

# A PHYSICAL METHOD FOR DERIVING THE ELECTROSTATIC INTERACTION BETWEEN ROD-LIKE POLYIONS AT ALL MUTUAL ANGLES

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**ABSTRACT** The screened Coulomb interaction between polyelectrolyte cylinders immersed in an ionic bath is examined. The electrostatic force and torque acting between a pair of unlike rods is formulated for all separations in which the electrostatic potential on some dividing surface between rods can be written as a linear superposition of isolated cylinder potentials. (The surface potential on the rods themselves may be much higher than that permitted by a superposition approximation.) The mutual energy in the case of skewed rods is found to be exponential in separation and proportional to  $1/\sin \theta$  where  $\theta$  is the twist angle of one rod relative to the other. Rods with similar charge repel each other with a torque acting to make the rods perpendicular while rods of opposite charge attract with the parallel arrangement preferred.

## INTRODUCTION

In this paper we derive several formulae for the electrostatic interaction between very long cylindrical particles in a salt solution. The mutual orientation of the rods may be parallel (as has been the case in previous analyses [1, 2]) or skewed at any angle (3). The particles themselves may be of differing charge and thickness.

For skewed rods the electrostatic force per interaction is purely exponential in separation and goes as  $1/\sin \theta$  in their mutual angle (Fig. 1), Eqs. 19 and 20.

In order to find these results we have devised a method that avoids the approximation of treating cylinder interactions as a modification of that between planes (3, 4). It also obviates the mathematical problems of integrating over the elements of a stress tensor (5) or over the states of a charging process (6). The method is actually an observation on the exact physical equivalence of several pictures of the interacting particles. It permits one to write down formulae almost directly for electrostatic interactions in other than cylindrical geometry. Physically the method is limited by the same restrictions inherent in the "linear superposition approxima-

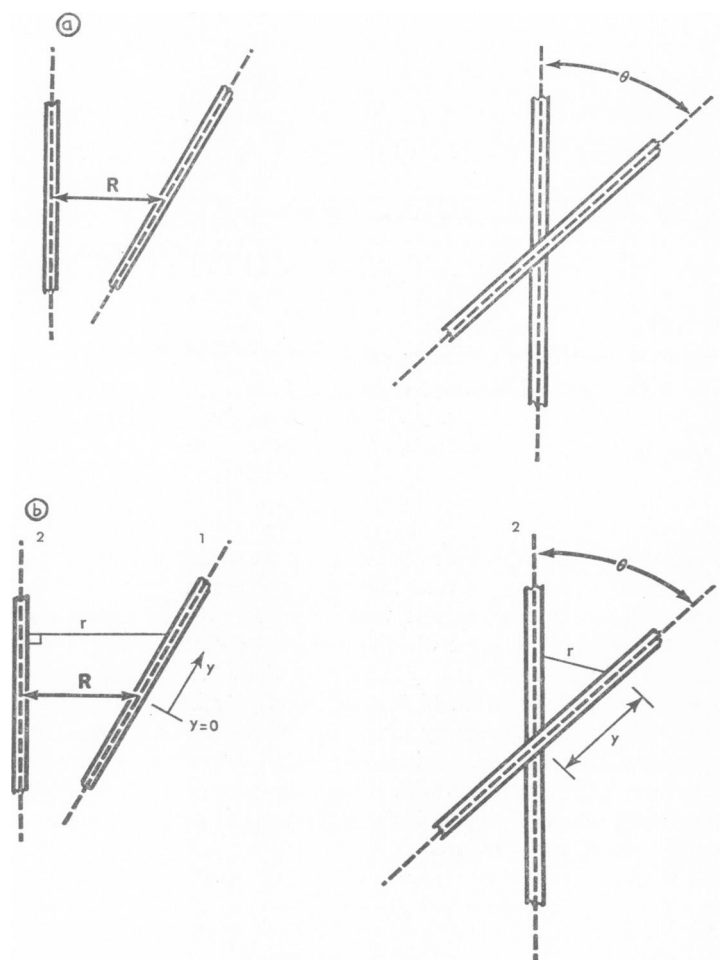


FIGURE 1 (a) Rods are separated by a minimum center-to-center distance  $R$  and make an angle  $\theta$  when viewed along  $R$ . (b) The distance  $r$  is the perpendicular distance from the axis of rod 2 to some point along the axis of rod 1. The distance along rod 1 is measured by  $y$  where  $y = 0$  is chosen at  $r = R$ . These distances and angle are related by  $r^2 = R^2 + (y \sin \theta)^2$ .

tion" of Bell et al. (5) (which of course holds well beyond the weak surface potentials usually associated with superposition of potentials in salt solution).

The breadth of situations allowed by the present formulation for rod-like particles should allow application to phenomena of phase separation and array formation. For example, tobacco mosaic virus, suspended in salt water, will divide into two phases, one a dilute solution of randomly oriented rods, the second an array of parallel viruses (7). Accurate theoretical expressions for attractive and repulsive forces between particles are necessary for understanding the distribution and

spacings of particles in these phases (3, 8–13). The structures of other systems such as collagen fibrils in corneal deposition (14–17), aggregation and orientation of sickle-cell hemoglobin (18), and the formation and mutual juxtaposition of muscle proteins (19–21) may also depend on electrostatic torques and forces.

In the following we first give a physical argument for reducing the mathematical problem of formulating electrostatic forces between rods. This method will apply when rod radii are much less than their separation or when the nearest rod-rod distance is not less than the Debye length of the salt medium. We then write down expressions for the force per unit length between dissimilar parallel rods, and the force, torque, and energy per interaction between skewed rods. These particular results hold when the skewed rods are effectively of infinite length although the general method may in principle be applied to particles of any length.

## METHOD

The electrostatic force on a charged body in a salt solution is most generally conceived as the total electric and osmotic stress integrated over any closed surface that includes the charged body but excludes other bodies acting on it. The magnitude of the electro-osmotic stress tensor depends on the electrostatic potential and potential gradient at each point on the enclosing surface. Unhappily integration of the stress over any surface set up for the interaction of two cylinders can be a mathematically arduous procedure (5). We therefore make the following observation:

The same electrostatic potential giving the stress between two charged rods of finite thickness can often be rewritten identically as a potential arising from two hypothetical rods of infinitesimal thickness. But now rather than using a stress tensor to formulate the mutual force exerted between these thin rods, one may in many cases write the force as the product of the field set up by one rod times the charge on the other thin rod.

That is, there are then three equivalent ways to visualize the force between two rods of finite thickness: (a) integration over a stress surface, (b) integrating over the same surface where the same electrostatic potential and potential gradient is expressed as emanating from two hypothetical but equivalent thin rods, or (c) multiplying the charge on one thin rod by the local electric field emanating from the other thin rod. When permitted, use of (c) relieves one of tedious spatial integrations required by (a) or (b). (Analogous reasoning for the interaction of spherical particles leads to the results derived by Bell et al. (5) by a single multiplication rather than integration (a).)

In order to follow procedure (c) it is sufficient that (1) the total potential on the stress surface be the superposition of potential fields due to the individual rods; (2) the component potential fields can be expressed as those occurring in the vicinity of the isolated rods. The first condition is implicit in any solution of a linearized potential equation (which need hold only on some surface between the interacting particles); the second condition is met when the minimum surface-to-surface distance of the two bodies is not less than the Debye length  $1/\kappa$  of the salt water medium (6) (see Eq. 3 below).

Between the rods we are interested in the formal solution of a linearized Poisson-Boltzmann equation for the electrostatic potential  $\Psi$ . The full PB equation,

$$\nabla^2 \Psi = -\frac{4\pi e}{\epsilon} \sum_i n_i^0 z_i e^{-z_i e \Psi / kT}, \quad (1)$$

is expanded in the exponentials to become

$$\nabla^2 \Psi = \kappa^2 \Psi. \quad (2)$$

When superposition holds the use of the linearized Poisson-Boltzmann equation is valid on the stress surface because the potential there is small ( $e\Psi \ll kT$ ) due to screening of the field emanating at the rod surfaces by the intervening salt solution. Here we define

$$\kappa^2 = 8\pi ne^2/\epsilon kT, \quad (3)$$

where  $\epsilon$  is the (uniform) dielectric constant of the bathing medium,  $-e$  is the electronic charge,  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $n$  is given by

$$n = \frac{1}{2} \sum_{\{n_i^0\}} n_i^0 z_i^2. \quad (4)$$

The set  $\{n_i^0\}$  designates the concentrations of the ionic species in the reference solution far from the charged bodies (where the potential is taken to be zero) with ions of valence  $z_i$  having concentrations  $n_i^0$  (ions per cubic centimeter).

For a single cylindrical rod of radius  $a$  the potential is radially symmetric varying only as the distance  $r$  from the rod axis. The solution of Eq. 2 is

$$\Psi(r) = AK_0(\kappa r) \quad (5)$$

where  $K_0$  is the zero order modified Bessel function of the second kind (22).

If we imagine that the single cylinder potential Eq. 5 arises from a hypothetical line charge of density  $\nu_h$  charge per unit length then coefficient  $A$  is  $2\nu_h/\epsilon$ . The potential sufficiently far from the rod axis is

$$\Psi = (2\nu_h/\epsilon)K_0(\kappa r). \quad (6)$$

the derivative electric field at those long distances is

$$E = -\partial\Psi/\partial r = (2\nu_h/\epsilon) \kappa K_1(\kappa r). \quad (7)$$

Several available methods (1, 23, 24) may be used for determining the effective charge  $\nu_h$  in particular applications. Alamov (25) and Philip and Wooding (26) describe techniques for matching solutions for potentials near a charged cylindrical body with the limiting large  $\kappa r$  form of Eq. 5. The variational method of Brenner and Roberts (27) may be readily adapted to cylinders for a closed-form analytic expression for the potential. Finally, direct iterative numerical solution of the full Eq. 1 is practical.

For the special case of cylinders of known radius  $a$  and low surface potential, Eq. 6 holds at all distances  $r > a$ . In that weak potential limit we have

$$\nu_h = 2\pi\sigma/\kappa K_1(\kappa a), \quad (8)$$

where  $\sigma$  is the actual charge per unit area of the cylinder and  $K_1$  is a Bessel function. In the additional limit where  $(\kappa a) \gg 1$ ,  $\nu_h$  becomes

$$\nu_h \rightarrow (2\sigma/\kappa) \sqrt{2\pi\kappa a} e^{\kappa a}. \quad (9)$$

Brenner and McQuarrie (6) have shown that to good approximation the total electrostatic

potential from two identical parallel rods of interaxial distance  $R$  is simply the sum of two solutions having the form of Eq. 5. They demonstrated that this will hold as long as the minimum distance ( $R - 2a$ ) is not less than  $1/\kappa$ , the Debye length of the medium.

## RESULTS

### *Parallel Rods*

The electrostatic force per unit length between two parallel rods "1" and "2" separated by intraxial distance  $R$  is the product of the electric field  $E_1(R)$  on rod 1 and the effective linear charge density  $\nu_{h2}$  on rod 2 (or vice versa)

$$f_1(R) = 2(\nu_{h1}\nu_{h2}/\epsilon)\kappa K_1(\kappa R), \quad (10)$$

while the mutual energy of interaction (relative to infinite separation) is

$$W_1(R) = 2(\nu_{h1}\nu_{h2}/\epsilon)K_0(\kappa R). \quad (11)$$

The functions  $K_0(\kappa R)$  and  $K_1(\kappa R)$  may be expanded in asymptotic series for large  $\kappa R$  (22)

$$K_0(\kappa R) = \sqrt{\pi/2} (e^{-\kappa R}/\sqrt{\kappa R}) \left(1 - \frac{1}{8\kappa R} + \frac{9}{2(8\kappa R)^2} - \dots\right) \quad (12)$$

$$K_1(\kappa R) = \sqrt{\pi/2} (e^{-\kappa R}/\sqrt{\kappa R}) \left(1 + \frac{3}{8\kappa R} - \frac{15}{2(8\kappa R)^2} + \dots\right). \quad (13)$$

For the limiting case of cylinders of known radii  $a_1, a_2$ , and low surface potential, the coefficients  $\nu_{h1}$  and  $\nu_{h2}$  for the hypothetical linear charge densities in Eqs. 10 and 11 are related to the actual charge per unit area by the relations in Eqs. 8 or 9.

Whenever the distance  $R - (a_1 + a_2)$  is *much* greater than the Debye length  $1/\kappa$ , Eq. 13 may be used for a limiting force law

$$f_1(R) \rightarrow \frac{\sqrt{2\pi} \nu_{h1}\nu_{h2}}{\epsilon} \kappa (e^{-\kappa R}/\sqrt{\kappa R}) \left(1 + \frac{3}{8\kappa R} - \frac{15}{2(8\kappa R)^2} + \dots\right). \quad (14)$$

This agrees with a result of Brenner and McQuarrie who used a lengthier method to find the leading term in the force between two like rods,

$$f_1(R) = \xi(e^{-\kappa R}/\sqrt{\kappa R}), \quad (15)$$

where  $\xi = \xi(\kappa, a)$  for a given charge density and dielectric constant.

### *Skewed Rods*

For two skewed infinitely long rods of minimum interaxial separation  $R$  and mutual angle (of rotation from parallel configuration)  $\theta$ , it is convenient to write first the

energy of electrostatic interaction  $W_{12}(R, \theta)$  (Fig. 1). This energy is the integral of line charge on one rod times the potential of the second thin rod exerted at each point on rod no. 1.

If we let  $y$  measure this distance along rod no. 1 (where  $y = 0$  is the point of minimum distance from rod no. 2) the required integral is

$$W_{12} = \nu_{h1} \int_{-\infty}^{+\infty} \Psi_2 dy, \quad (16)$$

as shown in Fig. 1. From Eq. 9 we must integrate

$$\begin{aligned} W_{12} &= \frac{2\nu_{h1}\nu_{h2}}{\epsilon} \int_0^{\infty} K_0(\kappa r) dy \\ &= \frac{2R\nu_{h1}\nu_{h2}}{\epsilon \sin \theta} \int_0^{\infty} K_0(\kappa R \cosh \beta) \cosh \beta d\beta. \end{aligned} \quad (17)$$

Here the variable of integration  $r$  is the perpendicular distance from each point  $y$  on rod no. 1 to the axis of rod no. 2. Since  $r$  and  $y$  are related by

$$r^2 = R^2 + (y \sin \theta)^2,$$

we have defined a new variable of integration  $\beta$  such that  $r = R \cosh \beta$ . Eq. 17 may be integrated in closed form using a technique due to Nicolson (28) to give

$$W_{12} = (\pi\nu_{h1}\nu_{h2}/\epsilon\kappa)(e^{-\kappa R}/\sin \theta). \quad (18)$$

The electrostatic force per interaction  $f(R, \theta)$  and the torque  $\tau(R, \theta)$  are:

$$f(R, \theta) = -(\partial W_{12}/\partial R)_{\theta} = (\pi\nu_{h1}\nu_{h2}/\epsilon)(e^{-\kappa R}/\sin \theta), \quad (19)$$

$$\tau(R, \theta) = -(\partial W_{12}/\partial \theta)_R = (\pi\nu_{h1}\nu_{h2}/\epsilon\kappa)(\cos \theta/\sin^2 \theta)e^{-\kappa R}. \quad (20)$$

These electrostatic forces are purely exponential in separation and decrease with increasing mutual angle. The forces seem to diverge as  $\theta$  goes to zero because they are forces *per interaction* and we have assumed rods have infinite length; in fact the interaction of parallel rods is finite but is properly expressed as a force *per unit length* (Eq. 10).

As should be expected, the torque acts to twist rods of like charge sign away from the parallel orientation toward a perpendicular configuration. The electrostatic attraction or rods of unlike charge sign acts to align the particles (similar to the torque created by the electrodynamic or van der Waals attraction between thin rods [29]). Obviously, attraction tends to align rods while repulsion tends to minimize contact between them.

An expression similar to Eq. 18 was derived by Onsager (3) using an approximate method due to Derjaguin (4). The difference from our Eq. 18 is in the coefficient  $\pi\nu_{h1}\nu_{h2}/\epsilon\kappa$ . It had not been apparent on the basis of the earlier work that the spatial

and angular dependence,  $e^{-\kappa R}/\sin \theta$ , was the result of a certain approximate treatment or in fact a general property of rod interactions.

## DISCUSSION

How widely can the present formulae be used to compute the electrostatic interaction of two cylindrical particles? As long as the potential on some surface between the particles be a sum of unperturbed potentials from the two rods, the underlying assumptions will be satisfied. Should those individual unperturbed potentials very near the rods be a solution of the full nonlinear equation (Eq. 1), one only requires suitable definition of the coefficient  $\nu_h$  to match the assumed form Eq. 6 far from the rod surface. (A similar modification has already been suggested for the case of spheres [5].) Rods of differing radii and charge density may be treated within this framework.

Qualitatively, as long as interaxial separation  $R$  is much greater than cylindrical radii or as long as the minimum surface-to-surface distance is not less than the Debye length, the computations of Brenner and McQuarrie (6) would suggest that it is appropriate to treat the interacting cylinders as if they were equivalent thin rods. The present expressions reduce rigorously to give the correct result for the interaction of two thin charged rods in a salt-free dielectric.

For rods bearing weak potentials (such that  $e\Psi/kT \ll 1$ ) or in media having high salt concentrations (such that  $\kappa R \gg 1$ ), the simultaneous interaction of several charged rods will be the pairwise sum of individual rod-rod interactions. For low salt concentrations and high charge densities on the rods, one must solve for the electrostatic potential in a way that accounts for the simultaneous position of several rods (30, 31); the electrostatic energy in the array is not then the pairwise sum of rod-rod interactions.

The one major restriction in the application of these formulae is the assumption that rod length  $L$  be much greater than the interaxial distance  $R$ . It is clear that for finite rods of length  $L$  (at any angle) separated by  $R \gg L$  the resultant equations will be essentially those characterizing point charges of magnitude  $\nu L$ . For rods whose length  $L \gg R$  and whose ends are far from the position of closest approach of the rods, we have the case considered in this paper. For  $R \simeq L$  the analysis is difficult but we expect a smooth transition from infinite rod to point particle behavior.

We are currently studying implications for the present results for the packing of tobacco mosaic virus particles in gels and for the orientation of linear polyelectrolytes in ordered arrays.

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