

## LETTER TO THE EDITOR

## Long-Range Electrostatic Attractions between Identically Charged Particles in Confined Geometries: An Unresolved Problem

**Long-range electrostatic attractions between identical colloidal particles in confined geometries have been observed experimentally by many workers. A satisfactory theoretical explanation for this behavior has proven elusive. Recent numerical calculations and reports (*Nature* 393, 621–623, 663–665 (1998)), however, have suggested that this problem is closed by demonstrating that this surprising effect is to be found naturally within the well-established Poisson–Boltzmann (PB) theory. We rigorously prove that these claims are false; within the framework of the PB theory, the interaction between identical colloidal particles is always repulsive, irrespective of whether the particles are isolated or confined. A satisfactory theoretical explanation of this surprising phenomenon thus remains an unresolved problem.** © 1999 Academic Press

**Key Words:** confined geometries; electrostatic attraction; Poisson–Boltzmann.

Recently, a great deal of effort has been focused on the experimental measurement (1–6) and theoretical validation (7–10) of the surprising phenomenon of long-ranged electrostatic attraction between identically charged colloidal particles, immersed in an electrolyte, and confined by a third charged body. These observations are at odds with the well-established theory of Derjaguin–Landau–Verwey–Overbeek (DLVO) (11, 12) for the pairwise interaction of two isolated identically charged particles, which predicts a repulsion. Experimental results suggest, however, that the source of this dichotomy lies in the influence of a third charged body (1, 3, 5, 6): an attraction is apparent when the particles are in the vicinity of a charged wall, whereas the pairwise interaction is purely repulsive when the particles are isolated. It has been suggested (1, 3, 5, 6, 13) and demonstrated via numerical calculation (10) that this attractive interaction can be obtained using the well-known Poisson–Boltzmann theory, provided the particles are confined. Here we rigorously prove that this is not the case; within the framework of the nonlinear Poisson–Boltzmann theory, the pairwise interaction of two identically charged particles confined or in the vicinity of an arbitrary third charged body, whose sides are parallel to the line joining the centers of the particles, is always repulsive (14). Consequently, our results show that the experimentally observed attractive interactions (1–6) are not to be found within this theoretical framework, and suggest either (a) the need for revision of the existing and established colloidal theories or (b) a reassessment of the experimental techniques and the corresponding interpretation of experimental observations.

The problem to be considered is that of two identically charged particles, immersed in an electrolyte, and confined to or in the vicinity of an arbitrary charged surface  $\Sigma$  which is parallel to the line connecting the centers-of-mass of the two particles. The particles need not be spherical and may have arbitrary charge properties. The only requirement is that the electric potential possesses mirror symmetry about the midplane between the particles. We emphasize that this specification encompasses many cases of practical interest including that of two particles in the vicinity of a single planar wall (6), particles confined between two walls (1–5), or particles confined in a cylindrical pore (10) (see Fig. 1). The electrolyte is confined to the interior of the surface  $\Sigma$  where the particles lie, and the region exterior to the electrolyte has constant permittivity. The surface  $\Sigma$  maintains either constant potential or constant charge density or is charge regulating (15, 16).

To calculate the force between the particles, we require the electric potential in the electrolyte. Within the framework of the nonlinear Poisson–Boltzmann theory, the electric potential  $\Psi$  in a symmetric 1:1 electrolyte and the electric potential  $\phi$  outside the surface  $\Sigma$  (i.e., exterior to the electrolyte) satisfy

$$\nabla^2 \Psi = \left( \frac{kT}{e_0} \right) \kappa^2 \sinh \left( \frac{e_0 \Psi}{kT} \right), \quad \nabla^2 \phi = 0, \quad [1]$$

where  $\kappa$  is the Debye screening parameter. All variables not defined in the text are given in the Appendix. To determine the general nature of the force between the particles, we do not need to solve [1].

A formally exact expression for the electrostatic force  $f$  between the particles, acting along their line-of-centers, is obtained by integrating the Maxwell stress tensor (15) over an appropriate surface  $S$  enclosing one of the particles within the electrolyte,

$$f = \int_S \mathbf{n} \cdot \left[ \left( \Pi + \frac{1}{2} \epsilon E^2 \right) \mathbf{I} - \epsilon \mathbf{E} \mathbf{E} \right] \cdot \mathbf{k} dS, \quad [2]$$

where  $\Pi = 2n_0 kT \cosh(e_0 \Psi / kT)$  is the osmotic pressure, and  $\mathbf{E} = -\nabla \Psi$  is the electric field. A repulsive force between the particles corresponds to  $f$  being positive.

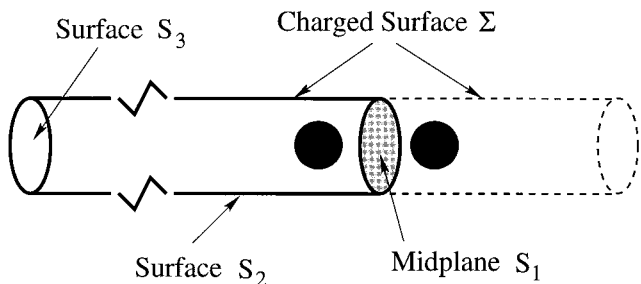
The choice of the surface  $S$  is completely arbitrary and will give the same result provided it completely encloses one of the particles. For convenience we choose the surface  $S$  to be a cylinder of arbitrary cross section with (a) one face of  $S$  coinciding with the midplane between the particles, denoted  $S_1$ , (b) the sides of cylinder  $S$ , denoted  $S_2$ , are parallel to the line-of-centers of the particles and are lying either on the charged surface  $\Sigma$  or at an infinite distance from the particles (e.g., in the case  $\Sigma$  is a single flat wall), and (c) the remaining face of  $S$ , denoted  $S_3$ , is identical and parallel to the face at the midplane  $S_1$ , but located at an infinite distance along the cylinder axis from  $S_1$  and the interacting particles. A graphical example of this surface for two particles confined in a cylindrical pore is given in Fig. 1. The expression for the force, Eq. [2], is then separated into three integrals over  $S_1$ ,  $S_2$ , and  $S_3$ .

For the case where  $\Sigma$  is held at constant potential, we note that the components of the electric field at  $S_1$ ,  $S_2$ , and  $S_3$  in the  $\mathbf{k}$  direction are zero. Consequently, the integral over  $S_2$  vanishes. Substituting  $y_{\text{diff}} = y - y_3$  into [2], making use of [1], and Green's theorem (17) we then obtain

$$f = \epsilon \left( \frac{kT}{e_0} \right)^2 \int_{S_1} \left\{ \kappa^2 [\cosh(y_3 + y_{\text{diff}}) - \cosh y_3 - y_{\text{diff}} \sinh y_3] + \frac{1}{2} \left| \nabla_y y_{\text{diff}} \right|^2 \right\} dS_1, \quad [3]$$

where  $y_3$  is identical to the reduced electric potential distribution due to the charged surface  $\Sigma$  in isolation, i.e., with the particles removed. Since the integrand in [3] is always positive, irrespective of the signs and magnitudes of  $y_3$  and  $y_{\text{diff}}$ , it then follows that  $f$  is always positive; i.e., the force is repulsive.

The analysis for the case where  $\Sigma$  is held at constant charge density is performed in an analogous manner by making use of the dielectric boundary



**FIG. 1.** Schematic diagram of two identically charged particles (filled spheres) confined in a charged cylindrical pore  $\Sigma$ . The particles are immersed in an electrolyte which is bounded by the surface  $\Sigma$ . The region exterior to the electrolyte has constant permittivity. The integration surface  $S$  used in the evaluation of the force encloses one of the particles, and its subsurfaces  $S_1$ ,  $S_2$ , and  $S_3$  are indicated.

condition (15) at  $\Sigma$  and Green's theorem (17), which results in a line and a surface integral over the midplane  $A$ , exterior to the electrolyte. The line integral cancels with contributions from  $S_1$  to give

$$f = \epsilon \left( \frac{kT}{e_0} \right)^2 \left[ \int_{S_1} \left\{ \kappa^2 [\cosh(y_3 + y_{\text{diff}}) - \cosh y_3 - y_{\text{diff}} \sinh y_3] + \frac{1}{2} \left| \nabla_t y_{\text{diff}} \right|^2 \right\} dS_1 + \frac{\epsilon_{\text{ext}}}{2\epsilon} \int_A \left| \nabla_t p_{\text{diff}} \right|^2 dA \right]. \quad [4]$$

The integrands in [4] are always positive, and again we find that the force between the particles is always repulsive. We emphasize that [3] and [4] are completely general in that no approximations have been invoked in their derivation and are valid for all particles, irrespective of their charge and shape. An analogous analysis can be carried out for the case where the surface  $\Sigma$  is charge regulating (16), for which it is also found that the interaction is always repulsive.

Within the framework of the Poisson–Boltzmann theory, the interaction of two identical charged particles is always repulsive, irrespective of the charge on the particles and whether the particles are isolated or confined, provided the sides of the confining surface  $\Sigma$  are parallel to the line-of-centers of the particles. Therefore, the observed long-ranged attractive interactions (1–6) between like-charged particles cannot be accounted for using this well-established and tested theory, contrary to previous suggestions (1, 3, 5, 6, 13), and numerical calculations (10). An alternative theory has been proposed (7–9) to explain this attractive interaction, but it too gives results that are inconsistent with experimental observations (3, 6). One can then only speculate about the origin of such attractive interactions, whether it lies in effects not taken into account in the existing and established theories, or perhaps in experimental phenomena which have not been interpreted correctly.

## APPENDIX: NOMENCLATURE

$e_0$	Proton charge
$k$	Boltzmann constant
$T$	Absolute temperature
$\epsilon$	Permittivity of electrolyte
$\epsilon_{\text{ext}}$	Permittivity exterior to the electrolyte
$n_0$	Bulk ion number density of the electrolyte
$\mathbf{n}$	Unit normal vector directed toward the enclosed particle from the surface $S$
$\mathbf{I}$	Unit tensor
$S_i$	Subsurfaces of integration surface $S$

$A$	Midplane between the particles, exterior to the electrolyte
$\mathbf{k}$	Unit vector pointing away from the unenclosed particle in [2], that is in the line joining the centers of the particles
$\nabla_t$	Transverse gradient operator parallel to the midplane between the particles
$y = e_0 \Psi / kT$	Reduced electric potential in electrolyte
$y_i = e_0 \Psi_i / kT$	Reduced electric potential in electrolyte at the surface $S_i$
$y_{\text{diff}} = y - y_3$	Difference between the reduced potential in the electrolyte and that due to the surface $\Sigma$ in isolation
$p_{\text{diff}}$	Difference between the reduced potential exterior to the electrolyte and that due to the surface $\Sigma$ in isolation

## ACKNOWLEDGMENTS

We thank Professor Tom Healy for drawing our attention to this problem. This research was supported by the Advanced Minerals Product Centre of the Australian Research Council and by the Australian Research Council Small Grants scheme.

## REFERENCES

- Kepler, G. M., and Fraden, S., *Phys. Rev. Lett.* **73**, 356–359 (1994).
- Crocker, J. C., and Grier, D. G., *Phys. Rev. Lett.* **73**, 352–355 (1994).
- Crocker, J. C., and Grier, D. G., *Phys. Rev. Lett.* **77**, 1897–1900 (1996).
- Murray, C. A., and Grier, D. G., *Ann. Rev. Phys. Chem.* **47**, 421–462 (1996).
- Carbajal-Tinoco, M. D., Castro-Roman, F., and Arauz-Lara, J. L., *Phys. Rev. E* **53**, 3745–3749 (1996).
- Larsen, A. E., and Grier, D. G., *Nature* **385**, 230–233 (1997).
- Sogami, I., *Phys. Lett. A* **96**, 199–203 (1983).
- Sogami, I., and Ise, N., *J. Chem. Phys.* **81**, 6320–6332 (1984).
- Tata, B. V. R., and Arora, A. K., *Phys. Rev. Lett.* **75**, 3200 (1995).
- Bowen, W. R., and Sharif, A. O., *Nature* **393**, 663–665 (1998).
- Derjaguin, B. V., and Landau, L., *Acta Physicochim. (USSR)* **14**, 633–662 (1941).
- Verwey, E. J., and Overbeek, J. Th. G., “Theory of the Stability of Lyophobic Colloids,” Elsevier, Amsterdam, 1948.
- Grier, D. G., *Nature* **393**, 621, 623 (1998).
- Recent numerical calculations of the interaction between two identical charged cylinders confined between two charged plates are in agreement with this finding. See: Ospeck, M., and Fraden, S., *J. Chem. Phys.* **109**, 9166–9171 (1998).
- Russel, W. B., Saville, D. A., and Schowalter, W. R., “Colloidal Dispersions,” Cambridge Univ. Press, Cambridge, UK, 1989.
- Reiner, E. S., and Radke, C. J., *J. Chem. Soc. Faraday Trans.* **86**, 3901–3912 (1990).
- Jeffreys, H., and Jeffreys, B., “Methods of Mathematical Physics,” Cambridge Univ. Press, Cambridge, UK, 1992.

John E. Sader<sup>1</sup>  
Derek Y. C. Chan

Department of Mathematics and Statistics  
University of Melbourne  
Parkville, 3052  
Victoria, Australia

Received October 6, 1998; accepted January 28, 1999

<sup>1</sup> To whom correspondence should be addressed. E-mail: j.sader@ms.unimelb.edu.au.