

Charge-Fluctuation Forces between Rodlike Polyelectrolytes: Pairwise Summability Reexamined

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We formulate low-frequency charge-fluctuation forces between charged cylinders, parallel or skewed, in salt solution. At high-salt concentrations, forces are exponentially screened. In low-salt solutions, dipolar fluctuation energies go as R^{-5} or R^{-4} ; monopolar energies vary as R^{-1} or $\ln R$, where R is the minimal separation between cylinder axes. The most important result is not the derivation of long-sought pair potentials but rather the demonstration that pairwise summability of rod-rod ion-fluctuation forces is easily violated under low-salt conditions. [S0031-9007(97)05263-0]

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Models of assembly by rodlike particles such as DNA, tobacco mosaic virus, microtubules, or filamentous bacterial viruses often require closed-form expressions for molecular interaction. In addition to brute steric forces, hydration forces, and electrostatic double layer interactions [1] between charged rods, there are interactions of correlated charge fluctuations [2]. Most generally, these fluctuations can be either the dipolar events of traditional van der Waals forces [3] or monopolar charge fluctuations from transient changes in the density of mobile ions around a charged particle. The study of monopolar charge fluctuations in molecular interactions has a venerable history [4] with approximate but explicit formulation of fluctuation forces between two parallel polyelectrolyte rods [5], as well as more sophisticated and versatile analyses [6].

Between like particles, these correlated-fluctuation forces are attractive. There is always a question, though, whether one is allowed to compute these attractive forces in molecular arrays as though they were the sum of individual rod-rod interactions. The purpose of this paper is to assess the limits of validity of the pairwise additivity assumption in rod-rod fluctuation attraction with or without the added salt, as well as to derive the form of the effective fluctuation pair potential in parallel and skewed geometries, basing the theory of correlation attraction on the Lifshitz-Pitaevskii approach [3]. The perspective of this approach lets one speak of ion density fluctuations that extend simultaneously over many rodlike particles. The nonadditivity of rod-rod interactions in arrays, as addressed in this paper, is different and distinct from the nonadditivity of interactions between segments of rods in a two-rod theoretical framework [2].

We find that the conditions for the validity of pairwise additivity in an array can be quite restrictive. The ranges of validity of different theories [2,5] that formalize rod-rod counterion correlation forces are thus practically limited if the interacting polyelectrolytes are part of an ordered array or in a solution. We stress that the nonadditivities studied here are of a nature different from those encountered in analyses of electrostatic forces between charged surfaces

either via the solution of Poisson-Boltzmann equation or through more sophisticated statistical mechanical approximations [7,8]; nonadditivity in the present case does not depend on the amount of charge or magnitude of the mean electrostatic potential on the interacting particles. The interactions we are studying here are due to long wavelength mobile charge density fluctuations—similar to those discussed in qualitative terms in [9]—that can extend over many individual polyelectrolyte molecules.

The Lifshitz-Pitaevskii approach [3,10] begins with an artificial but easily formulated interaction between arrays of cylindrical rodlike molecules. Specifically, we examine the van der Waals (vdw) attraction between two like anisotropic media, \mathcal{L} and \mathcal{D} , containing parallel cylindrical particles embedded in a medium m (Fig. 1). \mathcal{L} and \mathcal{D} are separated by an isotropic region of salt solution devoid of cylinders. Pair potentials between individual particles in \mathcal{L} and \mathcal{D} are extracted in a dilute rod limit.

The anisotropic regions are composites of parallel cylindrical rods of effective dielectric cross section πa^2 at volume fraction $v = N\pi a^2$; N is the cross-sectional number density of N rods per unit area. The cylinders of dielectric material c have anisotropic intrinsic susceptibilities ϵ_{\perp}^c and ϵ_{\parallel}^c , perpendicular and parallel to the rod axis. For each region $r = \mathcal{L}, m, \mathcal{D}$ the effective dielectric and ionic properties of the composites can be written in terms of their local values. In this construction the axis parallel to the rod in region \mathcal{D} is rotated about axis z to create an angle θ with respect to the rod x axis in \mathcal{L} .

Because ionic fluctuations are slow [3], we consider only “zero-frequency” van der Waals interactions, describing thermal as opposed to quantum fluctuations. The wave equations in media $r = \mathcal{L}, m, \mathcal{D}$ follow

$$\nabla[\epsilon\nabla\phi(\mathbf{r})] = \frac{4\pi n_r e^2}{kT} \phi(\mathbf{r}), \quad (1)$$

where $\phi(\mathbf{r})$ is the electrostatic potential, with $n_r = \sum_Z Z^2 n_r(Z)$; and $n_r(Z)$ is the average number density of ions of valence Z taken over each region r . The average can be computed from an appropriate microscopic

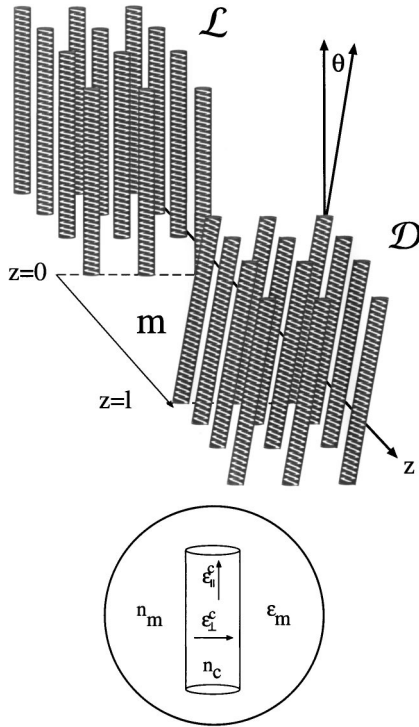


FIG. 1. Array-interaction geometry. Region \mathcal{L} is confined to $z < 0$, region \mathcal{D} to $z > l$; isotropic region m is the slab in between. The cylindrical array in \mathcal{D} is rotated about the z axis by an angle θ with respect to \mathcal{L} . Not only the dielectric constants of the composite media \mathcal{D} and \mathcal{L} but also the dielectric constants of the cylindrical rods (bottom) themselves are anisotropic; ϵ_{\parallel}^c , ϵ_{\perp}^c , n_c refer to the cylinder material.

model of mean ion distributions or taken from measured ion content of polyelectrolyte suspensions. For regions \mathcal{L} and \mathcal{D} , we distinguish the densities of mobile ions n_c associated with cylinders and n_m in the intervening space, respectively. For univalent counterions $n_c \pi a^2$ equals the linear density of fixed charges per unit length of the cylinder. The volume average $n_{\mathcal{L}}$ and $n_{\mathcal{D}}$ over the whole composite is $n_{\mathcal{L}} = n_{\mathcal{D}} = n_c v + n_m(1 - v) = n_m + v(n_c - n_m)$. The dielectric susceptibility tensor ϵ^r is taken only in the limit of zero frequency. For the composite regions $r = \mathcal{L}$ and \mathcal{D} ϵ^r has diagonal elements ϵ_x^r , ϵ_y^r , ϵ_z^r , with the axes x and y of \mathcal{D} rotated by an angle θ . For small enough volume fractions v , the components of the unrotated tensors for the composite media are [11] $\epsilon^{\mathcal{L}}$ and $\epsilon^{\mathcal{D}}$, where $\epsilon_{\parallel} = \epsilon_x^{\mathcal{L}} = \epsilon_x^{\mathcal{D}} = \epsilon_m(1 - v) + v\epsilon_{\parallel}^c = \epsilon_m(1 + v\Delta_{\parallel})$, $\epsilon_{\perp} = \epsilon_y^{\mathcal{L}} = \epsilon_y^{\mathcal{D}} = \epsilon_z^{\mathcal{D}} = \epsilon_m \left(\frac{1 + v\Delta_{\perp}}{1 - v\Delta_{\perp}} \right)$ with $\Delta_{\parallel} = \frac{\epsilon_{\parallel}^c - \epsilon_m}{\epsilon_m}$, $\Delta_{\perp} = \frac{\epsilon_{\perp}^c - \epsilon_m}{\epsilon_{\perp}^c + \epsilon_m}$, and $\Gamma = \Delta_{\parallel} - 2\Delta_{\perp}$. ϵ_m is the isotropic susceptibility in region m and in between cylinders in \mathcal{L} and \mathcal{D} ; superscript c refers to the response of the cylinder material. Because solutions of the wave equation require continuity of $\epsilon \nabla \phi$ perpendicular to the interfaces at $z = 0$ and l , it is the perpendicular response of $\epsilon^{\mathcal{L}}$ and $\epsilon^{\mathcal{D}}$ that determines the ionic screening lengths in both semi-

infinite regions. For small enough volume fractions v the inverse squared screening lengths in \mathcal{L} and \mathcal{D} are

$$\frac{4\pi n_{\mathcal{L}} e^2}{\epsilon_{\perp} kT} = \frac{4\pi n_{\mathcal{D}} e^2}{\epsilon_{\perp} kT} \approx \kappa^2 \left[1 + v \left(\frac{n_c - n_m}{n_m} - 2\Delta_{\perp} \right) \right],$$

where $\kappa^2 = \kappa_m^2 = \frac{4\pi n_m e^2}{\epsilon_m kT}$ is the square of the standard inverse Debye screening length in the region m .

The zero-frequency vdW interaction free energy per unit area between the two anisotropic semi-infinite regions \mathcal{L} and \mathcal{D} across a slab m of thickness l is [3]

$$\mathcal{F}(l, \theta) = \frac{kT}{8\pi^2} \int_0^{2\pi} d\psi \times \int_0^{\infty} \ln[1 - \Delta^2(\theta, \psi) e^{-2\sqrt{Q^2 + \kappa^2} l}] Q dQ, \quad (2)$$

where $\Delta^2(\theta, \psi) = \Delta_{\mathcal{L}m}(\psi) \Delta_{\mathcal{D}m}(\theta - \psi)$. To take account of anisotropy, ψ is for angular integration over all directions in radial wave vectors \mathbf{Q} . The functions $\Delta_{\mathcal{L}m}(\psi)$ and $\Delta_{\mathcal{D}m}(\theta - \psi)$ can be obtained in the standard way [3]. For small enough values of v , they can usually be expanded to terms linear in cylinder volume fraction v . To lowest order in density, the interaction energy goes as N^2 . In this dilute limit, rods in the two media interact pairwise across the gap l .

Extraction of the pairwise interaction potential follows one of two procedures, depending whether the rods in \mathcal{L} and \mathcal{D} are parallel ($\theta = 0$) or skewed. We connect the per-unit-area interaction $\mathcal{F}(l, \theta)$ between planar regions of embedded cylinders with the pair interaction potential $\mathcal{G}(l, \theta)$ between skewed cylinders or the pair interaction energy per unit length $g(l)$ between parallel cylinders. Note that \mathcal{G} and g have different units and are not always simply related (see below).

A sufficient condition for connecting the forces between two semi-infinite dilute macromolecular arrays and the corresponding pair potentials between macromolecules is that $\mathcal{F}(l, \theta)$ can be accurately expressed by the first, quadratic term in a series expansion in density N or volume fraction v . The Pitaevskii *ansatz* can be applied in two forms [10]. For *skewed* cylinders at a mutual angle θ , the connection is

$$\lim_{N \rightarrow 0} \frac{d^2 \mathcal{F}(l, \theta)}{dl^2} \Big|_{l=R} = N^2 \sin \theta \mathcal{G}(R, \theta), \quad (3)$$

while for *parallel* cylinders the connection is an Abel transform

$$\lim_{N \rightarrow 0} \frac{d^2 \mathcal{F}(l, \theta = 0)}{dl^2} \Big|_{l=R} = N^2 \int_{-\infty}^{+\infty} g(\sqrt{R^2 + y^2}) dy. \quad (4)$$

In both cases R is the minimal separation between the cylinder axes.

Expanding $\mathcal{F}(l, \theta)$ in Eq. (2) to the second order in v one obtains from Eq. (3) for *skewed* cylinders the relation

$$\mathcal{G}(R, \theta) = -\frac{kT}{2\pi^2} \frac{\kappa^4(\pi a^2)^2}{\sin \theta} \int_1^\infty p^3 dp e^{-2\kappa R p} \int_0^{2\pi} \Delta'^2(\theta, \psi) d\psi, \quad (5)$$

with $\Delta'^2(\theta, \psi) = \frac{\partial \Delta_{Lm}(\psi)}{\partial v} \frac{\partial \Delta_{Dm}(\theta - \psi)}{\partial v}$, while for *parallel* cylinders with the inverse Abel transform Eq. (4) gives

$$g(R) = -\frac{kT}{\pi^3} \kappa^5(\pi a^2)^2 \int_1^\infty p^4 dp K_0(2\kappa R p) \int_0^{2\pi} \Delta'^2(\theta, \psi) d\psi, \quad (6)$$

where $K_0(x)$ is the modified Bessel cylindrical function of order 0. There is no simple limit relating Eqs. (5) and (6), i.e., the skewed interaction energy and the parallel interaction energy per unit length for the case of infinitely long cylinders cannot be obtained from a continuous limiting process. Both skewed and parallel cases reflect three types of charge fluctuations, written as separate lines in Eqs. (7),(8): dipole-dipole, dipole-monopole, and monopole-monopole.

In the limit of *vanishing salt concentration in the medium*, $\kappa R \rightarrow 0$ and with $F(\theta) = (2 \cos^2 \theta + 1)/2^7$

$$\begin{aligned} \mathcal{G}(R, \theta) &\cong -\frac{3kT}{8\pi} (\pi a^2)^2 \left[\Delta_\perp^2 + \frac{1}{4} \Delta_\perp \Gamma + \Gamma^2 F(\theta) \right] \frac{1}{\sin \theta R^4} + \frac{kT}{4\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right) \left[\Delta_\perp + \frac{1}{8} \Gamma \right] \frac{1}{\sin \theta R^2} \\ &\quad + \frac{kT}{4\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right)^2 \frac{\ln(2\kappa R)}{\sin \theta} \\ g(R) &\cong -\frac{9kT}{32\pi} (\pi a^2)^2 \left[\Delta_\perp^2 + \frac{1}{4} \Delta_\perp \Gamma + \Gamma^2 \frac{3}{2^7} \right] \frac{1}{R^5} + \frac{kT}{8\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right) \left[\Delta_\perp + \frac{1}{8} \Gamma \right] \frac{1}{R^3} \\ &\quad - \frac{kT}{8\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right)^2 \frac{1}{R}. \end{aligned} \quad (7)$$

When all salt concentrations equal zero, interactions come only from differences in dielectric susceptibility. All monopolar terms vanish to leave only dipolar terms [10]. Equation (7) has already been derived and discussed [3].

In the opposite case of *strong ionic screening*, $\kappa R \gg 1$, the only terms surviving are those of longest range that nevertheless decay exponentially.

$$\begin{aligned} \mathcal{G}(R, \theta) &\cong -\frac{8kT}{\pi} \kappa (\pi a^2)^2 \Gamma^2 F(\theta) \frac{e^{-2\kappa R}}{\sin \theta (2R)^3} - \frac{kT}{2\pi} \kappa^2 (\pi a^2)^2 \Gamma \left(\frac{n_c - n_m}{2n_m} \right) \frac{e^{-2\kappa R}}{\sin \theta (2R)^2} \\ &\quad - \frac{kT}{\pi} \frac{\kappa^3 (\pi a^2)^2}{\sin \theta} \frac{e^{-2\kappa R}}{(2R)} \left(\frac{n_c - n_m}{2n_m} \right)^2 \frac{e^{-2\kappa R}}{\sin \theta (2R)} \\ g(R) &\cong -\frac{16\sqrt{2}kT}{\pi^{5/2}} \kappa^5 (\pi a^2)^2 \left[\Delta_\perp^2 + \frac{1}{4} \Delta_\perp \Gamma + \Gamma^2 \frac{3}{2^7} \right] \frac{e^{-2\kappa R}}{(2\kappa R)^{7/2}} \\ &\quad + \frac{8\sqrt{2}kT}{\pi^{5/2}} \kappa^5 (\pi a^2)^2 \left(\Delta_\perp + \frac{\Gamma}{16} \right) \left(\frac{n_c - n_m}{2n_m} \right) \frac{e^{-2\kappa R}}{(2\kappa R)^{5/2}} \\ &\quad - \frac{2\sqrt{2}kT}{\pi^{5/2}} \kappa^5 (\pi a^2)^2 \left(\frac{n_c - n_m}{2n_m} \right)^2 \frac{e^{-2\kappa R}}{(2\kappa R)^{3/2}}. \end{aligned} \quad (8)$$

When all ϵ 's are *equal* but when there are differences in ionic densities n_c and n_m , only monopolar terms endure. For this case in 0.1 M uni-univalent salt and with monovalent counterions the interaction between two rods at right angle would amount to at the most a fraction of kT at a surface to surface separation of one Debye length or to $\sim kT$ per persistence length if parallel. This is at least about an order of magnitude smaller than other interactions (hydration and electrostatic) [12]. Higher valency counterions, however, would give much larger interactions, proportional to Z^4 .

There is a curious further limit—*unscreened monopole-monopole correlated fluctuations*—where $n_m \rightarrow 0$ but cylinders still carry counterions n_c ,

$$\mathcal{G}(R, \theta) \cong \frac{kT}{4\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right)^2 \frac{\ln(R)}{\sin \theta} \quad (9)$$

(to within additive constants) and

$$g(R) \cong -\frac{kT}{8\pi} (\pi a^2)^2 \left(\frac{4\pi n_c e^2}{\epsilon_m kT} \right)^2 \frac{1}{R}. \quad (10)$$

In the case of DNA even for monovalent counterions these forces would be quite large, amounting to $\sim 500kT$ per persistence length at near contact, overshadowing all other interactions [12]. We now show why this particular limit is in fact unattainable and why Eqs. (9) and (10) give severe overestimates for the correlation interactions.

The $n_m \rightarrow 0$ form for parallel rods has been obtained analytically [5] before and is also closely related to recent

results [2,13], provided the counterion liquid structure factor introduced in [2] is a constant. This correspondence is quite along the line of our present understanding of the state of condensed counterions [14], as well as completely consistent with recent direct measurements of the counterion structure function in DNA arrays [15].

When can one assume pairwise additivity? The central requirement of the Pitaevskii construction is to create composite media whose dielectric properties are linear in N . The interaction between composites then goes as N^2 . With salt solutions, requisite dependence on the square of densities requires [Eq. (2)]

$$v \left| \frac{(n_c - n_m)}{n_m} - 2\Delta_{\perp} \right| \ll 1. \quad (11)$$

What kind of restriction does this inequality impose for pairwise summability of ionic fluctuation forces in an array? We can read condition Eq. (11) (for simplicity we set $\Delta_{\perp} = 0$) as saying that there is only a small relative difference in the total density of ions in the regions with and without polyelectrolytes. Setting $n_c \pi a^2 \sim b^{-1}$ and taking $v \sim (\frac{a}{R})^2$ we have

$$n_m \gg n_c \frac{v}{1+v} \gg \frac{1}{b\pi(R^2 + a^2)} \quad (12)$$

with b the length per unit fixed charge along the rod surface ($b = 1.7 \text{ \AA}$ for DNA). We can thus estimate the salt concentration at which for different values of R pairwise additivity seriously breaks down. For R in the range where spontaneous DNA aggregation is observed [16], we find that pairwise additivity of rod-rod interactions will break down below 1 M uni-univalent salt for $R \sim 50 \text{ \AA}$, below 0.1 M salt for $R \sim 100 \text{ \AA}$, and below 0.01 M salt for $R \sim 300 \text{ \AA}$. For polyelectrolyte densities away from close packing ($v \ll 1$) and ionic concentrations above ~ 1 M, the additivity condition is trivially satisfied. If pairwise summability of interactions were nevertheless assumed for conditions where $v \frac{n_c}{n_m} \sim 1$, the pair interaction energy Eqs. (9) and (10) would be very large, on the order of $\sim kT$ per 10 \AA length, and thus qualitatively misleading.

On the other hand in the limit of vanishing salt with only counterions present in the system the condition Eq. (11) would never be satisfied. Strictly speaking the term pair potential in a polyelectrolyte array or a solution thus applies only to screened interactions, Eq. (8), and should not be used in connection with Eqs. (9) or (10) or with counterion-only two-rod formulations [2].

Traditional van der Waals forces, due to differences in dielectric susceptibility, may also not be pairwise additive. For low-frequency fluctuations even in the absence of counterions, the dielectric part of the inequality Eq. (11) can easily be violated [10]. Finite values of the medium salt concentration always create an exponentially damped contribution when $\kappa R \gg 1$. Though screening severely weakens forces, it does act to make pairwise summation more accurate.

If many-body effects cannot be neglected, how can one formulate the ion fluctuation free energies of aggregated arrays? In its ability to speak of electromagnetic fluctuations that encompass the entire macromolecular aggregate, the Lifshitz approach appears to be most appropriate. In its language, the free energy connected with electromagnetic field fluctuations can be seen to vary with macroscopic dimensions and even shape of the aggregate [17]. In an anisotropic polyelectrolyte array the energy of formation will also depend on the orientation of macroscopic facets with respect to anisotropic molecular axes. The different macroscopic shapes of the DNA aggregates might already be indicating such shape dependence [18].

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