Charge oscillations and many-body effects in bundles of like-charged rods

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We study charge correlations in bundles of like-charged rods that attract each other via counterion-mediated interactions, using a Debye-Hückel approach. We first show that the approach can predict oscillatory charge correlations in electrolyte solutions once the nonzero ion size is taken into account. We then apply the approach to bundles of rods, and find that the charge correlation function exhibits oscillatory decay due to many-body effective interactions among the rods. [S1063-651X(98)12511-4]

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I. INTRODUCTION

Like-charged stiff polyelectrolytes can attract each other in solution to form dense bundles when multivalent salts are added [1,2]. Recent simulations [3,4] and theories [5,3,6,7] of charged rods suggest that the mechanism of the short-ranged attraction is similar to the van der Waals attraction: fluctuations in the density of condensed counterions along the axes of the rods lead to charge fluctuations that become correlated when the rods are sufficiently close to each other. In addition, rods are affected by a long-ranged repulsion due to the fact that they carry the same sign of charge. If the interactions were pairwise additive, this would imply that the bundle size would be limited by the long-ranged repulsion. However, these interactions are not pairwise additive [7,8]. Explicit calculation [8] of the interactions in N-rod bundles shows that electrostatics prefer the bundle size to be infinite. At very low temperatures, this is not surprising because the system orders into an ionic crystal [3], and electrostatics do not limit the size of an ionic crystal. At the temperatures we have studied, however, the counterions are not ordered periodically, so it is less clear why electrostatics should prefer an infinite bundle size. By studying charge correlations in the bundle, we can gain insight into the result that the preferred bundle size is infinite. Another benefit is that we can make connection to experiments: charge correlations can be measured by x-ray scattering from the counterions.

In this paper we present a formulation that allows calculation of charge correlations in a bundle of like-charged rods with condensed counterions. We find that both the intrarod and inter-rod charge correlations are oscillatory within an exponentially decaying envelope. These oscillations can be viewed as a precursor to the ionic crystal; as the temperature is lowered, the exponential decay length diverges at the transition to an ionic crystal. We find that the oscillations extend over several rods, which explains why many-body effects are so important in this system.

In order to calculate the attractive interactions between rods and the corresponding charge correlations, we use an extension of Debye-Hückel theory. It is well known that standard Debye-Hückel theory fails to describe the attractions necessary to the formation of bundles. In fact, even the nonlinear Poisson-Boltzmann equation predicts repulsions for multivalent as well as monovalent counterions [9]. However, the Manning-Oosawa approach to counterion condensation allows the counterion to exist in two states: free or condensed. Condensed counterions modify the local charge while free counterions are treated within Debye-Hückel theory. There is chemical equilibrium between free and condensed counterions; this leads to fluctuations in the charge density along the rods. Our approach to this model is to use one-dimensional Debye-Hückel theory to treat the charge fluctuations along the rods [8]. The one-dimensional Debye-Hückel system on each rod is coupled via a three-dimensional Debye-Hückel system of free counterions and added salt ions to the one-dimensional Debye-Hückel systems on the other rods in the bundle. We have shown that this approach describes the interaction between two rods at a quantitative level when compared to simulations [6]. Here, we show that this approach predicts *oscillatory* decay of the *inter-rod* charge correlations. However, we must extend it to capture the proper oscillatory *intrarod* correlations. Recently, Lee and Fisher [10] generalized Debye-Hückel theory to capture oscillatory charge correlations in electrolyte solutions. Their approach, however, cannot be applied readily to the case of a bundle of rods with one-dimensional charge fluctuations. We have therefore adopted an alternate approach that is more amenable to rods. In Sec. II we introduce the approach and demonstrate its validity by applying it to an electrolyte solution consisting of positively and negatively charged spheres. In qualitative agreement with recent results of Lee and Fisher [10], we find that the charge correlations are oscillatory at sufficiently high densities within an exponentially decaying envelope. At very high densities, we also observe a transition to an ionic crystal, although the theory is certainly not accurate by that point.

In Sec. III we apply the same approach to a bundle of rods with charge fluctuations. The specific system we have in mind is a polyelectrolyte with condensed counterions [11,12], where the charge fluctuations originate from density fluctuations in the condensed counterions along the axes of the rods [13]. In the bundle, we consider both inter-rod and intrarod charge correlations, and show that the correlations are again oscillatory with an exponential decay. The oscillations are a precursor to the ionic crystal at low temperatures, where the exponential decay length diverges. We also show that pairwise additivity of effective two-rod interactions (mediated by the counterions) leads to monotonic decay of the inter-rod charge correlation function. Thus many-body inter-

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actions must be retained in order for the inter-rod correlations to be oscillatory.

II. CHARGE CORRELATIONS IN AN ELECTROLYTE SOLUTION

The conventional Debye-Hückel approach predicts monotonic decay of charge correlations. However, Lee and Fisher [10] have proposed a generalization of Debye-Hückel theory that predicts oscillatory correlations at high densities, by calculating the response to spatially varying fluctuations in the charge density. Here, we develop the momentum-space counterpart to their approach and show that it yields qualitatively similar results. We start with the restricted primitive model (RPM) of hard spheres of diameter d. We assume that there are N spheres carrying charge qe and N spheres carrying charge $-qe$. To calculate the free energy of the system, we define local number densities of the positively and negatively charged spheres as follows:

$$\hat{n}_+(\mathbf{r})=\sum_{i+}^{N}\delta(\mathbf{r}-\mathbf{r}_{i+}),$$

$$\hat{n}_-(\mathbf{r})=\sum_{i-}^{N}\delta(\mathbf{r}-\mathbf{r}_{i-}), \tag{1}$$

and the local charge density is

$$\rho(\mathbf{r})=q\hat{n}_+(\mathbf{r})-q\hat{n}_-(\mathbf{r}). \tag{2}$$

The electrostatic Hamiltonian is

$$\beta\mathcal{H}_{\mathrm{el}}=\frac{1}{2}\ell_B\int d^3r\int d^3r'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{3}$$

where $\ell_B=e^2/\epsilon k_BT$ is the Bjerrum length. Here, ϵ is the dielectric constant of the solvent. There is also a single particle Hamiltonian H_0 that ensures that ions are correlated into a sphere of diameter d. This is infinite for points outside the sphere and zero for points inside the sphere. We now introduce the Hubbard-Stratanovich transformation to replace the two-body interaction, Eq. (3), with a one-body interaction of the charge in an effective field $\Phi(\mathbf{r})$, and use the Gaussian approximation to obtain the free energy. The Gaussian approximation corresponds to Debye-Hückel theory in that the effective potential due to all the other particles is assumed to be weak compared to the thermal energy. The resulting free energy density for *point particles* is exactly the Debye-Hückel limiting law:

$$\beta F_{\mathrm{el}}=-\kappa_D^3/12\pi, \tag{4}$$

where $\kappa_D^2=4\pi\ell_Bq^2n_0$ is the Debye screening parameter that depends on the total number density of ions n_0. For spheres of diameter d, the electrostatic contribution to the free energy (per unit volume) is given within the same approach [15] by

$$\beta F_{\mathrm{el}}=\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\left[\ln\left(1+\frac{\kappa^2(k)}{k^2}\right)-\frac{\kappa^2(k)}{k^2}\right], \tag{5}$$

where

$$\kappa^2(k)=\kappa_D^2g(k), \tag{6}$$

where $g(k)=3(\sin kd-kd\cos kd)/(kd)^3$ is the form factor of a sphere of diameter d. We will refer to this as extended Debye-Hückel theory.

To examine charge correlations, we apply an electrostatic potential $-ih(\mathbf{r})$ that is conjugate to the charge density $\rho(\mathbf{r})$, so that the free energy is

$$\beta F[h]=-\ln\left\langle\exp\left[i\int d^3r\rho(\mathbf{r})h(\mathbf{r})\right]\right\rangle. \tag{7}$$

Then the Fourier transform of the charge correlation function is

$$G(k)\equiv\langle\rho(\mathbf{k})\rho(\mathbf{k})\rangle=-\frac{\partial^2F[h]}{\partial h(\mathbf{k})\partial h(-\mathbf{k})}. \tag{8}$$

The resulting expression within the extended Debye-Hückel approach is

$$G(k)=\frac{n_0k^2g(k)}{k^2+\kappa^2(k)}, \tag{9}$$

with $\kappa^2(k)$ given by Eq. (6). Note that in the limit of point particles $[d\to 0$ or $g(k)\to 1]$, the expression reduces to the Fourier transform of the usual Debye-Hückel prediction, which decays monotonically with distance. Note also that the expression Eq. (9) automatically satisfies both the charge neutrality zero moment condition and the Stillinger-Lovett second moment condition [16]. This can be seen by expanding the expression for small k [10]:

$$G(k)=(\epsilon k_BT/4\pi q^2e^2)k^2+O(k^4). \tag{10}$$

In order to analyze the asymptotic long-distance behavior of the charge correlation function, we find the pole k_0 of $G(k)$ that is closest to the origin in the complex k plane. For small values of $x=\kappa_Dd$, we find that the charge correlations decay monotonically, but for $x>x_K$, we obtain oscillatory decay. Our estimate of the Kirkwood value is

$$x_K\approx 2.06. \tag{11}$$

This is substantially larger than the predictions of other approaches [10], which lie in the range $1.0<x_K<1.3$. The behavior of k_0 as a function of $x=\kappa_Dd$, however, is qualitatively identical to that predicted by Lee and Fisher [10]. We have plotted the results in Fig. 1, which should be compared to Fig. 1 of Ref. [10]. For $x>x_K$, the charge correlation function oscillates within an exponentially decaying envelope. The real part of k_0, which controls the wavelength of oscillations, is shown as a solid line, while the imaginary part, which controls the decay, is a dotted line. As x increases, the wavelength of the oscillation decreases and the decay length increases. At $x=x_X$, the imaginary part vanishes and the decay length diverges, signalling the onset of crystallization. Our estimate of the onset is $x_X=19.1$, which is also outside the expected range of $2.8<x_X<17.7$ obtained by other methods [10]. We have neglected ion clustering, so

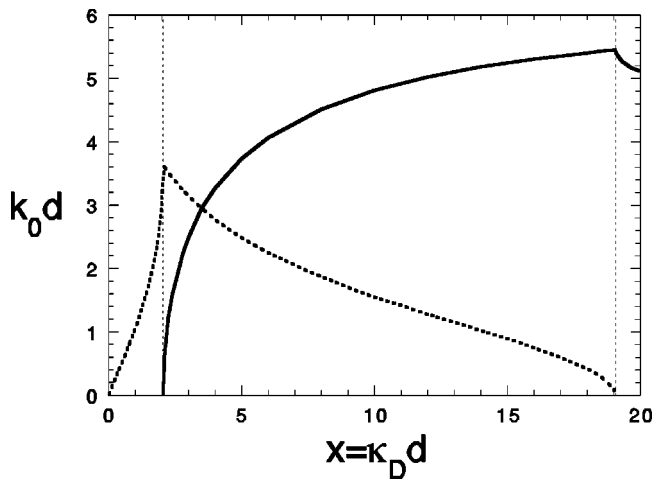

FIG. 1. The leading pole k_0 for an electrolyte solution of spheres of diameter d, as a function of the dimensionless quantity $x = \kappa_D d$. The behavior is qualitatively the same as predicted by Lee and Fisher [10]. The real part of k_0 (solid line) characterizes oscillations in the charge correlation function, while the imaginary part (dashed line) controls the decay. At x_K, marked by the dotted vertical line on the left, the correlation function becomes oscillatory. At x_X, marked by the vertical dotted line on the right, the system crystallizes. Note that our figure looks somewhat different from the one in Ref. [12] because we have only plotted the leading pole, while Lee and Fisher have also sometimes plotted the subleading pole.

the theory is certainly not valid at such high values of x. However, it is reassuring that our approximations lead to qualitatively correct behavior.

There are several possible reasons for the discrepancy between earlier results and our numerical predictions for x_K and x_X. Perhaps the most important one is that we do not cut off the electrostatic interactions at length scales inside the sphere. This can be done in an approximate way by introducing a high wave-vector cutoff at $\Lambda = \pi/d$ in the integral in Eq. (5), but the resulting expression for $G(k)$ will then be more complicated. Since we are not trying to obtain a quantitatively accurate description of the electrolyte, we will not attempt to improve on the estimate here. Rather, our aim is to develop an approach that can be generalized to a bundle of rods. The main point of this section is that we can capture oscillatory charge correlations by taking into account the nonzero size of the ions via the form factor $g(k)$.

III. CHARGE CORRELATIONS IN A BUNDLE OF POLYELECTROLYTE RODS

We consider a model of N parallel rods of length L aligned in the z direction, organized on a square lattice of spacing a. The counterions have diameter d. Each rod consists of M cylindrical monomers of length $b = L/M$. Each monomer s on rod j carries a random charge $q_j(s)$, in units of the elementary charge e. The electrostatic interactions are

$$\beta\mathcal{H} = \frac{1}{2}\ell_B \sum_{ij}^{N} \sum_{ss'}^{M} \frac{q_i(s)q_j(s')}{|\mathbf{r}_i(s) - \mathbf{r}_j(s')|}. \tag{12}$$

Following the same approach as in the preceding section, we introduce an electrostatic potential $-ih(\mathbf{r})$ that is conjugate to the charge density $\rho(\mathbf{r})$, so that the free energy is

$$\mathcal{F}[h_i(s)] = -\ln\left\langle \exp\left\{ -i\sum_{j=1}^{N}\sum_{s=1}^{M} q_j(s)h_j(s)\right\}\right\rangle. \tag{13}$$

Again, we make the Hubbard-Stratanovich transformation and truncate at Gaussian level [6,8]. This corresponds to treating the one-dimensional charge fluctuations on each rod within Debye-Hückel theory. The connected charge correlation function is then given by

$$\begin{aligned} G_{ij}(s,s') &= \langle q_i(s)q_j(s')\rangle - \langle q_i(s)\rangle\langle q_j(s')\rangle \\ &= -\left.\frac{\partial^2\mathcal{F}[h_i(s)]}{\partial h_i(s)\partial h_j(s)}\right|_{\{h_i(s)\}=0} \\ &= \boldsymbol{Q}_{ij}^{-1}(s,s'), \end{aligned} \tag{14}$$

where $\boldsymbol{Q}$ is a block matrix whose matrix element $\boldsymbol{Q}_{ij}$ is a submatrix defined by

$$\boldsymbol{Q}_{ij}(s,s') = \Delta^{-1}\delta_{ij}\delta_{ss'} + \frac{\ell_B}{\sqrt{R_{ij}^2 + |s-s'|^2}}, \tag{15}$$

where R_{ij} is the separation between rods i and j. As in our previous calculations [8], the quantity $\Delta = Z^2 f_c$ is the variance in the monomeric charge, where Z is the counterion valency and f_c is the fraction of condensed counterions per monomer. Note that charges at different sites are uncorrelated in the absence of electrostatic interactions: $G_{ij}(s,s') = \Delta\,\delta_{ij}\delta_{ss'}$ for $\ell_B = 0$ [17]. Once electrostatic interactions are turned on, however, charges on different sites are correlated via the electrostatic interaction $\ell_B/\sqrt{R_{ij}^2 + |s-s'|^2}$.

The expression for the charge correlation function, Eq. (15), could be evaluated numerically for a given rod length and lattice spacing. In order to obtain analytic expressions for the charge correlations, however, it is useful to take the continuum limit along the z direction. The straightforward limit of replacing the sums over s and s' by integrals and the Kronecker delta function $\delta_{ss'}$ by the Dirac delta function in Eq. (15) is analogous to the point-particle limit in the Debye-Hückel treatment of an electrolyte solution, and neglects important local correlations. We therefore retain the rodlike structure of the monomer by introducing the one-dimensional form factor $g(s,s') = \Theta(|s-s'| - d)/d$ where d is the size of the condensed counterions [18]. This is directly analogous to the sphere form factor that appears in Eq. (6). Once we have allowed for this short length-scale structure, we take the continuum limit on s and obtain

$$G_{ij}(s,s') = \int_0^L ds'' g(s,s'')\mathcal{Q}_{ij}^{-1}(s'',s'), \tag{16}$$

where

$$\mathcal{Q}_{ij}(s,s') = \Delta^{-1}\delta_{ij}\delta(s,s') + \ell_B\int_0^L ds'' \frac{g(s,s'')}{\sqrt{R_{ij}^2 + |s''-s'|^2}}. \tag{17}$$

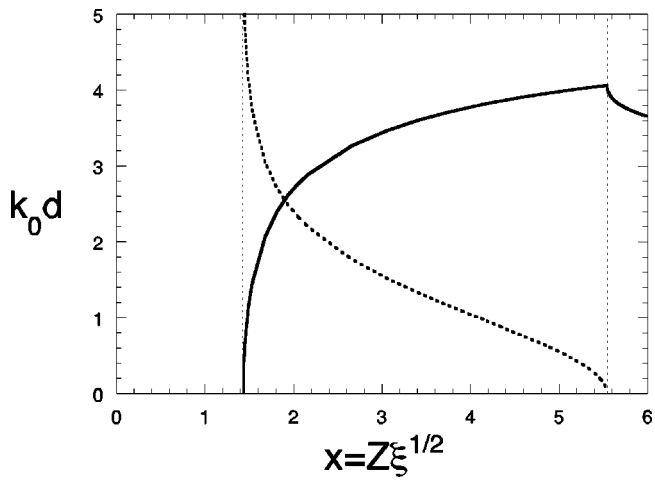

FIG. 2. The leading pole k_0 for charge correlations along a single rod, as a function of $x = Z\sqrt{\xi}$, where $\xi = \ell_B/b$ is the Manning parameter and $Z=2$ is the counterion valency. We have assumed $b=1.7$ Å and $d=4.2$ Å. The real part of k_0 (solid) controls the oscillations and the imaginary part of k_0 (dashed) controls the decay of the charge correlations. The onset of counterion condensation is at $x_C = \sqrt{2}$ and is marked by the vertical dotted line on the left. The onset of crystallization is at x_X and is marked by the dotted line on the right.

In the limit $L \to \infty$, we can introduce the Fourier transform in the z direction:

$$G_{ij}(s,s') = \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \cos k_z(s-s') \mathcal{Q}_{ij}^{-1}(k_z), \tag{18}$$

where

$$\mathcal{Q}_{ij}(k_z) = \Delta^{-1} g^{-1}(k_z)\delta_{ij} + 2\xi K_0(k_z R_{ij}), \tag{19}$$

where the dimensionless parameter $\xi = \ell_B/b$ is the Manning parameter, $g(k_z) = \sin k_z d / k_z d$ is the Fourier transform of $g(z)$, and $K_0(x)$ is the zeroth-order modified Bessel function of the second kind. In the case of two monomers on the same rod, where $i=j$, we set $R_{ii}=b$ to prevent a divergence when $s=s'$.

Given the general form of the correlation function in Eq. (18), we can now examine its behavior in various limits. We first consider charge correlations along the length of a single isolated rod. In that limit, the lattice spacing a diverges, so that $R_{ij} \to \infty$ in Eq. (19) unless $i=j$, and Eq. (18) reduces to

$$G^{-1}(k_z) = \Delta^{-1} g^{-1}(k_z) + 2\xi K_0(k_z b). \tag{20}$$

To obtain the asymptotic large z behavior of the correlation function, we extract the pole k_0 of $G(k_z)$ that lies closest to the origin in the complex k_z plane. This is plotted in Fig. 2 as a function of $x = Z\sqrt{\xi}$. As in the three-dimensional case, x increases as the temperature is lowered or the charge density along the rod increases. In our numerical calculations, we have chosen parameters consistent with our previous work:[6,8] $Z=2$, $b=1.7$ Å, and $d=4.2$ Å. The real part of k_0 is shown as a solid curve, and the imaginary part as a dotted curve. The real part controls the wavelength of the oscillations in the charge correlation function; thus the oscillation wavelength decreases as x increases. The imaginary part of k_0 is the inverse of the exponential decay length of the correlation function; this vanishes at $x = x_X = 5.4$, signalling the onset of long-range order [19].

Comparing Fig. 2 to Fig. 1, we see that the behavior is qualitatively different at small x. In the $d=3$ system, k_0 is purely imaginary and correlations decay monotonically at small x. One might also expect correlations to decay monotonically in the $d=1$ case for small x (high temperatures or low charge densities). To elucidate the origin of this difference between the $d=1$ and $d=3$ cases, we have expanded the Fourier transform of Eq. (20) in powers of the Manning parameter $\xi = \ell_B/b$ (recall that $x = Z\sqrt{\xi}$):

$$G(z,z') \cong \Delta\,\delta_{zz'} - \frac{\xi\Delta^2}{\sqrt{|z-z'|^2+b^2}} + \frac{1}{6}\Delta^3\xi^2 \boldsymbol{K}\left(-\frac{|z-z'|^2}{4b^2}\right), \tag{21}$$

where $\boldsymbol{K}(x)$ is the complete elliptic integral of the first kind.

According to the first few terms of the perturbation expansion, the charge correlations should decay algebraically, as $1/\sqrt{z-z'}$, instead of exponentially, as predicted by the full expression as shown in Fig. 2. If we take only the first two terms of the expansion, consistent with small values of x, we find a monotonic decay from below, similar to the result for $d=3$. However, the variance in the monomeric charge, Δ, is related to the amount of counterion condensation by $\Delta = Z^2 f_c$, where f_c is the fraction of condensed counterions per monomer. We find $\Delta = 0$ for $x < x_C$, where $x_C = \sqrt{Z}$ is the counterion condensation threshold; this is identical to Manning's result [11,12]. Therefore $G(z,z') = 0$ for $x < x_C$. For $x \geqslant x_C$, we find that the perturbation expansion diverges, so Eq. (21) is not useful. This explains why the one-dimensional case is so different from the three-dimensional electrolyte solution: below x_C, there are no condensed counterions so the charge is uniformly negative and completely correlated ($k_0 = 0$). Once some fraction of counterions have condensed ($x > x_C$), they repel each other and the correlation function exhibits oscillatory decay ($\mathrm{Re}\,k_0 \neq 0$).

When two rods are brought together, the correlations between charges on a rod depend on the separation between the two rods. To study these correlations, we consider two parallel rods separated by a distance R, and study $G_{11}(R, z-z')$, the correlation between a monomer at z on one rod with a monomer at z' on the *same* rod. As before, we examine the Fourier transform in the z direction

$$G_{11}^{-1}(R,k_z) = \Delta^{-1} g^{-1}(k_z) + 2\xi K_0(k_z b) - \frac{[2\xi K_0(k_z R)]^2}{\Delta^{-1} g^{-1}(k_z) + 2\xi K_0(k_z b)}. \tag{22}$$

For large separations z, this correlation function exhibits oscillatory decay. The position k_0 of the pole of $G_{11}(R,k_z)$ closest to the origin in the complex k_z plane is plotted in Fig. 3 as a function of b/R, where R is the inter-rod spacing. For this figure, we have chosen $x = Z\sqrt{\xi} = 4.087$. In the limit $R \to \infty$, k_0 approaches its single-rod value. As b/R increases, however, the real part of k_0 increases, showing that the wavelength of the oscillation decreases. In addition, the imaginary part of k_0 decreases, indicating that the correla-

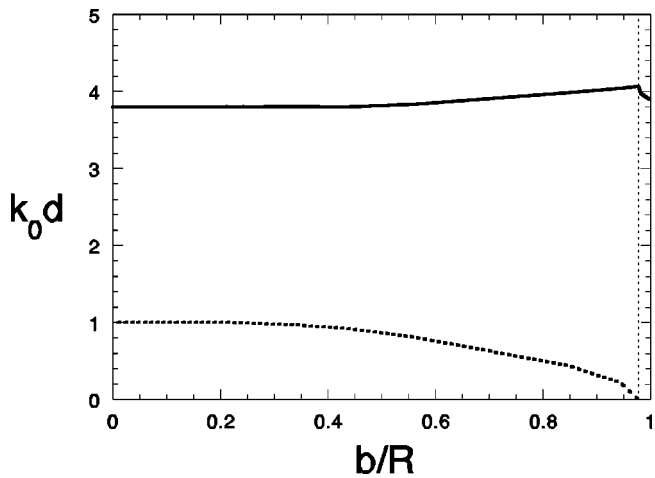

FIG. 3. The leading pole k_0 for charge correlations along the axis of one rod, as a function of the distance R between the rod and a second rod, in units of the monomer length b. Here, we have chosen $x=Z\sqrt{\xi}=4.087$ and $\Delta=1.761$. We have plotted the real (solid) and imaginary (dashed) parts of k_0 as a function of b/R. When $b/R\rightarrow 0$, our result approaches the single-rod limit. When the two rods are extremely close together at a spacing R_X (marked by the vertical dotted line), the charges crystallize.

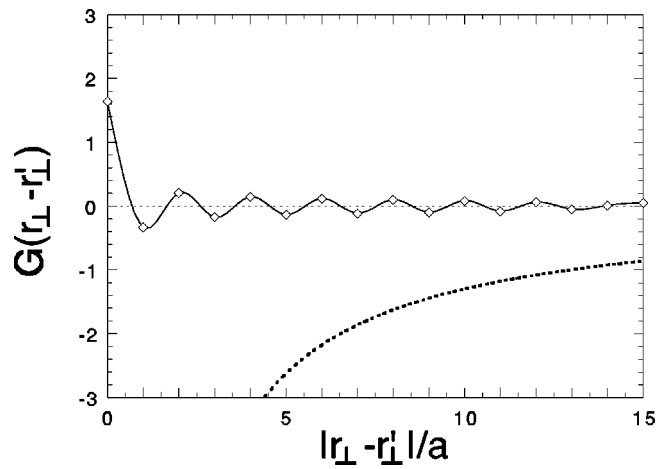

FIG. 4. The charge correlation function (diamonds) in the xy plane for a square bundle of 32×32 rods as a function of $|\mathbf{r}_\perp-\mathbf{r}'_\perp|$, in units of the lattice spacing a, at $x=Z\sqrt{\xi}=4.087$ and $\Delta=1.761$. The solid line is to guide the eye. Note that adjacent rods are anticorrelated and that the correlation function extends over many (approximately 12) rods. The charge correlation function within the truncated (pairwise-additive) theory is also shown as a dotted line. Note that it is monotonic.

tions in the z direction grow longer ranged as the spacing between the rods decreases. When the two rods are extremely close together at $b/R\approx 1$, the imaginary part vanishes, suggesting the onset of long-range order in the z direction. At this distance, however, effects that we have neglected, such as hard-core interactions, will be important.

Charge correlations *between* two rods also depend strongly on rod separation. Note that the rods are placed a nonzero distance apart and are discrete from each other, so we do not need to extend Debye-Hückel theory as in Sec. II in order to obtain oscillatory inter-rod correlations. To study these, we construct the function $G_{12}(R,z-z')$, which describes correlations between a monomer at z on one rod with a monomer at z' on the other rod. We find

$$G_{12}^{-1}(R,k_z)=-\frac{[\Delta^{-1}g^{-1}(k_z)+2\xi K_0(k_zb)]^2}{2\xi K_0(k_zR)}+2\xi K_0(k_zR). \tag{23}$$

Note that $G_{12}(R,k_z)$ is negative for all k_z, which implies $G_{12}(R,z-z'=0)<0$. In other words, the charge on one rod at position z is anticorrelated with the charge on the other rod at position z. This is the origin of the attraction between the two rods.

Finally, we consider charge correlations in a square bundle of parallel rods running in the z direction on a square lattice of lattice constant a. To calculate the charge correlations, we impose periodic boundary conditions on the bundle in the x and y directions, and introduce the discrete Fourier transform in the xy plane. The allowed values for the wave vector $\mathbf{k}_\perp$, which is conjugate to the position $\mathbf{r}_\perp=(x,y)$, are then given by $\mathbf{k}_\perp=(2\pi/\sqrt{N})(n_x,n_y)$ where n_x,n_y can assume the values $0,1,\ldots,\sqrt{N}-1$. The connected charge correlation function is

$$G(\mathbf{r}_\perp-\mathbf{r}'_\perp,s-s')=\frac{1}{N}\sum_{\mathbf{k}_\perp}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{\cos[k_z(s-s')+\mathbf{k}_\perp\cdot(\mathbf{r}_\perp-\mathbf{r}'_\perp)]}{\Delta^{-1}g^{-1}(k_z)+2\xi K_0(k_z,\mathbf{k}_\perp)}, \tag{24}$$

where the discrete Fourier transform of $K_0(k_z,\mathbf{r}_\perp)$ is denoted as

$$K_0(|k_z|,\mathbf{k}_\perp)=\sum_{j_xj_y=0}^{\sqrt{N}-1}K_0(|k_z|a|\mathbf{j}_\perp|)\cos(\mathbf{k}_\perp\cdot\mathbf{j}_\perp a), \tag{25}$$

where $\mathbf{j}_\perp=(j_x,j_y)$ and $j_x,j_y=0,1,\ldots,\sqrt{N}-1$. By convention, $K_0(k_za|\mathbf{j}_\perp=0|)=K_0(k_zb)$.

We now use Eq. (24) to study the correlations between charges at the same height z (i.e., $s=s'$), but on different rods within the bundle. Because the rods are placed on a discrete lattice, we do not have to extend Debye-Hückel theory, as in Sec. II, to obtain oscillatory decay. In our numerical calculations, we have studied a 32×32 bundle of rods consisting of $M=10^4$ monomers each, on a square lattice with a lattice spacing of $a=15$ Å. We have chosen a Manning parameter of $\xi=4.176$, a charge variance of $\Delta=1.761$, and a monomer length of $b=1.7$ Å (these are parameters characteristic of DNA at room temperature). To avoid singularities in the k_z integration, we integrate from $k_z=\pi/L$ to π/b, rather than $k_z=0$ to ∞. Since we are examining correlations in the xy plane, however, the function $\cos k_z(s-s')$ is set to unity, and the k_z integration is not sensitive to the numerical values of the upper and lower cutoffs. The resulting correlation function $G(\mathbf{r}_\perp-\mathbf{r}'_\perp)$ (solid line) is plotted in Fig. 4 as a function of the separation between the rods in units of the lattice spacing, $|\mathbf{r}_\perp-\mathbf{r}'_\perp|/a$. Evidently, the charge correlation function exhibits oscillatory decay, with an oscillation wavelength that is comparable to the lattice

spacing. Adjacent rods are anticorrelated. This result shows that the correlations extend over many rods.

We can calculate the same quantity within a perturbation expansion in powers of the Manning parameter ξ. If the expansion is truncated at lowest nonvanishing order, then the effective interactions between rods are pairwise additive [8]. At this order, however, the correlation function decays monotonically; we find $G(\mathbf{r}_\perp - \mathbf{r}'_\perp) \cong -\xi\Delta^2/|\mathbf{r}_\perp - \mathbf{r}'_\perp|$ for $\mathbf{r}_\perp \neq \mathbf{r}'_\perp$. This result is plotted as a dotted line in Fig. 4. Not only does the truncated theory predict monotonic instead of oscillatory decay, but it also predicts that the magnitude of the charge correlation function is much too high compared to the exact result (solid line). This is consistent with our earlier finding for the two-rod case, where the truncated expression predicts a much stronger and much longer-ranged attraction than the full series [6]. The truncated theory fails because it is pairwise additive and neglects many-rod interactions. The charge fluctuations on the rods are correlated over many rods, not just pair by pair. This leads to a more effective screening and a lower free energy for a large bundle.

IV. DISCUSSION

In this paper we have presented an extension of the Debye-Hückel approach that allows calculation of charge correlation functions in electrostatic systems. The Debye-Hückel approach yields monotonically decaying correlations unless the discrete nature of the charges is explicitly included. Recently, Lee and Fisher [10] showed that by calculating the response to an oscillatory charge density within Debye-Hückel theory, one can obtain oscillatory decay of the correlation function. The random phase approximation is the same in spirit, and represents a momentum-space version of their real-space theory when the discrete nature of the charges is included. We have shown that our approach yields qualitatively identical results to earlier calculations of charge correlations in electrolytes.

The main advantage of our approach is that it can be applied easily to other problems. In particular, we are interested in charge correlations in a bundle of like-charged rods that are held together by counterion-mediated attractions. In our picture, condensed counterions give rise to charge fluctuations along the rods. The attraction arises from correlations of the charge fluctuations on different rods. Earlier, we showed that many-body effective interactions among rods are extremely important to this system [8]; pairwise summation of the effective interactions leads to a preferred bundle size that is finite, while explicit calculation (including many-body interactions) predicts that the preferred bundle size is infinite. Here, we have shown that the very terms in the free energy that give rise to these many-body interactions are also required in order to obtain oscillatory charge correlations. These oscillations are a precursor to the ionic crystal, which one would expect to be infinite. Thus our result yields insight into the physical reason why electrostatics prefer an infinite bundle size.

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[13] Our formulation is general and can be applied to any system of randomly charged rods. For example, the charge fluctuations could arise from dissociation of some of the charges due to pH in a polyacid or polybase. Alternatively, it could arise from charge fluctuations in a polyampholyte [14] (i.e., a chain that contains charged groups of both signs).

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[19] Although the rod is a one-dimensional system, the electrostatic interactions are repulsive so the system can form a one-dimensional ionic crystal at low temperatures.