

## Wall-Mediated Forces between Like-Charged Bodies in an Electrolyte

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(Received 24 September 1998)

The Poisson-Boltzmann model of colloidal bodies in electrolyte is the basis of a recent numerical calculation predicting attraction between two colloidal spheres confined in a cylinder. The present study formulates an analytical proof that this model cannot predict attraction. Our exact result, not contingent upon approximations, suggests that a new model is needed to explain experimental results. [S0031-9007(98)08326-4]

PACS numbers: 82.70.Dd

Recent experiments demonstrate attraction between two colloidal spheres in a thin layer of electrolyte bound by glass walls [1,2]. The effect of walls is crucial since the experiment and theory both concur that the force between two like-charged spheres in unbounded electrolyte is repulsive [1,2]. Additional experiments suggest that the nearby presence of densely packed spheres affects the pair interaction in a manner similar to walls—by inducing a long range attractive force [1,2]. Collectively, these experiments demonstrate that densely packed spheres in electrolyte constitute a nonpairwise many body problem.

In a recent publication, Bowen and Sharif numerically simulate the electrostatic interaction between colloidal spheres confined by a cylinder [3]. They report a range of intersphere distances for which the computed force is attractive. This study presents an analytical proof that the equations behind the Bowen and Sharif simulation predict only repulsive interaction. The argument presented here is not contingent upon approximations of an asymptotic or numerical character and applies not only to the specific setup analyzed in [3], but more generally: The colloidal particles need not be spherical and the confining cylinder can have any cross section. A pair of colloidal particles between confining planes would be a special case of the analysis presented here. In addition, the ionic composition of the solution can be generalized from the simple 1:1 electrolyte treated in [3]. Any mixture of ions with different charge numbers is admissible, as long as electroneutrality is maintained.

In [3], the physics of the interaction is expressed mathematically by a boundary value problem for the electrostatic potential  $\psi(\mathbf{x})$  in the electrolyte. Let  $\mathcal{R}$  represent the region occupied by electrolyte. In a dimensionless formulation,  $\psi(\mathbf{x})$  satisfies the Poisson-Boltzmann equation (PBE)

$$\Delta\psi - V'(\psi) = 0 \quad (1)$$

in  $\mathcal{R}$ . The function  $V(\psi)$  is determined by the ionic composition of the electrolyte. Physically,  $-V'(\psi)$  is the local charge density. Given  $N$  ion species with charge numbers  $z_i$  and relative concentrations  $c_i$ , the local charge density seen in thermal equilibrium is the linear

combination of Boltzmann factors

$$-V'(\psi) = \sum_1^N c_i z_i e^{-z_i \psi}.$$

Integration with respect to  $\psi$  gives

$$V(\psi) = \sum_1^N c_i e^{-z_i \psi}. \quad (2)$$

The (irrelevant) constant of integration is set equal to zero. For the case treated in [3], i.e., a simple electrolyte with two kinds of ions of charge numbers  $+1$  and  $-1$ ,  $V'(\psi) = \sinh \psi$  and  $V(\psi) = \cosh \psi$ . The differential equation (1) is supplemented with boundary conditions: On any component of boundary  $\partial\mathcal{R}$  where the electrolyte interfaces with one kind of material,  $\psi$  is a uniform constant. On the surfaces of colloidal bodies all made of one material, there is one uniform potential  $U$ , and another value  $U_w$  on confining walls of some other material. In summary, the boundary value problem for  $\psi$  consists of the Poisson-Boltzmann equation (1) subject to the given uniform values of  $\psi$  on colloidal bodies and/or walls.

Given the solution for  $\psi$ , the Poisson-Boltzmann approximation to the force acting on a colloidal particle with surface  $S$  is [4]

$$\mathbf{F} = \frac{1}{2} \int_S \psi_n^2 \hat{n} da. \quad (3)$$

Here,  $\hat{n}$  is the unit normal outward from the body,  $\psi_n$  is the normal derivative of  $\psi$ , and  $da$  is the element of surface area on  $S$ . Physically, the surface integral in (3) represents the electrostatic force acting on the surface charge. In addition, the counterion cloud about  $S$  induces a pressure force on the body. But this pressure is uniform on  $S$ , and so its contribution to the net force is zero. In [3], the force  $\mathbf{F}$  (3) is computed using a numerical solution for  $\psi$  which corresponds to the given geometry of two spheres confined in the cylinder.

The analysis of this Letter is based upon an alternative evaluation of the force  $\mathbf{F}$  by means of a stress tensor  $T$

$$T \equiv \nabla\psi \otimes \nabla\psi - fI, \quad (4)$$

$$f \equiv \frac{1}{2} |\nabla\psi|^2 + V(\psi). \tag{5}$$

Here,  $I$  is the identity matrix. If  $\psi(\mathbf{x})$  is any solution of the PBE (1), then the stress tensor is divergence free. This is verifiable by a simple calculation. But it also follows from a basic result of variational calculus: The quantity  $f$  in (5) is a Lagrangian density for the PBE (1). It turns out that  $T$  in (4) is precisely the divergence free stress tensor which follows from the space translation invariance of  $f$ . The relevance of  $T$  is the following: On the colloid surface  $S$  where  $\psi$  is uniform,  $\nabla\psi = \psi_n \hat{n}$  and  $V(\psi)$  is a uniform constant. It readily follows that

$$\int_S T \hat{n} da = \frac{1}{2} \int_S \psi_n^2 \hat{n} da = \mathbf{F}.$$

But due to the divergence free character of  $T$ , the surface of integration can be deformed from  $S$  to another surface  $S'$  in the electrolyte which encloses  $S$ , but no other colloidal body. That is,

$$\mathbf{F} = \int_{S'} T \hat{n} da. \tag{6}$$

This method of computing  $\mathbf{F}$  is applied to a setup which contains the setup treated in [3] as a special case. As shown in Fig. 1, the cylinder containing the electrolyte and colloidal bodies can have a noncircular cross section. Cross section planes orthogonal to the cylinder axis are labeled by axial displacement  $z$ , and the 2-vector  $\mathbf{y}$ , confined to a given two-dimensional region  $D$ , denotes positions in a given cross section plane. Two colloidal bodies of the same shape are placed in the cylinder so that  $z = 0$  represents a plane of mirror symmetry.

Consider the axial ( $\hat{z}$ ) component of force on the colloid in  $z > 0$ ,

$$\hat{z} \cdot \mathbf{F} = \int_{S'} \hat{z} \cdot T \hat{n} da. \tag{7}$$

The surface of integration  $S'$  encloses the colloidal surface  $S$  as shown in Fig. 1. It consists of the cylinder section between  $z = 0$  and  $z = L$ , together with the two cross

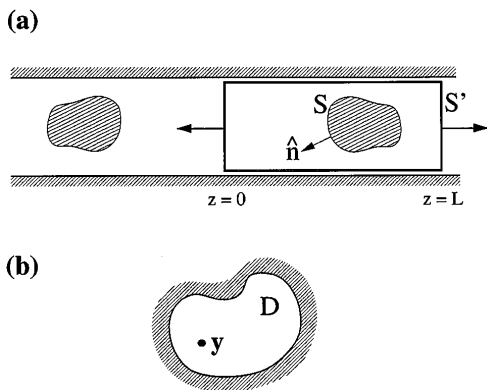


FIG. 1. Two colloidal bodies in a cylinder. (a) Side view. (b) Cross section of the cylinder.

sections  $z = 0$  and  $z = L$ . On the cylinder section,  $\psi$  is uniform so  $\nabla\psi$  has no  $\hat{z}$  component. Also, the unit normal  $n$  on the cylinder wall is orthogonal to  $\hat{z}$ . It follows that  $\hat{z} \cdot T \hat{n} = 0$  on the cylinder, so the cylinder contribution to (7) vanishes. This leaves contributions from cross sections  $z = 0$  and  $z = L$ . On the  $z = L$  cross section,  $\hat{n} = +\hat{z}$ , and it follows from the definition of  $T$  in (4) that

$$\hat{z} \cdot T \hat{n} = \psi_z^2(\mathbf{y}, L) - f(\mathbf{y}, L).$$

On the  $z = 0$  cross section,  $\hat{n} = -\hat{z}$  and

$$\hat{z} \cdot T \hat{n} = f(\mathbf{y}, L).$$

There is no  $-\psi_z^2(\mathbf{y}, 0)$  term because  $\psi_z = 0$  on  $z = 0$  due to the mirror symmetry. In summary, the net axial force acting on  $S$  is

$$\hat{z} \cdot \mathbf{F} = \int_D \{\psi_z^2(\mathbf{y}, L) + f(\mathbf{y}, 0) - f(\mathbf{y}, L)\} d\mathbf{y}. \tag{8}$$

The integral on the right-hand side has to be independent of  $L$ . It is convenient to evaluate it in the limit  $L \rightarrow \infty$ . In the limit  $L \rightarrow \infty$ ,  $\psi(\mathbf{y}, L)$  becomes asymptotic to the solution  $\Psi(\mathbf{y})$  of the two-dimensional boundary value problem

$$\Delta\Psi - V'(\Psi) = 0 \quad \text{in } D, \tag{9}$$

$$\Psi = U_w \quad \text{on } \partial D. \tag{10}$$

One has  $\psi_z(\mathbf{y}, L) \rightarrow 0$  as  $L \rightarrow \infty$ , and  $\psi_z(\mathbf{y}, 0) = 0$  due to mirror symmetry. Hence, (8) reduces to

$$\hat{z} \cdot \mathbf{F} = \int_D \{f(\mathbf{y}, 0) - f(\mathbf{y}, L)\} d\mathbf{y} = \varphi[\psi^0] - \varphi[\Psi]. \tag{11}$$

Here,  $\varphi[h]$  is the functional

$$\varphi[h] \equiv \int_D \left\{ \frac{1}{2} |\nabla h|^2 + V(h) \right\} d\mathbf{y}, \tag{12}$$

defined on scalar fields  $h(\mathbf{y})$  in two-dimensional region  $D$ , and  $\psi^0(\mathbf{y}) \equiv \psi(\mathbf{y}, 0)$ .

For an attractive interaction between the colloidal bodies, the axial force in (11) must be negative. It is not hard to see that the formulation (9)–(12) does not

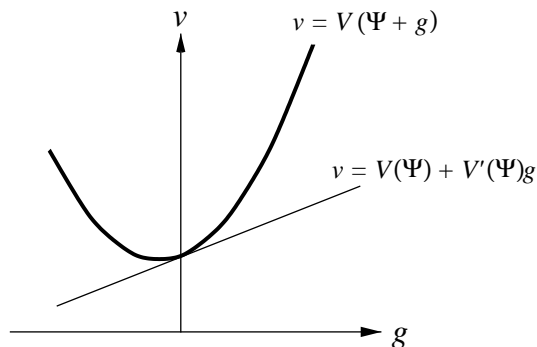


FIG. 2. Convex  $V(\Psi)$ .

confirm such a notion. Note that the solution  $\Psi(\mathbf{y})$  of the two-dimensional boundary value problem (9),(10) is a stationary point of the functional  $\varphi[h]$  in the space of  $h$ 's with  $h \equiv U_w$  on  $\partial D$ . In fact,  $\Psi(\mathbf{y})$  is a *global*

*minimum* of  $\varphi$ . It follows that the axial force (11) cannot be negative and is most likely positive.

The details of the global minimum argument are very simple: Let  $g(\mathbf{y}) \equiv \psi^0(\mathbf{y}) - \Psi(\mathbf{y})$ . From the definition of  $\varphi$  it follows that

$$\begin{aligned} \varphi[\psi^0] - \varphi[\Psi] &= \int_D \left\{ \frac{1}{2} |\nabla g|^2 + \nabla \Psi \cdot \nabla g + V(\Psi + g) - V(\Psi) \right\} dy \\ &= \int_D \left\{ \frac{1}{2} |\nabla g|^2 - \Delta \Psi g + V(\Psi + g) - V(\Psi) \right\} dy \\ &= \int_D \left\{ \frac{1}{2} |\nabla g|^2 + V(\Psi + g) - V(\Psi) - V'(\Psi)g \right\} dy. \end{aligned} \quad (13)$$

The second line follows from a standard Green's identity calculation and the boundary condition  $g = \psi^0 - \Psi = 0$  on  $\partial D$ . The third line is obtained by substitution of  $V'(\Psi)$  for  $\Delta \Psi$  as permitted by differential equation (9). If  $V$  is a convex-up function of its argument, then

$$V(\Psi + g) - V(\Psi) - V'(\Psi)g \geq 0$$

for any  $g$ , with equality only when  $g = 0$ . Figure 2 illustrates this argument. It is clear that the right-hand side of (13) is positive definite in  $g$  if  $V(\psi)$  is convex up. It follows that there is a possibility for attractive interaction only if  $V(\psi)$  is not convex up. Recall the explicit expression (2) for  $V(\psi)$ . Each exponential  $e^{-z_i \psi}$  is convex up regardless of the signs of charge numbers  $z_i$ . The coefficients  $c_i$  representing concentrations are necessarily positive. The verdict:  $V(\psi)$  is convex up. Consequently, electrostatic force  $\mathbf{F}$  between two colloidal bodies is non-negative, and hence, nonattractive.

It is not clear why numerical simulations presented in [3] produced attractive interaction. However, answers to this question have no relevance to the real issue. The rigorous mathematical argument presented here demonstrates that the theory of colloid interaction based upon the Poisson-Boltzmann boundary value problem in [3] cannot predict an attractive force between pairs of colloidal spheres, even if that interaction is mediated by a confining cylinder.

What are the alternatives? Has Poisson-Boltzmann theory been totally ruled out as an explanation of an attractive interaction between colloidal bodies? In an absolutely rigorous sense, not quite: The proof presented here applies only to specific boundary conditions, namely, uniform potentials on the solid surfaces. Even though such boundary conditions can be criticized on physical grounds, they are retained in this Letter in order to focus on the assessment of Bowen and Sharif's results [3]. It remains to examine if the analysis of this Letter generalizes to other boundary conditions, such as might result from an explicit model of ion absorption on the solid surfaces. Admittedly, such a generalization is not straightforward. However, even if a Poisson-Boltzmann model based on

modified boundary conditions predicts wall-mediated attraction between colloidal bodies, it is unlikely that a real contact can be made with Larsen and Grier's experimental data [1]. The energy and length scales observed in this experiment seem out of reach. In [1], Larsen and Grier present the wall-mediated interaction energy between two colloidal spheres of radius  $0.5 \mu\text{m}$  as a function of center-to-center separation. There is a potential well  $\approx 1.5kT$  deep at a separation of  $\approx 3.5 \mu\text{m} = 3500 \text{ nm}$ . Even with a probably optimistic  $400 \text{ nm}$  estimate of the Debye length given in [1], the  $3500 \text{ nm}$  separation represents several Debye lengths. It is hard to see how a Poisson-Boltzmann model can account for such a deep potential well at such a large separation. The need to go beyond Poisson-Boltzmann theory seems compelling. One possible extension was initiated by Onsager [5] and Kirkwood [6], and summarized in the recent monograph of Schmitz [7]. These works suggest that intercolloidal attractions might be a fluctuation-based phenomenon. Models of fluctuation-mediated interactions between polymer chains are presented in a review article by Barrat [8]. Nevertheless, the origin of the attractive force between colloidal bodies remains an open question.

The author of this work acknowledges Professor George Oster at UC Berkeley for bringing this problem to his attention.

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