich distribution is not exactly Gaussian.

must retain the third term for it may sometimes be O(1). Equations (1), (4) and (5) then yield tot leading order

$$\psi_{R}(\kappa s) \sim \frac{(2\pi)^{1/2} \xi_{\text{eff}} \exp\left(-\kappa s + \frac{1}{4}\kappa^{2}d^{2}\right)}{(\kappa s)^{1/2} \left(1 + \frac{1}{2}\kappa d^{2}s^{-1}\right)^{1/2}} \qquad (6)$$

This exhibits a potentially large renormalizing factor  $\exp \frac{1}{4}\kappa^2 d^2$ .

In view of the screening, a test polyion in a certain configuration experiences on the average only six potentials  $\psi_R$  exerted by its six neighbours in the hexagonal lattice. If we now average over all the undulations of the test macro-molecule, we derive the lead term for the electrostatic free energy of interaction per unit length of polyion \*

$$\Delta F_{\rm el}/k_{\rm B}T = 3v_{\rm eff} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy G(x, y) \\ \times v_{R} \Big( \kappa \Big[ (R+y)^{2} + x^{2} \Big]^{1/2} \Big) \\ \sim \frac{3(2\pi)^{1/2} \xi_{\rm eff}^{2} \exp(-\kappa R + \frac{1}{2}\kappa^{2}d^{2})}{Q(\kappa R)^{1/2} (1 + \frac{1}{2}\kappa d^{2}R^{-1})}$$
(7)

Note that a second renormalization has taken place with respect to eq. (6).

## 4. Minimization of the total free energy

The correct variational principle is as follows: we have to minimize the total Helmholtz free energy  $F_{\text{tot}} = \Delta F_{\text{con}} + \Delta F_{\text{el}}$  with respect to d at a fixed volume of the system i.e. at a fixed spacing R of the polyelectrolyte gel. Equations (3) and (7) then yield to the leading order

$$\frac{d^{8/3} e^{\frac{1}{2}\kappa^2 d^2}}{\left(1 + \frac{1}{2}\kappa d^2 R^{-1}\right)} = \frac{2cQR^{1/2} e^{\kappa R}}{9(2\pi)^{1/2} \xi_{\text{eff}}^2 P^{1/3} \kappa^{3/2}}$$
(8)

The osmotic pressure  $\pi_{os}$  is derived by using an expression valid for an hexagonal gel [5]

$$\pi_{\rm os} = -\frac{\partial F_{\rm tot}(d(R), R)}{3^{1/2}R \ \partial R} \tag{9}$$

The contribution from the implicit differentiation vanishes. Hence, we have

$$\pi_{\rm os} = \frac{2ck_{\rm B}T}{3^{3/2}\kappa Rd^{8/3}P^{1/3}} \tag{10}$$

where d has to be determined numerically from eq. (8). The relative error in eqs. (7), (8) and (10) is estimated to be of order  $d/\lambda$  or  $(d/P)^{1/3}$  and is caused by the neglect of orientational fluctuations in the electric repulsion.

## 5. Discussion

Equation (8) shows a strong non-linear coupling of electrostatic interactions and chain undulations through the renormalizing factor  $\exp \frac{1}{2}\kappa^2 d^2$ . This factor arises for two reasons: (1) the six worms surrounding a test polyion undulate; and (2) the test chain itself undulates too. It is remarked that the correlations among the respective configurational fluctuations are here accounted for only in a mean-field fashion via the Ansatz eq. (1). When the persistence length becomes large, the "tube diameter" d in eq. (8) becomes much smaller than the Debye length  $\kappa^{-1}$  so that eq. (10) reduces to the pressure exerted by an hexagonal array of perfectly rigid, cylindrical polyions [3], as it should. When the "tube diameter" is of the order of the Debye length, the pressure is substantially enhanced but the import of the non-linear eq. (8) is best gauged

## 5.1 DNA in aqueous NaCl

in a comparison with experiments.

Podgornik et al. [16] converted the experimentally determined osmotic pressure for DNA gels to the force f per unit length exerted on one DNA molecule by a neighbouring chain

$$f = 3^{-1/2} R \pi_{\rm os} \tag{11}$$

<sup>\*</sup> In eq. (7) a factor of 3 occurs instead of 6 because we have to correct for doublecounting: if we neglect end effects, there are 3M pairs of interacting macromolecules in an hexagonal array of M polyions.

Table 1

The theoretical values of the force per unit length f (dynes cm<sup>-1</sup>) compared with the experimental results  $f_{exp}$  of Podgornik et al. [6] (estimated from their Fig. 2) as a function of the interaxial spacing R, for DNA in 2 M salt. ( $\kappa^{-1} = 0.21$ nm;  $\xi_{eff} = 365$ ). The values of f if DNA were supposed infinitely stiff are given in parentheses. The effect of undulations is also monitored by the parameter  $\kappa d$ .

	<i>R</i> (nm)			
	3.0	3.5	4.0	
кd	0.96	1.70	2.45	
f	2.3 (1.5)	0.50 (0.13)	0.19 (0.11)	
$f_{\rm exp}$	2.5	1.0	0.32	

They obtained f as a function of the interaxial spacing R of the hexagonal DNA gel at a temperature T of 293 K. The Bjerrum length Q is then 0.72 nm and  $\kappa^{-1} = 0.30 n_s^{-1/2}$  nm if the NaCl concentration  $n_s$  is given in moles per liter. Estimates of their f are displayed in Tables 1 and 2 together with theoretical predictions calculated from eqs. (8), (10) and (11) employing the following representative values for the DNA parameters: linear charge density v = 1 charge per 0.17 nm, or  $\xi = 4.2$ ; diameter D = 2.4 nm; persistence length P = 50 nm. The effective charge parameter  $\xi_{\text{eff}} = Qv_{\text{eff}}$  has been evaluated in accordance with the procedure outlined in ref. [17] using the

Table 2

As in Table 1 but for NaCl concentrations,  $n_s$ : 0.8 M ( $\kappa^{-1}$  = 0.34 nm,  $\xi_{eff}$  = 45.6), 0.4 M ( $\kappa^{-1}$  = 0.47 nm,  $\xi_{eff}$  = 17.7), 0.3 M ( $\kappa^{-1}$  = 0.55 nm,  $\xi_{eff}$  = 12.3) and 0.2 M ( $\kappa^{-1}$  = 0.67 nm,  $\xi_{eff}$  = 8.4).

n <sub>s</sub> (M)		<i>R</i> (nm)			
		4.0	4.5	5.0	
0.8	кd	1.32	1.80	2.27	
	f	0.44 (0.19)	0.19 (0.042)	0.10 (0.009)	
	ferm	0.50	0.35	0.17	
0.4	кd	0.83	1.14	1.48	
	f	0.89 (0.63)	0.38 (0.21)	0.19 (0.07)	
	, fexn	0.63	0.45	0.32	
0.3	кd	0.67	0.90	1.17	
	f	1.21 (0.9)	0.55 (0.37)	0.27 (0.14)	
	fexn	0.79	0.56	0.45	
0.2	кd	0.52	0.68	0.87	
	f	1.71 (1.5)	0.83 (0.65)	0.43 (0.31)	
	$f_{\rm exp}$	1.12	0.63	0.50	

analytical calculations of Philip and Wooding [20]. In order to assess the influence of undulations. the predicted values of f for infinitely stiff polyions  $(P = \infty)$  have also been presented. The present theory incorporating undulations is in quite good agreement with the experiments on DNA [6] if we consider that no adjustable parameters have been used. Recall that the double-layer interaction is not always in perfect agreement with other experiments [21-23] even though undulations are expected to have a negligible effect when positional order is absent. Had we assumed the undulation enhancement to be non-existent  $(P = \infty)$  in the experiments at hand [6], we would have been at a loss to explain several of the anomalously low values of the force in Tables 1 and 2. The entry in Table 2 at 0.2 M and 4 nm separation may appear bothersome, but at this stage the double layers are starting to overlap so we are pushing the theory beyond its range of validity. For this reason the present author has not included data [6] for smaller R.

Another item of interest is that the values of drange from about 0.2 to 0.8 nm which is in fair agreement with the variation (0.3 to 0.9 nm) in the lattice fluctuations determined by Podgornik et al. [6] from the peak widths of the X-ray scattering. On the whole, it appears that the undulation-enhancement theory is on the right track for a biopolymer like DNA of medium stiffness. The restrictions inherent in the theory are adhered to in this case. In particular, the orientational fluctuations are always small (angle  $= d/\lambda = (d/P)^{1/3} \ll 1$  and  $d\kappa$  never greatly exceeds unity. The polyions are essentially parallel so the twisting force [15,17,24] should not appear (twist becomes important when the angle between two polyions becomes larger than  $1/\kappa\lambda$  for thin rods or  $D^{1/2}/\kappa^{1/2}\lambda$  for thick rods).

# 5.2 TMV in sodium phosphate buffer

The compressibility of TMV gels is reasonably well comprehended in terms of pure double layer and dispersion interactions [2–4]. However, at high ionic strengths anomalics occur for the osmotic pressure is systematically higher than expected. This is the regime where undulation enhancement of the electric forces, if applicable, should make its presence felt. Using parameter values typical of the buffered TMV gels [2] (D =18 nm, R = 21 nm, Q = 0.71 nm,  $\kappa^{-1} = 0.32$  nm and v = 70 nm<sup>-1</sup>), we obtain a pressure of 7 Torrs from eqs. (8) and (10) assuming an infinite persistence length, which increases to 28 Torrs if we set P equal to  $10^4$  nm. The latter value for Pis not unreasonable judging from the very slight undulations of TMV discernible in electron micrographs. The theory seems to rationalize somewhat the value of 40 Torrs found by Millman et al. [2]. We tentatively conclude that minute undulations in TMV may lead to experimentally observable effects.

## 5.3 Muscle thin filaments in KCl buffer

Millman has reviewed the  $\pi_{os}$ -R curves of various hexagonal muscle gels [4]. The experimental slope of <sup>10</sup>log  $\pi_{os}$  versus R is about -0.35 with slight variations depending on the type of muscle, whereas the Poisson-Bolzmann theory for an hexagonal array of rigid cylinders predicts a slope of about -0.65. Is enhancement of the electric forces by undulations possible in this case?

For instance, for a muscle thin filament discussed by Millman [4], we may set D = 9 nm,  $\nu = 15$  nm<sup>-1</sup>, Q = 0.71 nm,  $\kappa^{-1} = 0.80$  nm and  $\xi_{\rm eff} = 650$ . In Table 3, we show the pressures predicted by eq. (10) for several persistence lengths (the author is not aware of any measured P). At a spacing of 10 nm, the double layers

#### Table 3

The osmotic pressure  $\pi_{os}$  (in Torrs) versus the spacing R for muscle thin filament [4]. There are three sets of theoretical estimates depending on the persistence length P. The bottom entries are experimental figures taken from Fig. 2 of ref. [4] (no P value communicated)

P (nm)	<i>R</i> (nm)			
	10	15	17	
	104	10	0.8	
104	10 <sup>4</sup>	21	4.8	
10 <sup>3</sup>	104	28	7.6	
	$2 \cdot 10^{3}$	<b>~</b> 40	~ 20	

overlap so one expects the theory to break down, as it does in fact. At larger separations, undulations of the filaments may well enhance the electrostatic interactions. The magnitude of the pressure is clearly underestimated, though for  $P = 10^3$ nm the slope levels to -0.4 at large spacings, close to the experimental one.

## 6. Concluding remarks

In summary, whenever the unenhanced Coulomb repulsion is too low by an order of magnitude to explain the osmotic stress experiments on hexagonal biopolymer lattices, undulation of the charged chains turn out to be strong enough to enhance the predicted stress significantly. It is not hard to understand this enhancement effect qualitatively. At high salt concentrations, a slight deflection in a stiff chain of about one tenth of a nanometer is all that is needed to interfere with the screening because the Debye shielding length is small also. The screening is then diminished for there are a substantial number of configurations where a test polyion is closer to one or more others in the hexagonal array. Such minuscule undulations may occur even if the biopolymer is extremely stiff. At the other extreme, the details of the undulating chains become irrelevant at very low ionic strength so the electrostatic forces are not enhanced in that case.

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