ON THE ELECTROSTATIC INTERACTION ACROSS A SALT SOLUTION BETWEEN TWO BODIES BEARING UNEQUAL CHARGES

V. ADRIAN PARSEGIAN *and* DAVID GINGELL

From the Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20014. Dr. Gingell's present address is the Department of Biology Applied to Medicine, Middlesex Hospital Medical School, London W1P 6DB, England.

ABSTRACT We consider two parallel planar charged surfaces bearing unequal surface charge densities interacting across a region in ionic equilibrium with a neutral salt solution. Combining rules are derived appropriate for interactions across distances of separation greater than the characteristic Debye length. When ions are excluded from the regions behind the interacting surfaces there can be *repulsion* between *charged surfaces* of *opposite* sign; but surfaces bearing charges of the same sign never attract one another. Also, surfaces bearing electrostatic *potential* of *like* sign can *attract*.

INTRODUCTION

Much has been made of the confusing prediction that charged surfaces bearing different surface potentials of the same sign may attract across ionic solutions (Derjaguin, 1954). Such attraction has been considered a possible force between negatively charged biological cells (Pethica, 1961) and between nonidentical colloid particles (Bierman, 1955). In this paper we first obviate the superficial paradox in this attraction by showing that surfaces of like charge signs must repel in any case. In general, attraction between surfaces having potentials of the same sign can occur only when charges on each suface are of opposite sign and of different magnitude. That is, potential and charge on one of the surfaces must have opposite sign.

For a specific example we derive an expression for interactions between planar surfaces bearing fixed charge densities σ_1 and σ_2. We obtain useful combining rules for the force occurring at low surface potentials. This is done for the case where the mobile ions cannot penetrate behind the charged surfaces and where the intermediate salt solution is in ionic equilibrium with a reference salt solution. This constraint is characteristic of colloid and biological cell interaction. (In the Appendix we give formulae valid for situations where mobile charge may permeate freely behind the plane of fixed charge.)

We solve for the pressure between two plates where the potentials ψ_1 and ψ_2 are fixed during approach of the two bodies. Attraction between surfaces bearing fixed potentials is predicted under a wide variety of conditions. Indeed, for the present model, only when ψ_1 is approximately equal to ψ_2 will the two surfaces repel.

Like Charges Repel

We first consider the case of two planar surfaces bearing surface charge densities σ_1 and σ_2 separated by a distance l. The space between the surfaces is filled with a salt solution in ionic equilibrium with a reservoir containing defined concentrations of the ionic species. The region behind the charged surfaces is impermeable to ions (Fig. 1).

For the electrostatic potential ψ in the region of the surfaces we use the reduced one-dimensional Poisson-Boltzmann (P-B) equation

$$\frac{d^2y}{dx^2} = -\frac{4\pi e^2}{\epsilon kT} \sum_{\{n_i^0\}} n_i^0 z_i e^{-z_i y}, \tag{1}$$

where $y = e\psi/kT$ and ψ is the potential; T is the temperature, k is Boltzmann's constant, e is the electronic charge, and ϵ is the dielectric constant.

The set $\{n_i^0\}$ designates the concentrations of the ionic species in the reference solution where the potential is taken to be zero. By electroneutrality $\sum n_i^0 z_i = 0$. One integration of this equation gives

$$\left(\frac{dy}{dx}\right)^2 = \frac{8\pi e^2}{\epsilon kT}\left[\sum_{\{n_i^0\}} n_i^0 e^{-z_i y} + C\right] \tag{2}$$

where C is a constant of integration.

For the scheme described in Fig. 1 the boundary conditions for solving for y are

$$\left.\frac{dy}{dx}\right|_{x=0} = -\frac{4\pi\sigma_1 e}{\epsilon kT}, \tag{3a}$$

$$\left.\frac{dy}{dx}\right|_{x=l} = +\frac{4\pi\sigma_2 e}{\epsilon kT}, \tag{3b}$$

The pressure in the x direction at a given point in a solution relative to a reference point where the electrostatic potential and electric field are zero is

$$P = -\frac{\epsilon}{8\pi}\left(\frac{d\psi}{dx}\right)^2 + kT \sum_{\{n_i^0\}} n_i^0 (e^{-z_i y} - 1). \tag{4}$$

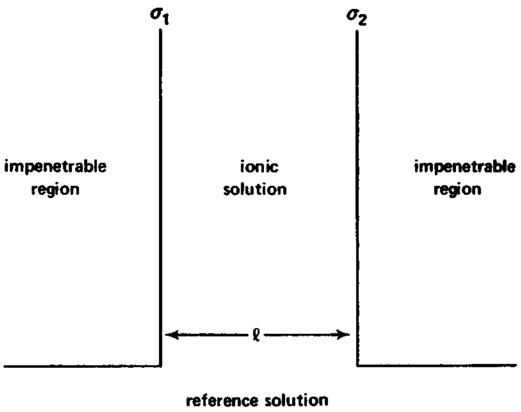

FIGURE 1 Schematic view of two parallel planar surfaces separated by distance l. The surfaces bear charge densities σ_1 and σ_2. Ions cannot penetrate behind the surfaces. The intermediate ionic solution is in equilibrium with a reference salt solution.

The first term is the Maxwell electric field stress tensor while the second is the osmotic pressure due to the redistribution of ion concentrations caused by the electrostatic potential.[1]

Since $y = e\psi/kT$, we have by definition $(\mathrm{d}y/\mathrm{d}x)^2 = (e/kT)^2(\mathrm{d}\psi/\mathrm{d}x)^2$. Putting this into equation 2, the first integral of the P-B equation, we obtain

$$\left(\frac{e}{kT}\right)^2\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2 = \frac{8\pi e^2}{\epsilon kT}\left[\sum_{\{n_i^0\}} n_i^0 e^{-z_i y} + C\right]; \tag{5}$$

we multiply both sides by $(\epsilon/8\pi)(kT/e)^2$ to obtain

$$\frac{\epsilon}{8\pi}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2 = kT\left[\sum_{\{n_i^0\}} n_i^0 e^{-z_i y} + C\right], \tag{6}$$

or

$$\begin{aligned} -kTC &= -\frac{\epsilon}{8\pi}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2 + kT\sum_{\{n_i^0\}} n_i^0 e^{-z_i y}, \\ &= P + kT\sum_{\{n_i^0\}} n_i^0 . \end{aligned} \tag{7}$$

We then have

$$P = -kT[C + \textstyle\sum n_i^0]. \tag{8}$$

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[1] Equation 4 neglects contributions to ρ due to compressibility of the solvent medium. This neglect is implicit in the formulation of equation 1.

P is constant everywhere in the region of the solution of equation 1. The quantities n_i^0 are defined by the problem. If there is a position where (dy/dx) is zero, we can write the value of y at that position as $\xi = e^y$ and introduce ξ into equation 2

$$0 = \frac{8\pi e^2}{\epsilon kT} [\sum n_i^0 \xi^{-z_i} + C]. \tag{9}$$

This yields an expression for C in terms of ξ:

$$C = -\sum n_i^0 \xi^{-z_i}. \tag{10}$$

Since $\xi \geq 0$, C is always less than or equal to $(-\sum n_i^0)$ (footnote 2). Hence the pressure P is subject to the inequality

$$P \geq 0. \tag{11}$$

$P \geq 0$ implies that an attractive force never occurs if dy/dx equals zero at any point between the charged surfaces. This condition will always be met if the surface charge densities σ_1 and σ_2 have the same sign.

To see this, observe that $dy/dx\,|_{x=0}$ and $dy/dx\,|_{x=l}$ will have opposite signs if σ_1 and σ_2 have the same sign. Since dy/dx is a continuous function, dy/dx must equal zero somewhere in the region $0 < x < l$. Thus, surfaces of like charge sign repel.

Under the condition set in this problem, that no mobile charge diffuse behind the charged surface, the converse need not hold: surfaces of unlike charge need not attract. If, for example, $\sigma_2 = 0$ but $\sigma_1 \neq 0$, the boundary condition, equation 2, requires $dy/dx\,|_{x=l} = 0$ so that repulsion is predicted if $y(l) \neq 0$. Or, if the ratio $|\sigma_2|/|\sigma_1|$ is infinitesimal, there will still be repulsion even if σ_2 and σ_1 are of opposite sign. This is because the condition confining the ionic double layer to the finite region of thickness l acts to increase the osmotic pressure in the region $0 \leq x \leq l$. In the case $\sigma_1 = -\sigma_2$ the potential y will be odd about the midpoint. At the midpoint $y = 0$ but $dy/dx > 0$; then there will always be attraction.

Combining Rules for the Interaction of Unlike Charged Surfaces

We consider further properties of the interaction in terms of a specific solution to the P-B equation. We can restrict ourselves to the condition $y \ll 1$ and still preserve the qualitative features of the electrostatic interaction between differently charged surfaces. Under this condition equation 1 becomes

$$\frac{d^2y}{dx^2} = \kappa^2 y, \tag{12}$$

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[2] C exhibits an extremum when $\partial C/\partial\xi = 0 = \sum n_i^0 z_i \xi^{-z_i-1}$. This occurs when $\xi = 1$ by the condition of electroneutrality. At $\xi = 1$, $-C = \sum n_i^0$, and $\partial^2 C/\partial\xi^2 = -\sum n_i^0 z_i(z_i - 1) = -\sum n_i^0 z_i^2 < 0$. Thus $C = -\sum n_i^0$ is a maximum value. Since C is a sum of monotonic increasing and monotonic decreasing terms there is only one maximum.

where

$$\kappa^2 = \frac{8\pi n e^2}{\epsilon kT}, \quad n = \frac{1}{2} \sum_{\{n_i^0\}} n_i^0 z_i^2,$$

with the solution

$$y = Ae^{\kappa x} + Be^{-\kappa x}. \tag{13}$$

At $x = 0$ the boundary condition is

$$\kappa(A - B) = -\frac{4\pi\sigma_1 e}{\epsilon kT}, \tag{14 a}$$

while the condition at $x = l$ gives

$$\kappa(Ae^{\kappa l} - Be^{-\kappa l}) = +\frac{4\pi\sigma_2 e}{\epsilon kT}. \tag{14 b}$$

The solutions for A and B are

$$A = \frac{4\pi e}{\epsilon kT\kappa} \frac{\sigma_2 + \sigma_1 e^{-\kappa l}}{e^{\kappa l} - e^{-\kappa l}}, \tag{15 a}$$

$$B = \frac{4\pi e}{\epsilon kT\kappa} \frac{\sigma_2 + \sigma_1 e^{+\kappa l}}{e^{\kappa l} - e^{-\kappa l}}. \tag{15 b}$$

Expanding the exponent in equation 4 and using the definition of n in equation 12 *b*,

$$P \approx -\frac{\epsilon}{8\pi}\left(\frac{kT}{e}\right)^2\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 + nkTy^2. \tag{16 a}$$

From equations 13 and 16 *a*, using the definition of κ (equation 12 *b*),

$$P = 4nkTAB. \tag{16 b}$$

Inserting A and B from equations 15 *a* and 15 *b* we have the full result:

$$P = \frac{8\pi}{\epsilon} \frac{\sigma_2^2 + \sigma_1\sigma_2(e^{\kappa l} + e^{-\kappa l}) + \sigma_1^2}{(e^{\kappa l} - e^{-\kappa l})^2}. \tag{17}$$

When $\sigma_1 \approx \sigma_2$ and $\kappa l \gtrsim 1$ so that $e^{\kappa l} \gg e^{-\kappa l}$ the pressure is

$$P \rightarrow \frac{8\pi}{\epsilon} \sigma_1\sigma_2 e^{-\kappa l}. \tag{18}$$

This is the relation when $e^{\kappa l} \gg 1$.

When $|\sigma_1| \ll |\sigma_2|$ we have

$$P \rightarrow \frac{8\pi}{\epsilon} \sigma_2^2 (e^{\kappa l} - e^{-\kappa l})^{-2},$$

$$\approx \frac{8\pi}{\epsilon} \sigma_2^2 e^{-2\kappa l}. \tag{19}$$

This is a repulsion independent of the sign of σ_1 or σ_2.

The general expression for the pressure on each plate,

$$P = \frac{8\pi\sigma_2^2}{\epsilon} \frac{1 + \frac{\sigma_1}{\sigma_2}(e^{\kappa l} + e^{-\kappa l}) + \left(\frac{\sigma_1}{\sigma_2}\right)^2}{(e^{\kappa l} - e^{-\kappa l})^2}, \tag{20}$$

is negative (attractive) when the numerator is negative. When the numerator is zero the pressure is zero. The zero condition, a function of σ_1/σ_2 for given κl, is found by solving the quadratic in σ_1/σ_2

$$\left(\frac{\sigma_1}{\sigma_2}\right)^2 + (e^{\kappa l} + e^{-\kappa l}) \frac{\sigma_1}{\sigma_2} + 1 = 0, \tag{21}$$

whence

$$\frac{\sigma_1}{\sigma_2} = -\cosh \kappa l \pm \sinh \kappa l,$$

$$= -e^{\pm \kappa l}. \tag{22}$$

Thus the curves $-e^{\kappa l}$ and $-e^{-\kappa l}$ plotted against κl delimit regions of attraction and repulsion, as shown in Fig. 2.

Within the region of attraction shown in Fig. 2, where will the surface potentials $y(0)$ and $y(l)$ have the same sign?

We let $J = (4\pi e\sigma_2/\epsilon kT\kappa)(e^{\kappa l} - e^{-\kappa l})^{-1}$ and speak of the signs of $y(0)$ and $y(l)$ relative to the sign of σ_2 taken to be positive. One may then consider the signs of the quantities multiplying the positive quantity J in

$$y(0) = A + B,$$

$$= J\left[2 + \left(\frac{\sigma_1}{\sigma_2}\right)(e^{\kappa l} + e^{-\kappa l})\right], \tag{23}$$

and in

$$y(l) = Ae^{\kappa l} + Be^{-\kappa l},$$

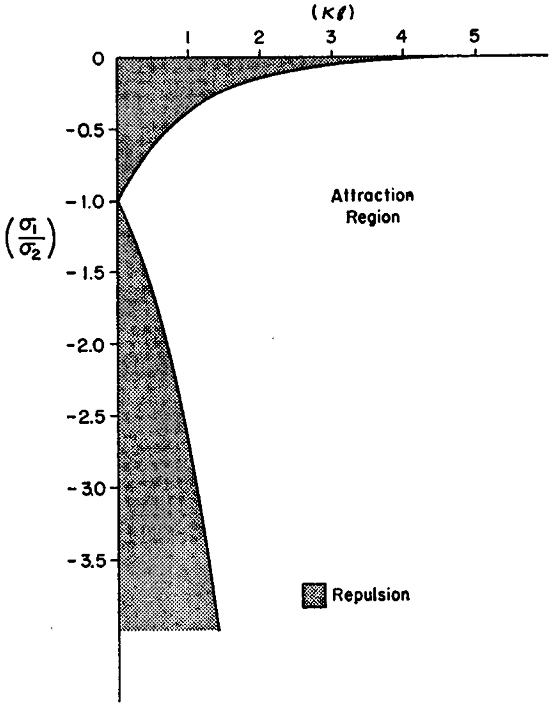

FIGURE 2 Regions of attraction and repulsion as a function of separation distance (κl) and ratio of surface charge densities (σ_1/σ_2) for the scheme described in Fig. 1. There is always repulsion between surfaces bearing charge densities of like sign [(σ_1/σ_2) positive, not shown]. Repulsion (dotted regions) occurs between charged surfaces of unlike sign when counterions and coions must be crowded into the region between σ_1 and σ_2 sufficient to neutralize the total fixed charge ($\sigma_1 + \sigma_2$). This repulsion will not occur when ions are allowed to move behind the charged surfaces (see Appendix). The scaling constant κ is defined in equation 12.

$$y(l) = J\left[2\left(\frac{\sigma_1}{\sigma_2}\right) + (e^{\kappa l} + e^{-\kappa l})\right], \tag{24}$$

giving $y(0)$, $y(l)$ in terms of σ_1/σ_2 and κl which are the axes of the graph, Fig. 3.

Since J is positive, $y(0)$ is negative when

$$\frac{\sigma_1}{\sigma_2} < -(\cosh \kappa l)^{-1}, \tag{25}$$

and zero or positive elsewhere; $y(l)$ is negative when

$$\frac{\sigma_1}{\sigma_2} < -\cosh \kappa l. \tag{26}$$

In Fig. 3 we plot the lines $(\sigma_1/\sigma_2) = -(\cosh \kappa l)^{-1}$ and $\sigma_1/\sigma_2 = -\cosh \kappa l$ dividing

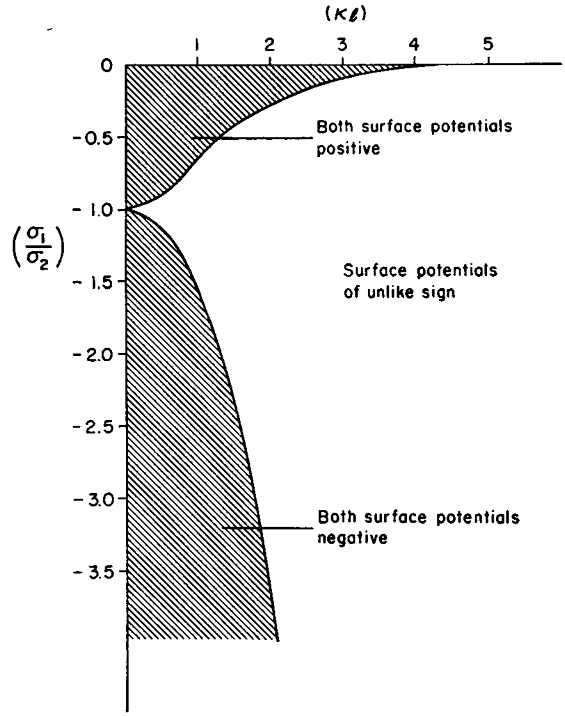

FIGURE 3 The relative sign of surface potentials $y(l)$ and $y(0)$ as a function of surface charge ratio (σ_1/σ_2) and separation (κl) for the scheme described in Fig. 1. Surface potentials are always of the the same sign when $(\sigma_1/\sigma_2) > 0$.

positive and negative regions of $y(0)$ and $y(l)$, respectively. We then add the regions where the surfaces attract (Fig. 4). There are two clear subregions where $y(0)$ and $y(l)$ have the same sign but there is attraction. These subregions are

$$-(\cosh \kappa l)^{-1} < \left(\frac{\sigma_1}{\sigma_2}\right) < -e^{-\kappa l}, \tag{27}$$

where both potentials are positive, and

$$-e^{\kappa l} < \frac{\sigma_1}{\sigma_2} < -\cosh \kappa l, \tag{28}$$

where $y(0)$ and $y(l)$ are negative.

The integral of P for electrostatic free energy per unit area is

$$G_\sigma(l) = \int_\infty^l -p \, \mathrm{d}l$$

$$= \frac{8\pi}{\epsilon\kappa} \frac{(\sigma_1^2 + \sigma_2^2)e^{-\kappa l}/2 + \sigma_1\sigma_2}{(e^{\kappa l} - e^{-\kappa l})}, \tag{29}$$

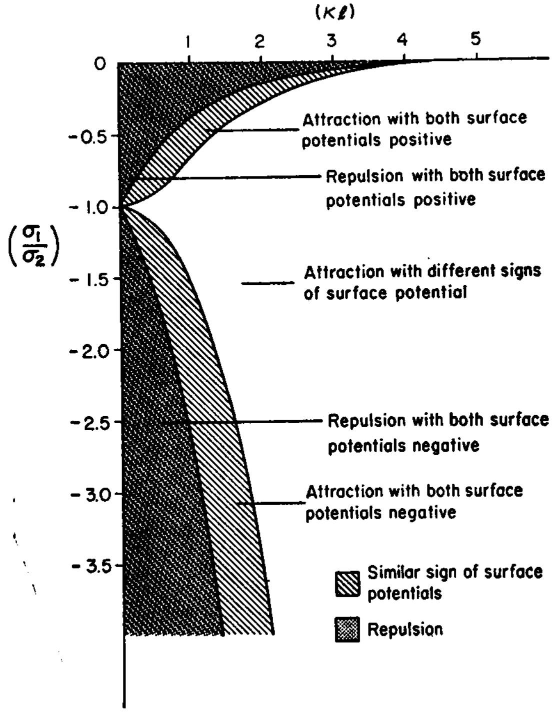

FIGURE 4 Superposition of Figs. 2 and 3. The conditions under which surface potentials have the same sign (Fig. 2) are not identical with the conditions for repulsion (Fig. 3). The regions where surfaces attract although bearing potentials of like sign (singly shaded areas) are described in equations 27 and 28.

assuming σ_1, σ_2 constant. For large distances equation 29 reduces to the intuitive relation

$$G_\sigma(l) = \frac{8\pi}{\epsilon\kappa}\sigma_1\sigma_2 e^{-\kappa l}. \tag{30}$$

Constant Surface Potential

What if the stipulated surface condition is that the two charged faces maintain constant potentials $y(0)$ and $y(l)$ during their approach? This is the assumption usually made in colloid science. The boundary conditions on $y(x)$ in equation 13 are, at $x = 0$,

$$y_0 \equiv y(0) = A + B, \tag{31}$$

and at $x = l$,

$$y_l \equiv y(l) = Ae^{\kappa l} + Be^{-\kappa l}. \tag{32}$$

We solve for A and B

$$A = \frac{y_0 - y_l e^{+\kappa l}}{(1 - e^{+2\kappa l})}, \tag{33 a}$$

$$B = \frac{y_0 - y_l e^{-\kappa l}}{(1 - e^{-2\kappa l})}, \tag{33 b}$$

and introduce these into equation 16, $P = 4nkT\,AB$, to obtain

$$P = 4nkT\,\frac{y_0 y_l (e^{\kappa l} + e^{-\kappa l}) - (y_0^2 + y_l^2)}{(e^{\kappa l} - e^{-\kappa l})^2}, \tag{34}$$

$$= \frac{4ne^2}{kT}\,\frac{\psi_0 \psi_l (e^{\kappa l} + e^{-\kappa l}) - (\psi_0^2 + \psi_l^2)}{(e^{\kappa l} - e^{-\kappa l})^2}. \tag{35}$$

This pressure is attractive when either of the surface potentials is zero or when there is a great disparity in magnitudes of potentials. It is repulsive only when $\psi(l) \approx \psi(0)$. A graph similar to Fig. 2 could be constructed for this case of constant potential. For

$$\frac{\psi(l)}{\psi(0)} > +e^{+\kappa l}, \qquad < e^{-\kappa l}, \tag{36}$$

there will be attraction; only when

$$e^{-\kappa l} < \frac{\psi(l)}{\psi(0)} < e^{\kappa l} \tag{37}$$

will surfaces of like potential repel.[3]

By integrating equation 35 for pressure at constant potential one can get a free energy $G_\psi(l)$

$$G_\psi(l) = \frac{4e^2 n}{kT\kappa}\,\frac{\psi_1 \psi_2 - (\psi_1^2 + \psi_2^2) e^{-\kappa l}/2}{(e^{\kappa l} - e^{-\kappa l})}. \tag{38}$$

At large distances this is

$$G_\psi(l) \approx \frac{4e^2 n}{kT\kappa}\,\psi_1 \psi_2 e^{-\kappa l}. \tag{39}$$

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[3] Further analysis, similar to that for the constant charge case, shows that surfaces of constant potential of different magnitude but similar sign never attract when the surface *charges* have similar sign.

DISCUSSION

The electrostatic pressure between two differently charged planar bodies having separation l interacting across a solution of monovalent ions is

$$P_\sigma(l) = \frac{8\pi}{\epsilon} \frac{(\sigma_2^2 + \sigma_1^2) + \sigma_1\sigma_2(e^{\kappa l} + e^{-\kappa l})}{(e^{\kappa l} - e^{-\kappa l})^2}, \qquad (40)$$

where σ_1 and σ_2 are surface charge densities, ϵ is the dielectric constant, and κ is a constant defined in equation 12. This result is rigorous at all distances as long as ionic energies at the surfaces are small compared with thermal energies ($\psi \lesssim 25$ mv). It is also a good approximation for higher surface potentials when the separation distances are large ($\kappa l \gtrsim 1$).

The surface charge densities may themselves be functions of the surface potentials which in turn depend on separation l. The pressure P will then necessarily include the dependence of σ on l. In the special case where the surface potentials are assumed fixed (the case in DLVO colloid theory), the electrostatic pressure may be written

$$P_\psi(l) = \frac{4e^2n}{kT} \frac{-(\psi_1^2 + \psi_2^2) + \psi_1\psi_2(e^{\kappa l} + e^{-\kappa l})}{(e^{\kappa l} - e^{-\kappa l})^2}. \qquad (41)$$

We have shown that two surfaces bearing potential of like sign can attract only if the surface charges are of unlike sign. In the case of nonidentical colloid particles considered by Bierman (1955), the attractive force was effected by postulating attractive sites to which counterionic charges could stick. This sticking by nonelectrostatic forces could cause the necessary charge reversal.

Similarly two biological cell surfaces cannot experience mutual attraction while both remain net negatively charged. Only if charge reversal occurs on one of the cells can they attract each other. Such reversal would require ion binding, which we have not treated, or differential dissociation of the fixed anionic and cationic groups in the cell surface. Low pH caused by elevated negative potentials of interaction (Gingell, 1967 *a*, *b*; Ninham and Parsegian, 1971) could conceivably cause sufficient reassociation of carboxyl groups of high pK_a to leave a dominant net positive charge on amino groups. In practice, however, there appears to be little evidence for sufficient ion binding under physiological conditions. Cell surfaces bear a considerable excess of covalently bound cationic groups of low p$K_a \sim 3$ (mostly carboxyls of sialic acid) and few or no anionic groups, depending on cell type. Consequently we feel that charge reversal is not likely to occur in normal ionic conditions. Our result, based on the constant surface charge assumption (Gingell, 1967 *a*, *b*; Ninham and Parsegian, 1971), is more appropriate for cells than the constant potential assumption used in colloid systems. Within the limits of our assumption we do not support the contention of Pethica (1961) that cells of similar charge sign but different magnitude could attract each other.

In the model considered (Fig. 1) the interaction pressure becomes repulsive at short enough distances if one insists on constant surface charge densities not equal in magnitude and of opposite sign (Figs. 2–4). In real systems the surface charge densities are likely to go to zero upon close approach. The way in which this happens is model dependent.

In the Appendix we treat the case where ions may freely permeate both sides of the charged surface. The mutual pressure between two charged plates σ_1 and σ_2 is then

$$P_\sigma(l) = \frac{2\pi}{\epsilon} \sigma_1\sigma_2 e^{-\kappa l}.$$

There is no extra osmotic repulsion due to confinement of ions between the two plates as was described in Figs. 1–4.

One may repeat all of the present analysis to include a more rigorous but tedious solution of the nonlinear P-B equation. That treatment, couched in the language of elliptic functions, would tend to obscure the basic physics revealed here. Further, nonlinear effects on forces between two plates probably become important only for short distances $\kappa l \lesssim 1$ where a continuum model itself is likely to be invalid (Ninham and Parsegian, 1971).

APPENDIX

The Interaction of Two Unlike Charged Surfaces with Fully Permeable Regions throughout the System

Consider the situation in Fig. A 1 where ionic double layers may exist on either side of the charged surfaces. The linearized P-B equation has the three solutions

$$y_L = A_L e^{\kappa x}, \tag{A 1}$$

$$y_M = A_M e^{\kappa x} + B_M e^{-\kappa x}, \tag{A 2}$$

$$y_R = B_R e^{-\kappa x}. \tag{A 3}$$

The boundary conditions at $x = 0$ give

$$y_L(0) = y_M(0) = A_L = A_M + B_M, \tag{A 4}$$

$$\left.\frac{\mathrm{d}y_M}{\mathrm{d}x}\right|_{x=0} - \left.\frac{\mathrm{d}y_L}{\mathrm{d}x}\right|_{x=0} = -\frac{4\pi e\sigma_1}{\epsilon kT} = \kappa(A_M - B_M) - \kappa A_L, \tag{A 5}$$

and at $x = l$

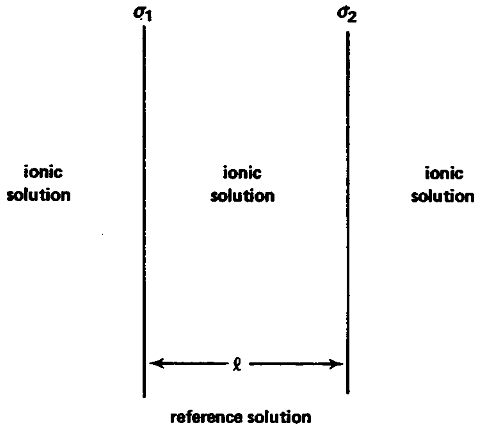

FIGURE A 1 Schematic view of two parallel planar surfaces separated by distance l, bearing surface charge densities σ_1 and σ_2. Ions are allowed to permeate the regions on either side of the surfaces and are in equilibrium with a reference salt solution.

$$y_M(l) = y_R(l) = A_M e^{\kappa l} + B_M e^{-\kappa l} = B_R e^{-\kappa l}, \tag{A 6}$$

$$\left.\frac{\mathrm{d}y_R}{\mathrm{d}x}\right|_{x=l} - \left.\frac{\mathrm{d}y_M}{\mathrm{d}x}\right|_{x=l} = -\frac{4\pi\sigma_2 e}{\epsilon kT} = -\kappa B_R e^{-\kappa l} - \kappa(A_M e^{\kappa l} - B_M e^{-\kappa l}). \tag{A 7}$$

Since y_R and $\mathrm{d}y_R/\mathrm{d}x$ go to zero as $x \rightarrow \infty$ and y_L and $\mathrm{d}y_L/\mathrm{d}x$ go to zero as $x \rightarrow \infty$, the pressure outside the plates defined by equation A 4 is zero. Between plates the pressure is

$$P = 4nkTA_M B_M. \tag{A 8}$$

Solving for A_M, B_M we obtain

$$A_M = \frac{2\pi e\sigma_2}{\epsilon kT\kappa} e^{-\kappa l}, \qquad B_M = \frac{2\pi e\sigma_1}{\epsilon kT\kappa}; \tag{A 9}$$

$$P_\sigma(l) = \frac{2\pi}{\epsilon} \sigma_1\sigma_2 e^{-\kappa l}. \tag{A 10}$$

This is always attractive for σ_1, σ_2 of unlike sign and always repulsive for σ_1, σ_2 of like sign.

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