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Comments
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Counterion-Mediated Attraction and Kinks on Loops of Semiflexible Polyelectrolyte Bundles

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The formation of kinks in a loop of bundled polyelectrolyte filaments is analyzed in terms of the thermal fluctuations of charge density due to polyvalent counterions adsorbed on the polyelectrolyte filaments. It is found that the counterion-mediated attraction energy of filaments depends on their bending. By consideration of curvature elasticity energy and counterion-mediated attraction between polyelectrolyte filaments, the characteristic width of the kink and the number of kinks per loop is found to be in reasonable agreement with existing experimental data for rings of bundled actin filaments.

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Charged polyelectrolyte filaments (DNA, F-actin, microtubules, viruses) form bundles in the presence of polyvalent counterions [1–3]. An explanation of these interesting phenomena based on the correlation effects of adsorbed counterions of high valency is given in Refs. [4–7]. When semiflexible polyelectrolytes are diluted to very low concentrations before addition of polyvalent counterions, they form rings or toroids, rather than bundles. In some cases the contours of the rings are not smooth, and sharp bends or kinks appear at approximately regular intervals around the circumference. Kinks can form in linear bundles of filaments held together by crosslinks because of interacting periodic potentials arising from the mutual displacement of periodic lattices on the filaments as they bend. Such kinks have been observed in bundles of F-actin and carbon nanotubes [8].

In Ref. [3] it is found that F-actin filaments form rings with several kinks—regions with strong variation of the tangent angle to the bundle. Such kinks are not observed for actin filament rings formed by the addition of actin crosslinking proteins [9]. We demonstrate in Fig. 1 the presence of kinks in actin filament rings formed by the addition of divalent cations, but not in rings formed by nonelectrostatic interactions. Rhodamine-phalloidin labeled and stabilized actin filaments diluted to 5 nM actin were induced to form rings by addition of high molecular weight dextran (MW 500 000, 350 mM KCl, 20 mM phosphate, pH = 7.5), which stabilizes actin bundling by depletion forces [Figs. 1(a)–1(c)] or by addition of 50 mM $MgCl_2$, 50 mM KCl, 20 mM phosphate, pH 7.5, which induces bundling due to counterion condensation effects [Fig. 1(d)]. Depletion forces lead to formation of either single actin filaments partially overlapping to form a ring [Fig. 1(a)] or multiple filaments bundled to form rings of greater fluorescence intensity and diameter than the single filaments observed in the background [Figs. 1(b) and 1(c)]. In all cases, the rings are smooth, and occasional irregularities, especially in single filament rings, are due to thermal fluctuations which are trapped when the ring is immobilized or visualized in a single frame. Video sequences (data not shown) show that bends in these rings are highly dynamic and disappear due to thermal motions. In contrast, actin rings formed by polyvalent counterions are invariably kinked, with several sharp bends spaced approximately equally over the circumference, at an average distance of a few microns [Fig. 1(d)].

We show here that the kink in a bundle of polyelectrolyte filaments arises from the interaction of 1D Wigner crystals of counterions condensed on the filaments. Our approach is related to the model described in Ref. [5] where the interaction energy of charged straight rods due to thermal fluctuation correlation effects of two lattices of 1D Wigner crystals is considered. To develop our model the structure factor of a 1D Wigner crystal is calculated and the energy of a bundle of two bent filaments due to the thermal fluctuation correlation effects of 1D Wigner lattices is considered. Estimates of the kink angle, the number of kinks per loop, and the size of a ring of bundled filaments in the presence of divalent counterions are compared with experimental data.

Because of the Manning condensation of counterions with valency Z on charged rods with linear charge density $-e/b$ the effective charge of the rod is diminished by $1/Z\xi$ and is small for large $Z\xi$. The parameter ξ represents the ratio of the Bjerrum length $l_B = e^2/(\epsilon k_B T)$ to the distance between fixed charges b. The period of the 1D Wigner crystal a is determined by the charge neutralization condition $a = Zb$. The ratio of the characteristic Coulomb energy to the thermal energy

$$\frac{(Ze)^2}{\epsilon k_B T a} = Z\xi$$

is assumed to be large. Neglecting higher order terms, the energy E of a 1D Wigner crystal per counterion can be estimated as the sum of the interaction energy of the polyion with charge Ze with a uniform neutralizing background (a_0 is cutoff)

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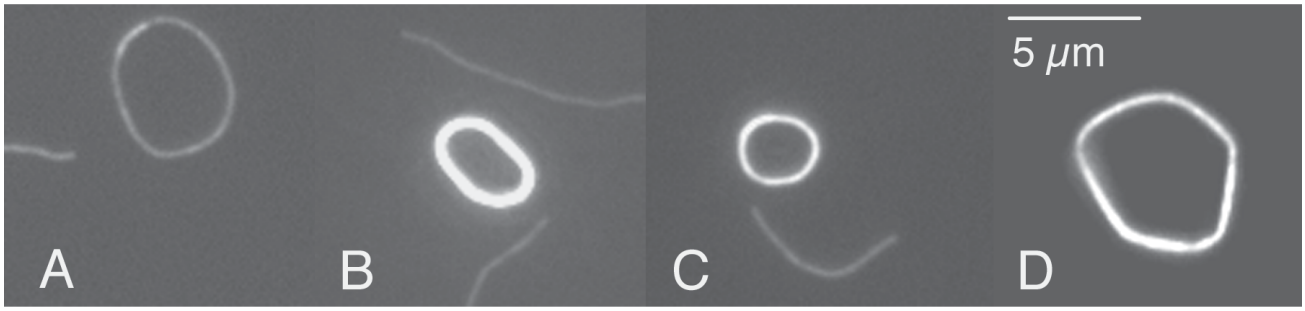

FIG. 1. Rings of actin filaments formed by excluded volume effects (a), (b), (c) are smooth, whereas those formed by counterion condensation (d) are kinked. Rings in panels (a), (b), (c) were made in a dilute solution of F-actin (5 nM actin monomers) by the addition of 3% dextran ($Mr = 500\,000$) in 350 mM KCl, 20 mM phosphate buffer, pH 7.0. The ring in panel (d) was made from the same concentration of F-actin by the addition of 50 mM $MgCl_2$ to a 50 mM KCl, 20 mM phosphate solution.

$$-\frac{2Ze^2}{\epsilon b}\int_{a_0/2}^{a/2}\frac{dr}{r}$$

and the Coulomb energy of the background

$$\frac{e^2}{2\epsilon b^2}\int_{-a/2}^{a/2}\int_{-a/2}^{a/2}\frac{drdr'}{|r-r'|}.$$

As a result

$$E = -\frac{Ze^2}{\epsilon b}\ln(a/a_0) - \frac{Ze^2}{\epsilon b}.$$

The linear energy density $e_l = En$, where $n = 1/a$ is the linear density of adsorbed polyions, then reads

$$e_l = \frac{Ze^2}{\epsilon b}n\ln na_0 - n\frac{Ze^2}{\epsilon b}. \tag{1}$$

The relation (1) allows calculation of the isothermal compressibility of a 1D Wigner crystal and its structure factor $S(k)$ $[nS(k) = \langle\delta|n_k|^2\rangle/L]$ in the long wavelength limit, where L is the length of filament and δn_k is a Fourier component of the density fluctuation:

$$S(0) = \frac{1}{Z\xi}. \tag{2}$$

The structure factor at finite wavelengths can be found by considering a 1D system of harmonic oscillators with energy ($x_0 = x_N$)

$$E_o = \frac{k_BT}{2\sigma^2}\sum_{i=0}^{N-1}(x_{i+1} - x_i - a)^2.$$

The correlation function of density fluctuations of this system is [10]

$$\langle\delta n(x)\delta n(x')\rangle = \frac{1}{2\pi}\int\frac{\sinh(\sigma^2k^2/2)}{\cosh(\sigma^2k^2/2) - \cos(ka)} \times \exp(ik(x-x'))$$

which for the structure factor of the system gives

$$S(k) = \frac{\sinh(\sigma^2k^2/2)}{\cosh(\sigma^2k^2/2) - \cos(ka)}. \tag{3}$$

Comparing the relation (3) in the limit $k \to 0$ with (2) we obtain $\sigma^2/a^2 = 1/Z\xi$.

Since the parameter $Z\xi$ in our case is quite large (for the case of F-actin filaments with the distance between elementary charges 0.25 nm and divalent counterions it is equal to 5.76) then according to Lindemann criteria [11] we should expect that a 1D system of the charges adsorbed on the actin filaments is below the melting temperature. Since in the bundle of actin filaments, in principle, we have a system of interacting 1D lattices of the charges pinned by actin filaments then several interesting issues may arise. The formation of 3D Wigner crystals in the bundle of the polyelectrolyte filaments is considered in Ref. [12]. Phase diagrams of 2D systems of particles pinned by 1D periodic potentials possess several interesting features. Among them a reentrant melting transition induced by the variation of the pinning potential [13,14] is observed in several experiments [15,16]. An important parameter responsible for a such a phenomenon is the ratio of the period of the 1D system and the characteristic Debye length $R_D = \kappa^{-1}$. Under our experimental conditions (50 mM $MgCl_2$ + 50 mM KCl) R_D is 0.68 nm, but a/R_D is approximately 0.74. This value is well below the critical value 5.6 [13,14] above which reentrant behavior should be observed. Since in our real experiment the Debye length is larger than the period of the 1D Wigner crystal and the distance between the filaments, then the assumption of Coulomb interactions

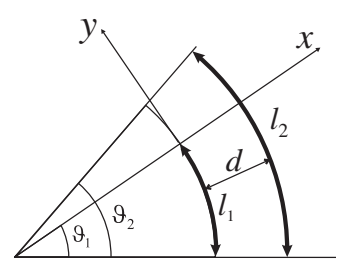

FIG. 2. Geometry of two interacting bent filaments.

between the charges on a single filament and between filaments looks quite reasonable. The issue of the reentrant melting transition for a system of the particles interacting by forces other than screened electrostatic repulsion is not yet sufficiently explored [14]. Appropriate here is the remark in Ref. [14] that reentrance behavior becomes less pronounced with increasing range of the interaction potential. Investigation of the all possibilities in systems of interacting 1D lattices of charges adsorbed on parallel actin filaments nevertheless is beyond the scope of our work. Here we consider the much simpler problem of the interaction between two bent filaments arising due to the correlation of the thermal fluctuations of the modulated 1D systems of charges. We illustrate that by a simple model it is possible to explain the formation of the kinks of actin filament bundles in the presence of polyvalent counterions observed experimentally.

The distance between two points specified by natural parameters l_1 and l_2 on slightly bent rods at distance d can be calculated as follows (Fig. 2). If R is the radius of curvature of the midline between the filaments then the projection of the radius vector between two points specified by natural parameters l_1 and l_2 on the y axis up to second order terms in $d, l_2 - l_1$ is expressed as $\Delta y \simeq R(\vartheta_2 - \vartheta_1) \simeq l_2 - l_1 - d\vartheta((l_1 + l_2)/2)$. Here ϑ is the tangent angle to the midline between the filaments. As a result for the distance between the two points on the filaments we have $\sqrt{(l_2 - l_1 + d\vartheta((l_1 + l_2)/2))^2 + d^2}$. Therefore the interaction energy between filaments due to fluctuating charge densities $Ze\delta n$ reads

$$H_I = \frac{(Ze)^2}{\epsilon} \int \frac{\delta n_1(l_1)\delta n_2(l_2) dl_1 dl_2}{\sqrt{[l_2 - l_1 + d\vartheta((l_1 + l_2)/2)]^2 + d^2}}.$$

Because of the correlations of fluctuations, the excess charge on one filament causes diminution of the charge on the other filament (correlation hole) and an effective attraction between filaments arises [5]. The magnitude of attraction in the frame of perturbation theory can be calculated according to

$$U = -\frac{\langle H_I^2 \rangle}{k_B T}$$

where the thermal average $\langle\rangle$ is taken with respect to the density fluctuations of both Wigner crystals. As a result, for attraction energy we have

$$U = -\frac{(Ze)^4}{\epsilon^2 k_B T} \frac{1}{L^2} \sum_{k_1,k_2} \int \exp(i(k_2 - k_1)l_r/2) \exp(i(k_1 + k_2)l) \exp(-i(k_2 - k_1)\tilde{l}_r/2)$$
$$\times \exp(-i(k_1 + k_2)\tilde{l}) n^2 S(k_1) S(k_2) dl_r dl \tilde{l}_r d\tilde{l} / [\sqrt{(l_r + d\vartheta(l))^2 + d^2} \sqrt{(\tilde{l}_r + d\vartheta(\tilde{l}))^2 + d^2}]. \quad (4)$$

By substituting $l_r' = l_r + d\vartheta(l)$; $\tilde{l}_r' = \tilde{l}_r + d\vartheta(\tilde{l})$ and accounting for the fact that $\Delta\vartheta = \vartheta(\tilde{l}) - \vartheta(l)$ is a function of $\tilde{l} - l$ only, we obtain

$$U = -\frac{4(Ze)^4}{\epsilon^2 k_B T} \frac{1}{2\pi} \int d(\tilde{l} - l)$$
$$\times \int dk \exp(ikd\Delta\vartheta(\tilde{l} - l)) n^2 S^2(k) K_0^2(kd) \quad (5)$$

where K_0 is the McDonald's function. The main contribution to the integral in relation (5) comes from the peaks of the structure factor around $k = k_0 = \pm 2\pi/a$. The height of these peaks is $Z\xi/\pi^2$ and the width of the approximating Lorentzian curve is $2\pi^2/(Z\xi a)$. As a result the interaction energy reads

$$U = -\frac{k_B T}{a} \frac{4(Z\xi)^3}{\pi^2} K_0^2(k_0 d) \int dl \cos(k_0 d\Delta\vartheta). \quad (6)$$

It should be remarked that relation (6) can be generalized for the case when the interactions of the fluctuating charges on the filaments are screened. In this case for the linear density of the interaction energy we have $U = -U_0 \cos(k_0 d\Delta\vartheta)$ where

$$U_0 = \frac{k_B T}{a} \frac{4(Z\xi)^3}{\pi^2} K_0^2(d\sqrt{\kappa^2 + k_0^2}). \quad (7)$$

In the case of straight filaments ($\Delta\vartheta = 0$) the interaction strength per unit length is proportional to $(Z\xi)^3$. The modulation of the interaction strength as a function of the tangent angle variation $\Delta\vartheta$ has a simple physical meaning. If a bundle of two filaments is bent, then due to the finite distance between 1D Wigner crystals on the filament, a displacement of their lattices by an amount $d\Delta\vartheta$ arises. If this displacement fits the period of Wigner

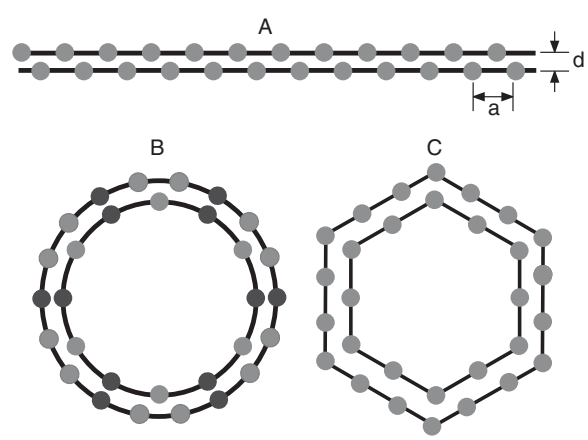

FIG. 3. The kink formation. A lattice of charges between two straight filaments is shown in (a). As these filaments are bent to form a ring (b) the lattice spacing is disrupted and unfavorable interactions (darker circles) arise. Formation of kinks (c) restores the lattice spacing of the straight filaments.

crystals the interaction energy is minimized again. A simple sketch of the physics behind the kink formation is given in Fig. 3. There it is seen that due to bending of two 1D lattices of counterions [Fig. 3(a)] an energetically unfavorable charge configuration arises [Fig. 3(b)], the energy of which can be minimized by the formation of kinks [Fig. 3(c)].

Bending a semiflexible filament by an angle $\Delta\vartheta$ is penalized by an increase of the elastic energy the of the part of the filament that is bent. Therefore the variation of the angle $\Delta\vartheta$ required to maintain the counterion spacing at its minimal energy configuration is confined to a finite interval of the bundle length. The corresponding variational problem for the Kirchhoff rod is considered in Ref. [8]. Here we have shown that the same problem appears quite naturally when attraction of the charged filaments mediated by the adsorbed polyions is considered. Discussion of kink formation in a specific system, rings of actin filaments, is carried out in the next section.

In Ref. [3] and Fig. 1 it is found that very low concentrations of F-actin filaments bundled in the presence of divalent counterions form rings on which several kinks are observed. The necessity of kink formation follows naturally from the analysis of the previous part of the work. When actin filaments are bent in the ring, energetically disadvantageous displacements of the lattices of the adsorbed polyions arise. These can be minimized by concentrating the tangent angle variation necessary for ring formation in a small region of the bundle and leaving the other parts of loop straight. The number of kinks on the closed loop can be estimated from $N\Delta\vartheta = 2\pi$, where $\Delta\vartheta$ is the tangent angle variation at one kink. The distance between elementary charges of actin filament is estimated as 0.25 nm [2,3]. If the distance between the filaments is estimated as 0.5 nm then the angle between straight segments of the kink is about 57° and corresponds to 6 kinks per loop. This value is close to what is observed in experiment; see Fig. 1 and Ref. [3].

The shape of the bundle in the region of the kink may be found by minimizing the energy of the bundle E at boundary conditions $d\vartheta(\infty) = a$ and $d\vartheta(-\infty) = 0$

$$E = \int\left(\frac{1}{2}K\vartheta_{,l}^2 - U_0\cos(2\pi d\vartheta/a)\right)dl \qquad (8)$$

where U_0 characterizes the attraction energy due to the adsorbed polyions. The solution of the variational problem is

$$\vartheta(l) = \frac{2a}{\pi d}\arctan(\exp(\pi d\sqrt{2U_0/K}l/a)). \qquad (9)$$

The width of kink is $\sqrt{K/2U_0}a/\pi d$. The expression for the interaction potential (6) and persistence length of the actin filament $l_p = 17\ \mu$m allows one to estimate the width of kink as

$$\frac{a}{\pi d}\frac{\sqrt{l_p a}}{(Z\xi)^{3/2}K_0(2\pi d/a)}.$$

The characteristic Coulomb energy $(Ze)^2/\epsilon a k_B T = Z\xi$ in $k_B T$ units for the case of an F-actin filament and divalent counterions is 5.7. With this value the characteristic width of the kink is estimated as 2.35 μm, which is in reasonable agreement with experimental data [3].

Comparing the energy of the kink $2a\sqrt{2U_0K}/d\pi$ calculated according to the relation (7) with the thermal energy $k_B T$ it is possible to estimate the ionic strength of the solution at which the kink is smeared out by thermal fluctuations. Then $U_0 \simeq k_B T/l_p$ in the case of the physical parameters given above gives $\kappa = 4.28\ \mathrm{nm}^{-1}$, which is much above the value of the screening parameter 1.47 nm^{-1} for our experimental sample. For the parameters given above we should expect that kinks disappear for concentration of $MgCl_2$ about 450 mM at 350 mM KCl. These concentrations are well above those used in the experiment.

It should be noted we considered a bundle of two filaments, whereas the real bundles may contain many filaments. Nevertheless the results show that an approach based on a model of polyvalent counterion-mediated attraction between charged polyelectrolyte rods gives a consistent explanation of the phenomena observed in the experiments; see Fig. 1 and Refs. [2,3].

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