Orientation-dependent electrical double-layer interactions. I. Rodlike macroions of finite length

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(Received 7 December 1994; accepted 31 January 1995)

The orientation-dependent electrical double-layer interaction between two thin rodlike macroions of finite length is considered. Starting from an expression for the interaction free energy as a double integral of the Green’s function for the linearized Poisson–Boltzmann equation, we obtain several useful analytical approximations. For certain rod configurations, we obtain simple analytical approximations to the double-layer interaction that are quantitatively accurate at physically relevant rod separations and electrolyte concentrations. For a general rod configuration, specified by the separation and three angles, we develop a generalized multipole expansion of the double-layer interaction energy, which converges rapidly if the rod length is not much larger than the center-of-mass rod separation or the Debye length. The orientation dependence of the double-layer repulsion can then be quantitatively accounted for in terms of the screened charge–quadrupole and quadrupole–quadrupole interactions. Furthermore, we show that the double-layer repulsion between finite rods depends on the rod orientations even at arbitrarily large separation.

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I. INTRODUCTION

The electrical double-layer interaction, i.e., the configuration-dependent electrostatic free energy of two macroions immersed in an electrolyte solution, is of central importance in colloid science. For nonspherical macroions, the orientation-dependent double-layer repulsion induces orientational correlations which, under certain conditions, lead to the formation of ordered phases. Such orientationally ordered (nematic, cholesteric, or smectic) phases occur in aqueous dispersions of various supramolecular structures, including surfactant micelles, polynucleotide fragments, and virus particles.

The extensive literature on the theory of the electrical double-layer interaction is devoted almost exclusively to spherical or infinitely long rodlike macrorods. In contrast, relatively little is known about the double-layer interaction between nonspherical macroions of finite dimensions. In fact, not even the asymptotic form of the interaction is known for this case. Starting from well-explored territory, there are two ways of approaching the problem. In the present paper, we start from the infinite rod, examining how the double-layer interaction is altered when the rod length is made finite. In a subsequent paper, we shall study the effect on the double-layer interaction of deforming a sphere into a prolate spheroid.

The calculation of the double-layer interaction between two rodlike macroions of finite length is a problem of considerable complexity. Even at the level of the primitive model (continuum solvent) and the mean-field approximation (neglect of small-ion correlations), there are technical complications. One of these is the nonlinearity of the Poisson–Boltzmann (PB) equation, governing the self-consistent electrostatic potential field around the macroions. In the present work, we avoid this problem by using the linearized form of the PB equation, which should be adequate for all configurations where the double layers of the two macroions do not overlap strongly. Strongly overlapping configurations, where the double-layer repulsion is typically much larger than \( k_B T \), are in any case so rare that they hardly affect configuration-averaged equilibrium properties.

The other technical difficulty is of a geometrical nature. Even in the thin-rod limit, the double-layer repulsion depends on six variables: the rod length, the Debye length (determined by the electrolyte concentration), the center-of-mass separation of the two rods, and the three angles needed to specify the relative orientation of the rods. Although, at the level of approximation adopted here, the double-layer repulsion can be given a concise integral representation, this form is neither suitable for subsequent statistical-mechanical calculations, nor does it provide much physical insight about the dependence of the double-layer repulsion on the six variables. To overcome these limitations, we derive here a spherical harmonic expansion of the double-layer repulsion between two rods of finite length, based on a two-center expansion of the screened Coulomb potential, \( \exp(-kr)/r \).

The outline of the paper is as follows. In Sec. II we formulate the approximations used to calculate the double-layer interaction energy and discuss their validity. In Sec. III we consider the integral representation of the double-layer interaction for configurations where both rods are perpendicular to the separation vector joining their centers. For finite rods in the parallel and perpendicular configurations, we obtain analytical approximations which are considerably more accurate than the infinite-rod limiting forms under physically relevant conditions of rod separation and electrolyte concentration. In Sec. IV we derive the spherical harmonic expansion of the double-layer interaction, which reduces to the usual electrostatic multipole expansion in the limit of vanishing electrolyte concentration. We then examine the convergence properties and asymptotic behavior of this generalized multipole expansion, and show that the ori-
entation dependence of the double-layer repulsion can often be quantitatively rationalized in terms of the leading screened multipole interactions.

II. FORMULATION OF THE PROBLEM

We consider two identical rod-shaped macroions of length \(2a\) in a generic configuration, specified by the center-of-mass separation \(R\), the polar angles \(\beta_1\) and \(\beta_2\) of each rod relative to the separation vector \(\mathbf{R}\), and the dihedral angle \(\varphi\) between the planes spanned by rod 1 and \(\mathbf{R}\) and by rod 2 and \(\mathbf{R}\) (see Fig. 1). For brevity, we denote the configuration by \(X=(R,\beta_1,\beta_2,\varphi)\). In presenting numerical results, we will focus on the four symmetric configurations \(H, X, T, I\), defined in Table I.

![Diagram](https://example.com/diagram.png)

**FIG. 1.** Two identical thin rods of length \(2a\) in a configuration specified by the internal variables \(R,\beta_1,\beta_2,\varphi\). The position along rod 1 is specified by the variable \(z_1\), with \(-a < z_1 < a\), and similarly for rod 2. In general, the two rods do not lie in a common plane.

We assume that the electrostatic potential \(\psi\) at all points outside the macroions is sufficiently small to obey the linearized Poisson–Boltzmann (LPB) equation,

\[
\nabla^2 \psi = \frac{\kappa^2 \psi}{1},
\]

with \(1/\kappa\) the Debye screening length. If the rod radius is small compared to the Debye length, the electrostatic potential from a single rod can be represented as an integral, over the length of the rod, of the Green’s function for the LPB equation, i.e.,

\[
\psi(r) = \frac{1}{4\pi\varepsilon_0\varepsilon_r} \int_{-a}^{a} dz \lambda(z) \frac{\exp(-\kappa r(z))}{r(z)},
\]

with \(\lambda(z)\) the linear charge density of the rod, \(r(z)\) the distance from a point \(z\) on the rod to the field point, and \(\varepsilon_r\) the relative permittivity of the surrounding dielectric medium.

In the linear regime, where the LPB equation is valid, the free energy of interaction of two thin rodlike macroions can be obtained simply by integrating the product of linear charge density and electrostatic potential over the length of either rod,

\[
V(X) = \frac{1}{4\pi\varepsilon_0\varepsilon_r} \int_{-a}^{a} dz_1 \int_{-a}^{a} dz_2 \lambda(z_1) \lambda(z_2) \exp[-\kappa r(z_1, z_2; X)] / r(z_1, z_2; X),
\]

with \(r(z_1, z_2; X)\) the configuration-dependent distance between the points \(z_1\) and \(z_2\) on the two rods (see Fig. 1),

\[
r(z_1, z_2; X) = R^2 + z_1^2 + z_2^2 - 2R (z_1 \cos \beta_1 - z_2 \cos \beta_2)
\]

\[
-2z_1z_2 (\cos \beta_1 \cos \beta_2
\]

\[
+ \sin \beta_1 \sin \beta_2 \cos \varphi) \right]^{1/2}.
\]

In Eq. (2.3), we have assumed that the linear charge density \(\lambda(z)\) is independent of the configuration \(X\); in fact, in the following we shall assume that it is uniform, \(\lambda(z) = \lambda\). As discussed previously,\(^{17-21}\) in connection with infinitely long rods \((a \rightarrow \infty)\), the effects of a finite rod radius can be taken into account simply by reinterpreting \(\lambda\). For rods of finite length, however, the effective linear charge density then becomes nonuniform even if the surface charge density is uniform. Furthermore, Eq. (2.3) is not exact for rods of finite radius, but represents a linear superposition approximation,\(^{1,11,18,24}\) valid for configurations where the double layers of the two rods overlap only weakly (surface separation larger than the Debye length). We note also that nonlinear screening effects, not described explicitly by the LPB equation, can be approximately incorporated into Eq. (2.3) by replacing the actual linear charge density and Debye length by suitably renormalized quantities.\(^{27,28}\)

Although in principle straightforward to integrate numerically for an arbitrary configuration \(X\), the integral representation Eq. (2.3) of the double-layer interaction is cumbersome to use in statistical-mechanical calculations. A more convenient representation can be obtained by means of a spherical harmonic expansion of the screened Coulomb potential in the integrand of Eq. (2.3). Before deriving the expansion of the double-layer interaction, however, we shall consider some special cases and derive some useful approximations to the integral representation Eq. (2.3).

III. INTEGRAL REPRESENTATION

A. Rods perpendicular to their separation vector

In this section we restrict the configurational space to configurations with both rods perpendicular to their separation vector \(\mathbf{R}\), i.e., \(\beta_1 = \beta_2 = \pi/2\). This configurational subset includes as special cases the canonical configurations \(H\) and \(X\) (cf. Table I). The two remaining configurational variables are the center-of-mass separation \(R\), which is now also the distance of closest approach of the two rods, and the dihedral angle \(\varphi\). For infinitely long rods, these are the only configurational variables. The general expression (2.4) now reduces to

<table>
<thead>
<tr>
<th>Configuration</th>
<th>(\beta_1)</th>
<th>(\beta_2)</th>
<th>(\varphi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)</td>
<td>(\pi/2)</td>
<td>(\pi/2)</td>
<td>0</td>
</tr>
<tr>
<td>(X)</td>
<td>(\pi/2)</td>
<td>(\pi/2)</td>
<td>(\pi/2)</td>
</tr>
<tr>
<td>(T)</td>
<td>0</td>
<td>(\pi/2)</td>
<td>...</td>
</tr>
<tr>
<td>(I)</td>
<td>0</td>
<td>0</td>
<td>...</td>
</tr>
</tbody>
</table>
where \( \alpha = \kappa a / \sqrt{2 \kappa R} \) and \( \text{erf}(z) \) is the error function. To obtain Eq. (3.4), we have performed the integration over \( x_2 \) and then made the substitution \( u = \alpha x \). The approximation (3.4) is actually valid at any separation \( R \), provided that \( \kappa a \) is sufficiently large so that the \( x_2 \) integral in Eq. (3.2) is heavily dominated by small values of \( x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi \). For \( \varphi = 0 \), this is the case if \( \kappa a \gg a R \), i.e., if \( \kappa R \gg 1 \), whereas, if \( \varphi = \pi/2 \), \( \kappa a \gg 1 \) is sufficient. For brevity, we refer to Eq. (3.4) as the asymptotic approximation, although its validity is not restricted to the large-separation regime.

The asymptotic approximation (3.4) allows us to obtain simple analytical results for the \( H \) and \( X \) configurations. For the \( X \) configuration, Eq. (3.4) yields

\[
V(R, \pi/2) = \frac{\lambda^2}{2 \sqrt{\pi \varepsilon_0 \varepsilon_r \kappa}} \exp(-\kappa R) \cdot \text{erf}(\alpha) \cdot [\text{erf}(\alpha)]^2,
\]

(3.5a)

and for the \( H \) configuration (per unit rod length),

\[
r(z_1, z_2; R, \varphi) = (R^2 + z_1^2 + z_2^2 - 2 z_1 z_2 \cos \varphi)^{1/2}.
\]

Inserting this into Eq. (2.3) (with uniform \( \lambda \)) and changing the integration variable to \( x = z/a \), we obtain

\[
V(R, \varphi) = \frac{a \lambda^2}{4 \pi \varepsilon_0 \varepsilon_r} \int_{-1}^{1} dx_1 \int_{-1}^{1} dx_2 \exp[-\kappa a (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi) / (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi)^{1/2}]
\]

\[
\times \exp[-\kappa a (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi) / (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi)^{1/2}].
\]

(3.2)

For the \( X \) configuration (\( \varphi = \pi/2 \)), this double integral can be reduced to two single integrals by means of a transformation to polar coordinates in the \( x_1 - x_2 \) plane,

\[
V(R, \pi/2) = \frac{\lambda^2}{2 \varepsilon_0 \varepsilon_r \kappa} \exp(-\kappa R)
\]

\[
- \frac{2}{\pi} \int_{0}^{\pi/2} d \theta \exp[-\kappa R \left( 1 + \left( \frac{a}{R \cos \theta} \right)^2 \right)]
\]

\[
- \frac{2}{\pi} \int_{\pi/2}^{\pi} d \theta \exp[-\kappa R \left( 1 + \left( \frac{a}{R \sin \theta} \right)^2 \right)]
\]

(3.3)

B. Asymptotic approximation

In the large-separation regime, \( R \gg a \), we can expand the square root in Eq. (3.2) to obtain

\[
V(R, \varphi) = \frac{a^2 \lambda^2}{4 \pi \varepsilon_0 \varepsilon_r R} \int_{-1}^{1} dx_1 \int_{-1}^{1} dx_2 \exp[-\kappa a (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi) / (R^2/a^2 + x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi)^{1/2}] \times \exp[-\alpha^2 (x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi)]
\]

\[
= \frac{\lambda^2}{2 \sqrt{\pi \varepsilon_0 \varepsilon_r \kappa}} \exp(-\kappa R) \int_{-\alpha}^{\alpha} du \exp(-u^2 \sin^2 \varphi \text{erf}(u \cos \varphi + \alpha)),
\]

(3.4)

where \( \alpha = \kappa a / \sqrt{2 \kappa R} \) and \( \text{erf}(z) \) is the error function. To obtain Eq. (3.4), we have performed the integration over \( x_2 \) and then made the substitution \( u = \alpha x \). The approximation (3.4) is actually valid at any separation \( R \), provided that \( \kappa a \) is sufficiently large so that the \( x_2 \) integral in Eq. (3.2) is heavily dominated by small values of \( x_1^2 + x_2^2 - 2 x_1 x_2 \cos \varphi \). For \( \varphi = 0 \), this is the case if \( \kappa a \gg a R \), i.e., if \( \kappa R \gg 1 \), whereas, if \( \varphi = \pi/2 \), \( \kappa a \gg 1 \) is sufficient. For brevity, we refer to Eq. (3.4) as the asymptotic approximation, although its validity is not restricted to the large-separation regime.

The asymptotic approximation (3.4) allows us to obtain simple analytical results for the \( H \) and \( X \) configurations. For the \( X \) configuration, Eq. (3.4) yields

\[
V(R, \pi/2) = \frac{\lambda^2}{2 \varepsilon_0 \varepsilon_r \kappa} \exp(-\kappa R) \left[ \text{erf}(\alpha) \right]^2,
\]

(3.5a)

and for the \( H \) configuration (per unit rod length),

\[
\frac{u(R, 0)}{2a} = \exp(-\kappa R) \left[ \text{erf}(2\alpha) - \frac{1 - \exp(-4\alpha^2)}{2 \sqrt{\pi \alpha}} \right].
\]

(3.5b)

The accuracy of these approximations is illustrated in Fig. 2 in terms of contours of constant relative error in the \( \kappa a = R/a \) plane. The relative error (in percent) is defined as \( 100 \left( V_{\text{asymp}} - V_{\text{exact}} \right) / V_{\text{exact}} \), with \( V_{\text{exact}} \) computed numerically from Eqs. (3.2) or (3.3). The asymptotic approximation, which generally overestimates the double-layer repulsion, is seen to perform respectably in a large part of the physically relevant region of the parameter plane. An accuracy better than 10%, for example, requires \( \kappa R > 1 \) for the \( H \) configuration and \( \kappa a + R/a > 2 \) for the \( X \) configuration. In general, an accurate estimate of the double-layer interaction is only needed when \( V \) is of order \( k_B T \). Within the region bounded by the two gray curves in Fig. 2, corresponding to \( 0.1 < V/(k_B T) < 10 \) for a rod of length 200 Å bearing a net charge of 100 e, the asymptotic approximation is only a few percent above the exact result.

The parameter \( \alpha \) is a measure of the anisotropy of the double-layer interaction. When \( \alpha \ll 1 \), we can...
C. Infinite rods

The limiting case of infinitely long rods, \( a \to \infty \), is actually a special case of the asymptotic approximation, which is valid at all separations for \( \kappa a > 1 \) if \( \varphi \neq 0 \). Thus, for \( \varphi \neq 0 \), we obtain from Eq. (3.4),

\[
V_{\infty}(R, \varphi) = \frac{\lambda^2}{\sqrt{\pi \varepsilon_0 \varepsilon_r \kappa}} \exp(-\kappa R) \int_0^\infty \exp(-u^2 \sin^2 \varphi) \, \text{d}u = \frac{\lambda^2}{2 \pi \varepsilon_0 \varepsilon_r} \exp(-\kappa R) \frac{1}{\sin \varphi}, \tag{3.7a}
\]

which is simply the screened Coulomb interaction between two point charges \( Q = 2a \lambda \). The dashed lines in Fig. 2 represent the 1% and 10% relative error contours (corresponding to \( \alpha = 0.12 \) and 0.38, respectively) for the point-charge interaction (3.6). The general criterion for the validity of Eq. (3.6) is \( R/a > 1 + \kappa a/2 \), which essentially reduces to \( \alpha < 1 \) within the region of the parameter plane shown in Fig. 2.

\[
\begin{align*}
\text{FIG. 3. Contours of constant relative error for the infinite-rod approximation} \\
\text{(3.7) to the double-layer repulsion between rods of length } 2a \text{ in the } H \\
\text{(upper panel) and } X \text{ (lower panel) configurations. The dashed contours refer} \\
\text{to the point-charge limit (3.6). They gray curves correspond to a repulsion} \\
\text{of 0.1 and 10 } k_B T \text{ between rods of length 200 Å and net charge } 100e.
\end{align*}
\]

D. Dihedral torque

For the configurations \( \beta_1 = \beta_2 = \pi/2 \) considered throughout Sec. III, the only torque acting on the rods is the dihedral torque

\[
T_\varphi(R, \varphi) = -\frac{\partial}{\partial \varphi} V(R, \varphi). \tag{3.8}
\]

From a physical point of view, it is clear that this torque must be nonnegative, tending to twist the rods into the \( X \) configuration, which clearly minimizes the double-layer repulsion. Furthermore, the symmetry of the problem implies that \( V(R, -\varphi) = V(R, \varphi) \) and \( V(R, \pi - \varphi) = V(R, \varphi) \). Consequently, the dihedral torque must vanish in both the \( H \) and \( X \) configurations, \( T_\varphi(R, 0) = T_\varphi(R, \pi/2) = 0 \), and must exhibit a maximum at some intermediate dihedral angle.

Inserting Eq. (3.7a) into Eq. (3.8), we obtain for the dihedral torque on infinitely long rods,

\[
T_\varphi(R, \varphi) = \frac{\lambda^2}{2 \pi \varepsilon_0 \varepsilon_r} \exp(-\kappa R) \sin(\varphi) \cos \varphi. \tag{3.9}
\]

Since this result was derived assuming \( \varphi \neq 0 \), it does not contradict the symmetry requirement \( T_\varphi(R, 0) = 0 \). As an approximation for finite rods, however, Eq. (3.9) grossly overestimates the torque at small angles \( \varphi \) even for very long

\[
\text{FIG. 3. Contours of constant relative error for the infinite-rod approximation} \\
\text{(3.7) to the double-layer repulsion between rods of length } 2a \text{ in the } H \\
\text{(upper panel) and } X \text{ (lower panel) configurations. The dashed contours refer} \\
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\end{align*}
\]
rods at short separation. This is illustrated in Fig. 4, comparing the infinite-rod approximation (3.9) with the exact torque, computed numerically from Eqs. (3.2) and (3.8), at two separations, $R/(2a)=0.1$ and 1. Even when the separation is merely 1/10 of the rod length, Eq. (3.9) is accurate only for large angles. When the separation is comparable to the rod length, Eq. (3.9) fails altogether, the angular dependence being close to $\sin(2\varphi)$.

IV. SPHERICAL HARMONIC EXPANSION

A. Two-center expansion of $\exp(-\kappa r)/r$

We now return to the generic configuration, with arbitrary angles $\beta_1$ and $\beta_2$ (cf. Fig. 1). As shown in Appendix A, the function $\exp(-\kappa r)/r$ in Eq. (2.3) can be expressed as a spherical harmonic expansion, convergent for $R>|z_1|+|z_2|$,.

$$
\frac{\exp(-\kappa r)}{r} = \kappa \sum_{L_1} \sum_{L_2} (-1)^{L_2} (2L_1+1)(2L_2+1) \times \left[ C(L_1L_2L;00) \right]^2 \mathcal{J}_{L_1}(\kappa z_1) \mathcal{J}_{L_2}(\kappa z_2) \times \mathcal{K}_{L}(\kappa R) S_{L_1L_2}(\beta_1,\beta_2,\varphi),
$$

(4.1)

where the Clebsch–Gordan coefficient $C(L_1L_2L;M_1M_2)$, the modified spherical Bessel functions $\mathcal{J}_L(z)$ and $\mathcal{K}_L(z)$, and the rotational invariant $S_{L_1L_2}(\beta_1,\beta_2,\varphi)$ have all been defined in Appendix A. Apart from the scaling of all distances by the Debye length, this expression differs from Eq. (A17) in that the argument of the first two Bessel functions in Eq. (4.1) involves the $z$ component (which may be negative) of the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, rather than their lengths (cf. Figs. 1 and 10). Consequently, $\beta_1$ is now the polar angle of rod 1 rather than of the vector $\mathbf{r}_1$, as in Eq. (A17). In Eq. (A17) the inversion $\mathbf{r}_1 \rightarrow -\mathbf{r}_1$ changes the rotational invariant $S_{L_1L_2}(\beta_1,\beta_2,\varphi)$ into $S_{L_1L_2}(\pi-\beta_1,\beta_2,\varphi+\pi)$.

$$
= (-1)^{L_1} s_{L_1L_2}(\beta_1,\beta_2,\varphi),
$$

while in Eq. (4.1) it changes $\mathcal{J}_{L_1}(\kappa z_1)$ into $\mathcal{J}_{L_1}(-\kappa z_1)$ and $\mathcal{J}_{L_2}(\kappa z_2)$ into $\mathcal{J}_{L_2}(-\kappa z_2)$. The two conventions are thus equivalent. When Eq. (4.1) is substituted into Eq. (2.3), we obtain two integrals of the form

$$
\int_{a}^{b} d\zeta \mathcal{J}_{L}(\kappa \zeta) = \begin{cases} 2 \int_{0}^{a} d\zeta \mathcal{J}_{L}(\kappa \zeta), & \text{even } L, \\ 0, & \text{odd } L. \end{cases}
$$

(4.2)

Consequently, only terms with even $L_1$ and $L_2$ contribute in the expansion of $V(\mathbf{X})$. Furthermore, since the Clebsch–Gordan coefficient in Eq. (4.1) vanishes unless $L_1+L_2+L$ is even, it follows that also $L$ must be even. Physically, the restriction to even $L_1$, $L_2$, and $L$ is a consequence of the invariance of the interaction energy under inversion of either rod 1, rod 2, or the separation vector $\mathbf{R}$, respectively. Furthermore, the Clebsch–Gordan coefficient, which can be expressed on closed algebraic form, imposes the restriction $|L_1-L_2|\leq L \leq L_1+L_2$.

B. Expansion of the double-layer interaction energy

Substitution of Eq. (4.1) into Eq. (2.3) yields the spherical harmonic expansion of the double-layer interaction energy for two thin rods of finite length in a generic configuration $\mathbf{X}=(R,\beta_1,\beta_2,\varphi)$.

$$
V(\mathbf{X}) = \sum_{L_1} \sum_{L_2} \sum_{L} V_{L_1L_2}(R) S_{L_1L_2}(\beta_1,\beta_2,\varphi).
$$

(4.3)

where the primes denote the restriction to even integers. After some rearrangements, the interaction coefficients $V_{L_1L_2}(R)$ can be expressed as

$$
V_{L_1L_2}(R) = V_0(R) A_{L_1L_2} M_{L_1}(\kappa a) M_{L_2}(\kappa a) F_L(\kappa R),
$$

(4.4)

with $V_0(R)$ the point-charge interaction in Eq. (3.6). In analogy with the electrostatic multipole expansion, we have defined the combinatorial factor

$$
A_{L_1L_2} = 2^{L_1+L_2-1} \frac{L_1!L_2!(2L)!}{(2L_1)!L_2!(2L)!} \left[ \frac{C(L_1L_2L;00)}{2} \right]^2,
$$

(4.5)

and the generalized multipole moments (cf. Sec. IV D),

$$
M_L(\kappa a) = (2L+1)!! \frac{1}{\kappa a} \int_{0}^{\kappa a} dx \mathcal{J}_{L}(x)
$$

$$
= \sum_{n=0}^{\infty} \frac{(2L+1)!!(\kappa a)^L+2n}{(L+1+2n)(2L+1+2n)!}(2n)!!
$$

(4.6)

where we have used Eq. (A15d). Due to the double factorials in the denominator, the power series Eq. (4.6) converges rapidly even for large $\kappa a$. Alternatively, one can use a recurrence relation expressing $M_L(\kappa a)$ in terms of $\mathcal{J}_{L-1}(\kappa a)$ and $M_{L-2}(\kappa a)$. The generalized monopole moment is

FIG. 4. Double-layer torque on rods of length $2a$ oriented perpendicular to the separation vector and skewed at an angle $\varphi$, with $\kappa a=5$ and separation $R$ as indicated. The torque was calculated numerically from Eq. (3.2) and (3.8) and is given in units of $\sqrt{\kappa^2/(2 \pi e_0 \kappa \epsilon)} \exp(-\kappa R)$. The dashed curve corresponds to the infinite-rod limit (3.9).
The magnitudes of the generalized multipole moments, mass separation, interaction energy is strictly convergent only if the center-of-length, i.e., if

\[ \text{double-layer thickness is at least comparable to the rod length, i.e., if} \]

\[ \text{If the double-layer thickness is at least comparable to the rod length, i.e., if} \]

\[ \text{Since} \]

\[ L_1 \text{ and } L_2 \text{ appear symmetrically in Eqs. (4.4) and (4.5), it follows that} \]

\[ V_{L_1 L_2}(R) = V_{L_2 L_1}(R), \]

which is simply a statement of the invariance of the interaction energy under interchange of the two identical rods.

Explicit expressions for the interaction coefficients \( V_{L_1 L_2}(R) \) and the rotational invariants \( S_{L_1 L_2}(\beta_1, \beta_2, \varphi) \) are given in Appendix B for \( L_1, L_2 \leq 2 \).

### C. Convergence properties

Since the two-center expansion of \( \exp(-kr)/r \) is convergent for \( R \gg |z_1| + |z_2| \) (cf. Appendix A), it follows that the spherical harmonic expansion (4.3) of the double-layer interaction energy is strictly convergent only if the center-of-mass separation, \( R \), is at least as large as the rod length, \( 2a \).

In practice, however, the expansion is useful also at somewhat shorter separations. The crucial question is how many terms are needed to achieve the desired accuracy. This depends not only on the relative separation \( R/a \), but also on the magnitudes of the generalized multipole moments, \( M_i(\kappa a) \).

If the double-layer thickness is at least comparable to the rod length, i.e., if \( \kappa a \) is of order unity or smaller, then, as regards electrostatic interactions, the rods appear to be nearly spherical and the higher (large \( L \)) multipoles \( M_L(\kappa a) \) are small. In the opposite limit of large \( \kappa a \), the rods have a pronounced electrical anisotropy and the higher multipoles are large. As seen from Table II, the transition between these limits occurs abruptly at \( \kappa a \) values of order unity.

To illustrate the convergence properties of the spherical harmonic expansion (4.3), we show in Fig. 5 the relative accuracy achieved by truncating the expansion after \( L_1, L_2 \leq L_{\text{max}} \), with \( L_{\text{max}} = 2 \) or 10, for the \( H \) and \( X \) configurations. For \( \kappa a \approx 1 \), the \( L_{\text{max}} = 2 \) truncation is seen to be highly accurate in the range \( R > 2a \) and reasonably accurate at even smaller separations. At the smaller separations, however, the accuracy is “accidental” and deteriorates as more terms are included. This is a well-known feature of multipole expansions.

Comparing the \( L_{\text{max}} = 10 \) curves for the two configurations, we see that higher accuracy is obtained at smaller separations for the \( X \) configuration. This is because, in the \( X \) configuration, only the central portions of the rods (where \( z_1 \) and \( z_2 \) are small) contribute significantly to the double-layer repulsion. With increasing \( \kappa a \), a rapidly growing number of terms is needed for high accuracy. This point is more clearly illustrated in Fig. 6, showing the double-layer repulsion, in units of \( V_0 \), at various levels of truncation for the configurations \( H, X, T, \) and \( I \) at a separation \( R = 2a \). As expected on the basis of the rapidly rising numbers of terms, the accuracy for \( \kappa a \approx 1 \) is poor, but improves as \( \kappa a \) increases.

#### FIG. 5. Relative accuracy of the truncated spherical harmonic expansion of the double-layer repulsion between rods of length \( 2a \) in the \( H \) (upper panel) and \( X \) (lower panel) configurations vs the reduced separation \( R/a \). The expansion was truncated after \( L_1, L_2 = L_{\text{max}} \), with \( L_{\text{max}} = 2 \) (solid curves) or \( L_{\text{max}} = 10 \) (dashed curves). The four curves in each set refer, from left to right, to \( \kappa a = 0.1, 1, 2, \) and 4.
basis of the separation between different parts of the two rods, the convergence is faster for $X$ than for $H$, and faster for $T$ than for $I$.

D. Unscreened multipole limit

In the limit of vanishing electrolyte concentration, $\kappa \to \infty$, Eqs. (4.6) and (4.8) reduce to $M_\ell(\kappa a) = (\kappa a)^\ell/(L+1)$ and $F_\ell(\kappa R) = 1/(\kappa R)^\ell$. Since $V_{L_1L_2L}$ in Eq. (4.4) is then proportional to $K^{L_1+L_2-L}$, it vanishes unless $L=L_1+L_2$. With this restriction, Eq. (4.5) reduces to $A_{L_1L_2L} = (L_1+L_2)!/(L_1! L_2!)$, and we obtain with Eqs. (3.6) and (4.4),

$$\lim_{\kappa \to 0} V_{L_1L_2L}(R) = \delta_{L_1+L_2} \left( \frac{L_1+L_2}{L_1! L_2!} \right) \frac{\mu_{L_1} \mu_{L_2}}{4\pi \varepsilon_0 \varepsilon_r R^{L_1+L_2+1}} ,$$

(4.10)

which is the well-known electrostatic multipole interaction, the spherical multipole moments of the rod being $\mu_L = Q a^{L+1}/(L+1)$. In the presence of screening ($\kappa > 0$), the spherical harmonic expansion (4.3) is no longer an electrostatic multipole expansion in the strict sense. The constraint $L=L_1+L_2$, characteristic of an electrostatic multipole expansion, emerges only for a potential that satisfies Laplace’s equation. In the double-layer case, the potential satisfies Poisson’s equation, and the expansion includes all terms with (even) $L$ values from $|L_1-L_2|$ to $L_1+L_2$. However, the non-multipole terms, with $L \neq L_1+L_2$, are relatively insignificant for $\kappa a \lesssim 1$ (cf. Sec. IV F).

E. Asymptotic limit

The spherical harmonic expansion of the double-layer interaction reduces to a very simple, but nontrivial, result in the large-separation regime. If $\kappa R$ is sufficiently large, the power series (4.8) can be truncated after the first ($n=0$) term, with a relative error of $L(L+1)/(2\kappa R)$. Since $L \geq L_1+L_2$, this error is negligible if $\kappa a$ is not too large and $R/a$ not too small, so that the expansion (4.3) converges rapidly (cf. Sec. IV C). More precisely, if $R/a \gg 1 + \kappa a/2$ we can replace $F_\ell(\kappa R)$ by $1/(2L-1)!$. Using the orthogonality relation $^\dagger$

$$\sum_{L} C(L_1L_2L:M-M)C(L_1L_2L;00) = \delta_{M0} ,$$

(4.11)

and the addition theorem $^\dagger$

$$\sum_{L} (2L+1) \mathcal{J}_L(x) P_L(\cos \beta) = \cosh(x \cos \beta) ,$$

(4.12)

we then obtain from Eqs. (4.3)–(4.6),

$$V(X) = V_0 \mathcal{J}_0(\kappa a \cos \beta_1) \mathcal{J}_0(\kappa a \cos \beta_2) ,$$

(4.13)

with $\mathcal{J}(z) = \sinh(z)/z$. This result can also be obtained directly from Eq. (2.3) by noting that, at large separations, we can replace $r$ by $R - z_1 \cos \beta_1 + z_2 \cos \beta_2$ in the exponent and by $R$ in the denominator.

The important lesson to be learned from Eq. (4.13) is that two screened rods of finite length do not in general behave as two screened point charges when they are at infinite separation. The point-charge limit (3.6) can be recovered from Eq. (4.13) in three distinct ways. One way is obviously by letting the rod length go to zero. A second way is by letting the electrolyte concentration (and, hence, $\kappa$) go to zero. This is as expected, for only the Coulomb term survives in the usual (unscreened) multipole expansion at sufficiently large separation. The third way is to restrict both rods to be perpendicular to the separation vector ($\beta_1 = \beta_2 = \pi/2$). If one or both rods deviate from this orientation, the double-layer repulsion increases by a factor that depends on the ratio of the projected (on $R$) rod length to the Debye length. It is instructive to note that

$$Q \mathcal{J}_0(\kappa a \cos \beta_1) = \sum_{n=0}^\infty \frac{\kappa^{2n}}{(2n)!} \bar{\mu}_{2n} ,$$

(4.14)

where $\bar{\mu}_{2n} = Q(\cos \beta_1)^{2n}/(2n+1)$ is the projected multipole moment of the rod (cf. Sec. IV D). Consequently, the asymptotic result Eq. (4.13) may be viewed as an interaction between the projected multipole moments of the two rods, scaled by the Debye length. Alternatively, Eq. (4.13) may be regarded as a screened Coulomb interaction with effective charges $Q \mathcal{J}_0(\kappa a \cos \beta_1)$ that depend on the rod orientation and on the electrolyte concentration.
double-layer repulsion increases in the order $1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 0.076 \rightarrow 0.021 \rightarrow 0.002 \rightarrow 0.028 \rightarrow 0.076$.

TABLE III. Multipole contributions to the double-layer repulsion between two rods of length $2a$ in each of the four canonical configurations, all at a separation of $R = 2a$.

<table>
<thead>
<tr>
<th>$L_1$</th>
<th>$L_2$</th>
<th>$L$</th>
<th>$V_{L_1L_2}/V_0$</th>
<th>$V_{L_1L_2S_{L_1L_2}}/V_0$</th>
<th>$H$</th>
<th>$X$</th>
<th>$T$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.118</td>
<td>1.118</td>
<td>1.118</td>
<td>1.118</td>
<td>1.118</td>
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<td>2</td>
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<tr>
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<td>2</td>
<td>0</td>
<td>0.003</td>
<td>-0.003</td>
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<td>0.001</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
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<td>2</td>
<td>2</td>
<td>0.012</td>
<td>-0.006</td>
<td>0.012</td>
<td>-0.006</td>
<td>0.012</td>
<td>0.012</td>
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<tr>
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<td>2</td>
<td>4</td>
<td>0.255</td>
<td>0.096</td>
<td>0.032</td>
<td>-0.128</td>
<td>0.255</td>
<td>0.255</td>
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<tr>
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<td>4</td>
<td>0.077</td>
<td>0.058</td>
<td>0.058</td>
<td>0.106</td>
<td>0.154</td>
<td>0.106</td>
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<tr>
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<td>2</td>
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<td>0.000</td>
<td>-0.000</td>
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</tr>
<tr>
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<td>2</td>
<td>4</td>
<td>0.002</td>
<td>-0.002</td>
<td>-0.003</td>
<td>-0.000</td>
<td>0.004</td>
<td>0.004</td>
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<tr>
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<td>-0.013</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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</tr>
<tr>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
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<td>4</td>
<td>4</td>
<td>0.001</td>
<td>-0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>6</td>
<td>0.076</td>
<td>0.021</td>
<td>0.002</td>
<td>0.028</td>
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<td>higher</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.004</td>
<td>-0.006</td>
<td>-0.013</td>
<td>0.717</td>
</tr>
</tbody>
</table>

We display terms up to $L_1, L_2 = 4$, the sum of which yields better than 1% accuracy at $R = 2a$ and $\kappa a = 1$ for the $H, X,$ and $T$ configurations. (For the $I$ configuration, where the rods are touching at $R = 2a,$ the error is $\sim 30\%$.) The first thing to note is that all nonmultipole terms, i.e., those with $L \neq L_1 + L_2$, are negligibly small. This is a general feature for $\kappa a \leq 1$. We now discuss the multipole terms $(L_1, L_2, L_1 + L_2)$, highlighted in Table III.

A uniformly charged rod has an (axial) quadrupole moment of the same sign as its net charge (monopole). If the latter is taken as positive, the quadrupole can be schematically represented as $(+)(-)(+).$ For the $H$ and $X$ configurations, the charge–quadrupole interaction, denoted (202) for short, should thus be attractive and of equal magnitude, while the quadrupole–quadrupole interaction, (224), should be repulsive, more so for $H$ than for $X$. Since the (202) interaction should dominate over the (224) interaction, we expect that the double-layer repulsion should increase in the order $V(X) \leq V(H) \leq V_0$, as in Fig. 7. An inspection of Table III shows that this simple rationalization in terms of the two lowest orientation-dependent multipole interactions is essentially correct. For the $H$ configuration, the higher terms essentially cancel out, while for the $X$ configuration they add a repulsive contribution similar to that from (224), bringing $V(X)$ closer to $V(H)$.

The $T$ configuration is unique among the four in that the two rods are nonequivalent $(\beta_1 \neq \beta_2)$, whereby $S_{L_1L_2}(T) \neq S_{L_1L_2}(T)$. With the angles defined as in Table I, (202) is repulsive (same as for configuration $I$), while (022) is attractive (same as for $H$ and $X$). The sum of these two terms, which is the quantity displayed in Table III, gives a repulsive charge–quadrupole interaction. As well-known, the $T$ configuration is the most stable one for purely quadrupolar molecules, and, as seen from Table III, the attractive (224) interaction cancels a large fraction of the charge–quadrupole repulsion. The stronger double-layer repulsion for the $T$ configuration as compared to point charges is, however, due to roughly equal extent to a repulsive charge–hexadecapole interaction, (404), the higher terms being insignificant.

At a given center-of-mass separation, $R$, the $I$ configuration is generally the least stable of all possible configurations. This follows since the interaction coefficients $V_{L_1L_2S_{L_1L_2}}(R)$ are nonnegative [as are all factors appearing in the definition (4.4)] and since $S_{L_1L_2}(T) = 1$. It is therefore not surprising that higher multipoles than the hexadecapole are needed to quantitatively account for the double-layer repulsion at a separation $R = 2a$, where the ends of the two rods are touching.

G. Torques

Using the spherical harmonic expansions (4.3) and (A9), we can express the dihedral double-layer torque, $T_\varphi = -\partial V/\partial \phi$, exerted on two finite rods as

$$T_\varphi(X) = \sum_M (-1)^M MT_M(R, \beta_1, \beta_2) \sin(M \varphi),$$

with
thought that a large number of terms is needed to accurately
sin
b
sion varies much more strongly with the polar angles
dM
w

noticeable contribution from the sin
b
T M
w
w!

interaction coefficients up to the hexadecapole level,

w~

differed from, and orders of magnitude smaller than, the
infinite-rod torque (3.9). At \( \kappa a = 5 \) and the same separation,
\( T_\phi(\varphi) \) retains a roughly symmetrical shape, albeit with a
noticeable contribution from the \( \sin(4\varphi) \) term (cf. Fig. 4).

As can be inferred from Fig. 7, the double-layer repulsion
varies much more strongly with the polar angles \( \beta_i \) and
\( \beta_2 \) than with the dihedral angle \( \varphi \). Indeed, in the infinite-rod
limit, the repulsion is effectively infinite for the \( T \) and \( I \)
configurations. According to Eq. (4.3), the polar double-layer
torque on rod 1, \( T_{\beta_1} = -\partial V/\partial \beta_1 \), for a fixed orientation
of rod 2, is

\[
T_{\beta_1}(X) = \sum_{L_1} \sum_{L_2} \sum_{L} V_{L_1,L_2,L}(R) \\
\times \left[ \frac{\partial}{\partial \beta_1} S_{L_1,L_2}(\beta_1, \beta_2, \varphi) \right].
\]

By symmetry, this torque must vanish at \( \beta_1 = 0 \) and at
\( \beta_1 = \pi/2 \) if \( \beta_2 = 0 \) or \( \beta_2 = \pi/2 \). Furthermore, the polar torque is
then always positive, tending to increase \( \beta_1 \) at fixed \( \beta_2 \) and
\( \varphi \). For less symmetrical configurations \( (0 < \beta_2 < \pi/2) \), how-
ever, the torque may go through zero at intermediate \( \beta_1 \) val-
ues, corresponding to a minimum in the double-layer repul-
sion.

If rod 2 is oriented along the separation vector \( (\beta_2 = 0) \),
Eq. (4.19) reduces, with the aid of Eq. (A 10b), to

\[
T_{\beta_1}(R, \beta_1) = \sum_{L_1} \sum_{L_2} \sum_{L} V_{L_1,L_2,L}(R) \\
\times \frac{L_1[PL_{1-1}(\cos \beta_1) - \cos \beta_1 PL_{1}(\cos \beta_1)]}{\sin \beta_1}
\]

which is readily shown to vanish at \( \beta_1 = 0 \) and at \( \beta_1 = \pi/2 \), as
required by symmetry.

In the asymptotic limit, we obtain from Eqs. (4.13) and
(A 15c),

\[
T_{\beta_1}(R, \beta_1, \beta_2) = V_0 \kappa a \sin \beta_1 \sin(\kappa a \cos \beta_1) \sin(\kappa a \cos \beta_2),
\]

with \( \sin(\zeta) = \cosh(\zeta)/z - \sinh(\zeta)/z^2 \). In this limit, the torque
vanishes at \( \beta_1 = 0 \) and at \( \beta_1 = \pi/2 \) for any orientation of rod 2.

Figure 9 shows the polar torque on rod 1 as a function of
its polar angle \( \beta_1 \) for a fixed orientation of rod 2 at a separa-
tion \( R = 2a \). Since the \( H \) and \( X \) configurations have
nearly equal double-layer repulsion (cf. Fig. 7), it is not sur-
prising that, as these configurations are transformed into the
\( T \) configuration, the torques are nearly equal. At the shorter
separation \( R = 2a \), the \( T \rightarrow H/X \) curves are nearly the same as
in Fig. 9, while the maximum of the \( I \rightarrow T \) curve shifts to
smaller \( \beta_1 \), corresponding to a drastic increase of the torque
for a small deflection from the metastable \( I \) configuration.

V. CONCLUDING REMARKS

For the purpose of statistical-mechanical calculations or
computer simulations of dispersions of rodlike macroions,
one needs a mathematically simple, yet reasonably accurate,
representation of the double-layer repulsion. In this work, we
have obtained two such representations. For rods in the \( H \)
and \( X \) configurations, the so-called asymptotic approxima-
tion (3.5), while not significantly more mathematically com-
plex than the infinite-rod limit (3.7), yields accurate results

FIG. 8. Double-layer torque, in units of \( V_o \), on rods of length \( 2a \) oriented
perpendicular to the separation vector and skewed at an angle \( \varphi \), with \( \kappa a = 1 \)
and separation \( R = 2a \). The solid curve was calculated numerically from
Eqs. (3.2) and (3.8), while the dashed curve corresponds to the low-order
multipole approximation (4.18) with the interaction coefficients taken from
Table III.

\[
T_M(R, \beta_1, \beta_2) = \sum_{L_1} \sum_{L_2} \sum_{L} V_{L_1,L_2,L}(R) \\
\times \frac{C(L_1L_2L;M-M)}{C(L_1L_2L;00)} d^{L_1}_{M_1}(\beta_1) d^{L_2}_{M_2}(\beta_2).
\]

(4.17)

Since \( \varphi = \varphi_1 - \varphi_2 \), it follows that the dihedral torques on the
two rods are equal in magnitude, but of opposite sign. It is
evident from Eq. (4.16) that the torque vanishes at \( \varphi = 0 \),
corresponding to the maximum repulsion. If both rods are
perpendicular to the separation vector, then, since\( d_M^{L_1}(\pi/2) = 0 \) for odd \( M, \) only terms with even \( M \) contrib-
ute to the sum in Eq. (4.16). Consequently, the torque van-
ishes also at \( \varphi = \pi/2 \) for these configurations (cf. Sec. III D).

In view of the small difference in double-layer repulsion
between the \( H \) and \( X \) configurations (cf. Fig. 7), it may be
thought that a large number of terms is needed to accurately
describe the dihedral torques for configurations with
\( \beta_1 = \beta_2 = \pi/2 \). As seen from Fig. 8, however, a good approxi-
mation is provided, for \( R = 2a \) and \( \kappa a = 1 \), by the leading
\( \sin(2\varphi) \) term in Eq. (4.16), with the prefactor including in-
teraction coefficients up to the hexadecapole level,

\[
T_\varphi(\varphi) = \frac{1}{8} \left[ 6(V_{220} - V_{222}) + V_{224} - V_{426} \right] \\
+ V_{448} \sin(2\varphi).
\]

(4.18)

Except very close to \( \varphi = \pi/2 \), this torque is qualitatively dif-
ferent from, and orders of magnitude smaller than, the
infinite-rod torque (3.9). At \( \kappa a = 5 \) and the same separation,
\( T_\varphi(\varphi) \) retains a roughly symmetrical shape, albeit with a
noticeable contribution from the \( \sin(4\varphi) \) term (cf. Fig. 4).
for finite rods over most of the physically interesting part of the parameter space (cf. Fig. 2). The general form Eq. (3.4) of the asymptotic approximation might be used, for example, to calculate the second virial coefficient of solution of a system with short rodlike macroions, or to investigate end effects on the isotropic-nematic phase transition.

From a conceptual point of view, the principal result of this work is the generalized multipole expansion of the double-layer repulsion, which for relatively short rods can be truncated at the quadrupole level, yielding quantitatively accurate results even at separations comparable to the rod length. The analysis in terms of screened charge–quadrupole and quadrupole–quadrupole interactions provides a simple rationalization of the orientation dependence of the double-layer repulsion in such cases. Furthermore, we have established the asymptotic form Eq. (4.13) of the double-layer repulsion, which retains a dependence on the polar angles at arbitrarily large separation.

The present approach to the double-layer interaction problem, based on the two-center expansion of the Green’s function for the LPB equation, is rather general and can be applied also to macroions other than thin rods, e.g., cylinders of finite diameter or ellipsoids. By applying the boundary condition at the macroion surface, one then obtains a non-uniform effective linear charge density. In a subsequent report, we shall use this approach to calculate the double-layer repulsion between prolate-spheroidal macroions.

**ACKNOWLEDGMENT**

This work was supported by the Swedish Natural Science Research Council.

**APPENDIX A: TWO-CENTER EXPANSION OF \( \exp(-r)/r \)**

We derive here the spherical harmonic two-center expansion of the function \( \exp(-r)/r \), where \( r \) is the distance between two points specified by radius vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) associated with two different origins \( O_1 \) and \( O_2 \) connected by a vector \( \mathbf{R} \) (see Fig. 10). We use an approach originally developed to evaluate multicenter overlap integrals in quantum chemistry, and we follow closely the treatment of Briels, who derived the analogous expansion of \( \exp(-r) \).

This Appendix also serves as a repository of definitions and useful properties of the modified spherical Bessel functions and of the rotationally invariant angular functions used in Sec. IV.

We begin by expressing the function \( \exp(-r)/r \) as an inverse Fourier transform,

\[
\frac{\exp(-r)}{r} = (2\pi)^{-3} \int d\mathbf{k} \, \phi(k) \exp(i\mathbf{k} \cdot \mathbf{r}),
\]  

(A1)

with

\[
\phi(k) = \int d\mathbf{r} \, \frac{\exp(-r)}{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) = \frac{4\pi}{1+k^2}.
\]  

(A2)

Since \( \mathbf{r} = \mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1 \) (cf. Fig. 10), the exponential in Eq. (A1) can be factorized as \( \exp(i\mathbf{k} \cdot \mathbf{R}) \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_2) \). Each of these exponentials is then developed in a plane-wave expansion, e.g.,

\[
\exp(i\mathbf{k} \cdot \mathbf{R}) = \sum_{L=0}^{\infty} (i)^L (2L+1) j_{2L}(\kappa R)
\]  

\[
\times \sum_{M=-L}^{L} C_{LM}(\Omega) C_{LM}^*(\Omega_k),
\]  

(A3)

where the \( j_{2L}(z) \) are \( L \)th order spherical Bessel functions of the first kind and the \( C_{LM}(\Omega) \) are Racah’s modified spherical harmonics, the argument \( \Omega \) giving the spherical polar angles of the vector \( [\mathbf{R} \text{ or } \mathbf{k} \text{ in Eq. (A3)}] \) with respect to an external coordinate system.

The combination of Eqs. (A1)–(A3) yields

![FIG. 10. Vectors used for the two-center expansion. In general, the three vectors \( \mathbf{r}_1, \mathbf{r}_2, \) and \( \mathbf{R} \) are not coplanar.](Image 358x630 to 519x743)
\[
\frac{\exp(-r)}{r} = (2\pi^2)^{-1} \sum_{L_1} \sum_{L_2} \sum_{L} (-1)^{L_1} (1+L_1+L_2)(2L_1+1)(2L_2+1) \int_0^\infty dk \frac{k^2}{1+k^2} j_{L_1}(kr_1)j_{L_2}(kr_2) j_L(kR) \\
\times \left[ \int d\Omega_k C_{L_1M_1}(\Omega_k) C_{L_2M_2}(\Omega_k) C_{LM}(\Omega_k) \right]^* C_{L_1M_1}(\Omega_1) C_{L_2M_2}(\Omega_2) C_{LM}(\Omega), \quad (A4)
\]

where the factor \((-1)^{L_1}\) comes from \(j_{L_1}(-kr_1)\) \((-1)^{L_1}j_{L_1}(kr_1)\). The integral of a product of three spherical harmonics can be expressed in terms of Clebsch–Gordan coefficients as

\[
\int d\Omega_k C_{L_1M_1}(\Omega_k) C_{L_2M_2}(\Omega_k) C_{LM}(\Omega_k) = \delta_{-M,M_1+M_2} \frac{4\pi}{2L+1} \times C(L_1L_2;00) C(L_1L_2;M_1M_2). \quad (A5)
\]

Inserting Eq. (A5) into Eq. (A4) and noting that \(C_{LM}^*(-\Omega) = (-1)^M C_{LM}(\Omega)\), we get

\[
\frac{\exp(-r)}{r} = \sum_{L_1} \sum_{L_2} \sum_{L} (i)^{L_1+L_2-L_1}(2L_1+1)(2L_2+1) \\
\times [C(L_1L_2;00)]^2 \\
\times Y_{L_1L_2}(r_1,r_2,R) S_{L_1L_2}(\Omega_1,\Omega_2,\Omega), \quad (A6)
\]

where we have defined

\[
Y_{L_1L_2}(r_1,r_2,R) = \frac{1}{\pi} \int_{-\infty}^{\infty} dk \frac{k^2}{1+k^2} j_{L_1}(kr_1)j_{L_2}(kr_2) j_L(kR). \quad (A7)
\]

The integration range has been symmetrized here, which is possible since \((L_1+L_2+L)\) is an even integer, implying that the integrand is an even function of \(k\). Furthermore,

\[
S_{L_1L_2}(\Omega_1,\Omega_2,\Omega) = \sum_{M_1} \sum_{M_2} \frac{C(L_1L_2;M_1M_2)}{C(L_1L_2;00)} \\
\times C_{L_1M_1}(\Omega_1) C_{L_2M_2}(\Omega_2) C_{LM}^*(\Omega). \quad (A8)
\]

The real-valued quantity \(S_{L_1L_2}(\Omega_1,\Omega_2,\Omega)\) is invariant under rotation of the external coordinate system with respect to which the angles \(\Omega_1,\Omega_2,\Omega\) are measured. The expansion (A8) thus holds in any coordinate system. In particular, if the orientations of \(r_1\) and \(r_2\) are specified with respect to the internal frame, we obtain from Eq. (A8) and the relation \(C_{LM}(0) = \delta_{M0}\).

\[
S_{L_1L_2}(\beta_1,\beta_2,\varphi) = \sum_{M=0} \frac{(2-\delta_{M0})(-1)^M C(L_1L_2;M-M)}{C(L_1L_2;00)} \\
\times d_{M0}^{L1}(\beta_1) d_{M0}^{L2}(\beta_2) \cos(M\varphi), \quad (A9)
\]

with the internal orientational variables defined as in Fig. 1 and \(M = \min(L_1,L_2)\). The \(d_{M0}^{L}(\beta)\) are reduced Wigner functions, proportional to the associated Legendre functions. In the special case that \(r_1\) and \(r_2\) are parallel, making a common angle \(\beta\) with \(R\), the sum over \(M\) can be contracted \(29\) and Eq. (A9) reduces to

\[
S_{L_1L_2}(\beta,\beta,0) = P_L(\cos \beta). \quad (A10a)
\]

Similarly, if one of the rods is oriented along the separation vector, say \(\beta_2=0\), then Eq. (A9) reduces to

\[
S_{L_1L_2}(\beta_1,0,\varphi) = P_{L_1}(\cos \beta_1). \quad (A10b)
\]

Note that our definition of \(S_{L_1L_2}(\Omega_1,\Omega_2,\Omega)\) differs by a factor \(1/C(L_1L_2;00)\) from the usual convention.\(^{30}\) Our convention leads to simpler numerical factors in the spherical harmonic expansion coefficients.

To evaluate the integral in Eq. (A7) we substitute for the third Bessel function the Rayleigh formula\(^{31}\)

\[
j_L(z) = (-z)^L \left( \frac{1}{z} \frac{d}{dz} \right)^L \sin z, \quad (A11)
\]

whereby

\[
Y_{L_1L_2}(r_1,r_2,R) = \frac{(-R)^L}{\pi} \int_{-\infty}^{\infty} dk \frac{k^{1-L}}{1+k^2} j_{L_1}(kr_1)j_{L_2}(kr_2) \\
\times \left[ \frac{1}{R} \frac{d}{dR} \right]^L \sin(kR). \quad (A12)
\]

Since the \(k\)-dependent part of the integrand goes as \(k^{2+L_1+L_2-L}\) for small \(k\), and since \(L\leq L_1+L_2\) due to the triangle inequality implicit in the Clebsch–Gordan coefficient in Eq. (A6), it follows that the integrand is nonsingular. We can therefore interchange the order of integration and differentiation to obtain
Here we have also replaced \( \sin(kR) \) by \( \exp(i kR) / i \), which is permissible since the \( \cos(kR) \) part of the integrand is an odd function of \( k \) (\( L_1 + L_2 - L + 1 \) is an odd integer) and, hence, does not contribute to the integral.

The integrand in Eq. (A13) has simple poles at \( k = \pm i \) and as \( \rho \to \infty \) its magnitude goes as \( \exp(-R \rho) / \rho \), with the complex variable \( \rho = \rho \exp(i \theta) \). Provided that \( R \geq r_1 + r_2 \), the integrand thus vanishes as \( \rho \to \infty \) in the upper half of the complex plane (where \( \theta > 0 \)) and we can apply the residue theorem with the integration contour encircling the pole at \( k = i \). We thus obtain

\[
Y_{l_1 l_2}(r_1, r_2, R) = (-R)^L \left[ \frac{d}{dR} \sin \frac{R}{i} \right]^L \int_{-\infty}^{\infty} dk \frac{k^{1-L}}{1 + k^2} (l_1 \ell_1)(l_2 \ell_2)(2) \exp(i k R).
\]

(A13)

The unsymmetrical factor \( (-1)^L \) results from the convention of having the vector \( \mathbf{R} \) pointing from \( O_1 \) to \( O_2 \). Using Eqs. (A15d) and (A16d), one readily verifies that Eq. (A17) correctly reduces to \( \exp(-R) / R \) when \( r_1 = r_2 = 0 \). Using the spherical harmonic addition theorem, one can also show that Eq. (A17) correctly reduces, for \( r_2 = 0 \), to the well-known\(^{31}\) one-center expansion (valid for \( R \gg r_1 \)),

\[
\frac{\exp(-R)}{R} = \sum_{L} (2L + 1) J_L(r_1) \mathcal{H}_L(R) P_L(\cos \beta_1).
\]

(A18)

APPENDIX B: LEADING TERMS IN SPHERICAL HARMONIC EXPANSION

In this Appendix we give explicit expressions for the leading terms in the spherical harmonic expansion (4.3) of the double-layer repulsion between two finite rods. Including terms up to \( L_1, L_2 = 2 \), we have

\[
V = V_{000} + V_{022}(S_{022} + S_{022}) + V_{220}S_{220} + V_{222}S_{222} + V_{224}S_{224}.
\]

(B1)

According to Eqs. (4.4), (4.5), and (4.8), the interaction coefficients are

\[
V_{000} = M_0^2 V_0, \quad V_{202} = \frac{1}{3} M_0 M_2 \left[ 1 + \frac{3}{\kappa R} + \frac{1}{(\kappa R)^2} \right] V_0, \quad V_{220} = \frac{1}{45} M_2^2 V_0, \quad V_{222} = \frac{2}{63} M_2^2 \left[ 1 + \frac{3}{\kappa R} + \frac{3}{(\kappa R)^2} \right] V_0, \quad V_{224} = \frac{2}{35} M_2^2 \left[ 1 + \frac{10}{\kappa R} \right] V_0.
\]

(B2a)

(B2b)

(B2c)

(B2d)

The rotational invariants, defined by Eq. (A9), are

\[
S_{000} = 1, \quad S_{202} + S_{022} = P_2(\cos \beta_1) + P_2(\cos \beta_2), \quad S_{220} = P_2(\cos \beta_1) P_2(\cos \beta_2) + \frac{3}{4} \sin(2\beta_1) \sin(2\beta_2) \cos \varphi + \frac{1}{4} \sin^2 \beta_1 \sin^2 \beta_2 \cos(2 \varphi).
\]

(B3a)

(B3b)

(B3c)
\[ S_{222} = P_2(\cos \beta_1)P_2(\cos \beta_2) \]
\[ + \frac{3}{8} \sin(2\beta_1)\sin(2\beta_2)\cos \varphi \]
\[ - \frac{3}{4} \sin^2 \beta_1 \sin^2 \beta_2 \cos(2\varphi), \]
\[ S_{224} = P_2(\cos \beta_1)P_2(\cos \beta_2) \]
\[ - \frac{1}{3} \sin(2\beta_1)\sin(2\beta_2)\cos \varphi \]
\[ + \frac{1}{8} \sin^2 \beta_1 \sin^2 \beta_2 \cos(2\varphi). \]