

Attraction between negatively charged surfaces mediated by spherical counterions with quadrupolar charge distribution

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We observed monoclonal antibody mediated coalescence of negatively charged giant unilamellar phospholipid vesicles upon close approach of the vesicles. This feature is described, using a mean field density functional theory and Monte Carlo simulations, as that of two interacting flat electrical double layers. Antibodies are considered as spherical counterions of finite dimensions with two equal effective charges spatially separated by a fixed distance l inside it. We calculate the equilibrium configuration of the system by minimizing the free energy. The results obtained by solving the integrodifferential equation and by performing the Monte Carlo simulation are in excellent agreement. For high enough charge densities of the interacting surfaces and large enough l , we obtain within a mean field approach an attractive interaction between like-charged surfaces originating from orientational ordering of quadrupolar counterions. As expected, the interaction between surfaces turns repulsive as the distance between charges is reduced. © 2008 American Institute of Physics. [DOI: 10.1063/1.2972980]

I. INTRODUCTION

Electrostatic interaction between charged bodies is of fundamental importance in material science and biology.¹ In the presence of multivalent ions and/or extended charges, electrostatic correlations render the nature of this interaction nontrivial.^{2,3} For example, it is known that like-charged surfaces can be attracted to, and oppositely charged surfaces can be repelled from, each other in the presence of multivalent counterions (CIs).^{2,4,5} Short range attractions between equally charged mica or clay surfaces in a solution of divalent ions have been detected.⁶ Adsorption of polyelectrolytes on like-charged surfaces was observed.^{7,8} In biology, since many of the lipids and proteins have ionic groups that are easily dissociated in aqueous media, the role of electrostatics is crucial in deciding its structure and function.⁹ Condensation of DNA,¹⁰ which corresponds to the packing of DNA in viruses, network formation in actin solutions,¹¹ and aggregation of rodlike M13 viruses,¹² are some of the examples where electrostatic interactions mediated by multivalent ions are important. This has inspired many efforts to understand the interaction between objects with different shapes and charge distributions.¹³ For example, it is indicated that mediated interactions between structures containing negatively charged phospholipid molecules may play an important role in processes leading to blood clot formation.¹⁴

In this paper, we look at the interaction between two charged surfaces in the presence of extended CIs. We use a density functional theory and Monte Carlo simulations to calculate the interaction. The problem is motivated by an earlier experimental observation in which phospholipid vesicles, prepared as described in Ref. 14, were found to adhere to each other upon addition of monoclonal chimeric anti- β 2GPI antibodies (prepared as given in Ref. 15), (Fig. 1). The adhesion was assessed by the ratio between the contour length of the contacts between adhered vesicles and the whole contour length of the vesicles within a chosen video camera frame ($\delta_{\text{contour length}}$). It was found that there was no adhesion in the system of neutral vesicles, while for the charged vesicles, $\delta_{\text{contour length}}$ increased as the volume ratio between the charged and neutral phospholipids ($\delta_{\text{charged-neutral}}$) increased (Table I), indicating that the antibody-mediated adhesion is of electrostatic origin. We describe below two approaches, one based on the mean field theory and another on Monte Carlo simulations, to get insight into the attraction between the two surfaces.

II. FREE ENERGY FUNCTIONAL

Various mechanisms within the electric double layer theories were suggested to explain the attractive interactions between like-charged surfaces. At the simplest level, the interaction between two charged surfaces is described by the Poisson–Boltzmann (PB) theory, which assumes the surfaces to be uniformly charged and ions to be pointlike. This mean field theory, which is asymptotically exact in the limit of low electrostatic coupling (high temperature, low valency, and

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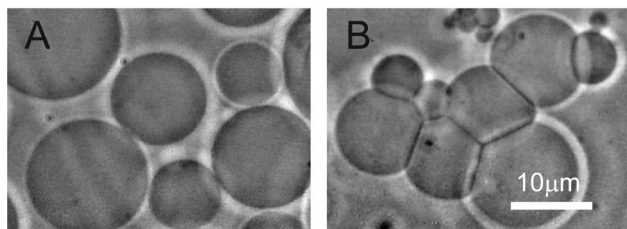


FIG. 1. Negatively charged giant phospholipid vesicles consisting from 40% of 1,1'2,2'-tetraoleoyl cardiolipin, 40% of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine, and 20% of cholesterol before (A) and 7 min after (B) the addition of monoclonal antiphospholipid antibodies.

low charge density), yields repulsion between like-charged surfaces.¹ At high electrostatic coupling, attractive interaction between like-charged surfaces, obtained by computer simulations,¹⁶ density functional theories,¹⁷ and experiments,¹⁸ demonstrated significant deviation from the PB theory predictions. Most of the attempts to understand these attractive electrostatic interactions dealt with multivalent point charges^{2,19} or multivalent fully flexible,²⁰ semiflexible,²¹ and stiff polymeric chains.²²

In a quadrupole-mediated interaction model,²³ the charge distribution within an ion (CI and coion) was described as two equal point charges separated by a fixed distance l . The orientationally averaged volume charge density and the energy of a CI were taken into account by expansion in terms of l up to the quadrupolar contribution. The free energy of the two interacting electric double layers was then minimized to yield consistently related equilibrium profiles of the electric potential, number density of CIs, and orientational order parameter of the system. For small electric potential energy of the ions, the linearized regime corresponding to small l was considered to yield an analytical solution of the problem.²³ An attractive interaction between like-charged surfaces was obtained for high enough charge on the surfaces and large enough extension between ions forming the quadrupole l . In further elaboration of this concept, the free energy for quadrupoles with an arbitrary length l was minimized by a rigorous solution of the variational problem stated by the integrodifferential equation for the electric potential.²⁴ Here again attraction between the like-charged surfaces was obtained. It was found that at equilibrium, for distances D between charged surfaces larger than the length of the rodlike CI, the CIs oriented, on the average, parallel to the charged surfaces. Upon close approach of the surfaces (D comparable to the length of the rodlike CIs), both the parallel and the perpendicular orientations were found to be energetically favorable. The orientation enables the coupled charges of the CIs to be as close to the (oppositely) charged surfaces

TABLE I. The relative contour of adhesion between giant phospholipid vesicles $\delta_{\text{contour length}}$ for different weight proportions of charged phospholipid $\delta_{\text{charged-neutral}}$.

$\delta_{\text{charged-neutral}}$	$\delta_{\text{contour length}}$
0	0
0.1	0.2
0.2	0.3

as possible. This was interpreted as an attractive interaction between the two electric double layers originating in energetically favorable ordering of CI quadrupoles. Below we show, using a method similar to the one described in Refs. 23 and 24, the attractive interaction between like-charged surfaces mediated by significant orientational ordering of globular CI with two monovalent charges situated at its poles.

In the model used here, the two interacting electrical double layers are formed by two flat surfaces, each of the area A , separated by a distance D . The surface area A is assumed to be large compared to the distance between surfaces D so that the end effects can be neglected. Each surface bears uniformly distributed charge with the surface charge density σ . The space between the charged surfaces is filled with the solution of CIs of a single species representing the solution of monoclonal antibodies. In our model, an antibody is described as a sphere of diameter l (globular protein) within which two positive charges, each of a valency Z , are separated by a distance l (Fig. 2). The charged surfaces are kept in the y - z plane and hence the electrostatic field varies only in the x -direction. We take that there are no external electric fields. The CIs are subject to positional and orientational degrees of freedom. For each CI, the center of the charge distribution (also its geometric center) is located at x . The two point charges are located at geometrically opposite points on its surface such that, when projected onto the x -axis, their positions are at $x+s$ and $x-s$, respectively, as shown in Fig. 2. The probability density $p(s|x)$ satisfies $(1/l)\int_{-l/2}^{l/2} p(s|x)ds=1$ and $p(s|x)=0$ for any x and $|s|>l/2$. The free energy of the system per unit area, in unit of kT , consists of three contributions: the electrostatic energy f_{el} , the positional entropy of CIs f_{ent} , and the orientational entropy of CIs f_{o} . Here k is the Boltzmann constant and T is the temperature of the system. The electrostatic contribution to the free energy f_{el} is given by

$$f_{\text{el}} = 1/8\pi l_B \int_0^D \Psi'(x)^2 dx, \quad (1)$$

where $\Psi = e_0\psi(x)/kT$, ψ is the electrostatic potential, e_0 is the elementary charge, $l_B = e_0^2/4\pi\epsilon\epsilon_0kT$ is the Bjerrum length, ϵ is the dielectric constant of the solution, and ϵ_0 is the permittivity of the vacuum. The prime denotes a derivative with respect to x . To calculate the positional entropy, the region of electrolyte solution is divided into layers of unit area and of thickness dx so small that all macroscopic quantities are con-

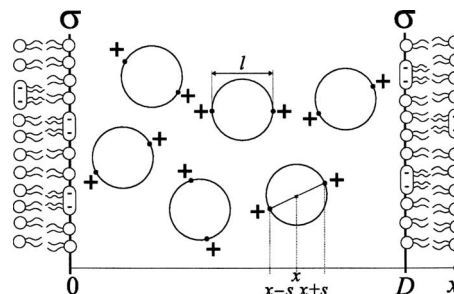


FIG. 2. Schematic illustration of two negatively charged planar surfaces separated by a solution containing spherical CIs with spatially distributed positive charge. The charges within a CI are separated by a fixed distance l .

sidered as constant and local thermodynamic equilibrium can be ascribed to each layer. A lattice of M equal volume elements (sites) with equal volumes v_0 is imagined within the cell so that $Mv_0=dV$, where dV is the volume of the layer. The CIs occupy N of the M sites in the cell. The contribution of the distributional entropy of a cell is $-\ln W$, where $W = M!/N!(M-N)!$. Using the Stirling approximation for large N and M and summing up (integrating) the contributions of all cells in the system gives

$$f_{\text{ent}} = \int_0^D \left[n \ln(nv_0) + \frac{1}{v_0}(1-nv_0)\ln(1-nv_0) \right] dx, \quad (2)$$

where $n=N/dV$. In the limit of infinite dilution ($nv_0 \ll 1$), we can use the approximation, $\ln(1-nv_0) \approx -nv_0$, to obtain²⁵

$$f_{\text{ent}} \approx \int_0^D [n \ln(nv_0) - n] dx. \quad (3)$$

It is taken such that $v_0 = \pi l^3/6$.

The contribution from the orientational ordering of the quadrupoles to the free energy of the system f_o is

$$f_o = \int_0^D n(x) \left(\frac{1}{l} \int_{-l/2}^{l/2} p(s|x) [\ln p(s|x) + U(x)] ds \right) dx. \quad (4)$$

The function

$$U(x) = \begin{cases} 0, & \frac{l}{2} \geq x \geq D - \frac{l}{2} \\ \infty, & \text{elsewhere} \end{cases} \quad (5)$$

is introduced in order to ensure that the CIs are confined within the region specified by the charged walls. The equilibrium state of the system is determined by the minimum of the total free energy, $f = f_{\text{ent}} + f_{\text{el}} + f_o$, subject to the constraints that (a) the system is electroneutral and (b) the orientational probability of the CIs, integrated over all possible angles, is 1. To solve this variational problem, a functional $\int_0^D \mathcal{L} dx$ is constructed,

$$\begin{aligned} \int_0^D \mathcal{L} dx = & f + \mu 2Z \int_0^D n(x) dx + \int_0^D n(x) \lambda(x) \\ & \times \left(\frac{1}{l} \int_{-l/2}^{l/2} p(s|x) ds \right) dx, \end{aligned} \quad (6)$$

where $\lambda(x)$ and μ are the Lagrange multipliers. In equilibrium, $\delta \int_0^D \mathcal{L} dx = 0$, which yields the equilibrium volume density of CIs $n(x)$

$$\begin{aligned} n(x) = & \frac{\exp(-2Z\mu)}{v_0 l} \int_{-l/2}^{l/2} \exp(-Z\Psi(x+s) \\ & - Z\Psi(x-s)) ds, \end{aligned} \quad (7)$$

and the equilibrium probability

$$p(s|x) = \frac{\exp(-Z\Psi(x+s) - Z\Psi(x-s))}{\int_{-l/2}^{l/2} \exp(-Z\Psi(x+\bar{s}) - Z\Psi(x-\bar{s})) d\bar{s}}. \quad (8)$$

The function $n(x)$ is defined only in the interval of $l/2 \leq x \leq D-l/2$. Inserting Eq. (7) into the Poisson equation $\psi''(x) = 8\pi l_B Z n(x)$ leads to the integrodifferential equation

$$\begin{aligned} \Psi''(x) = & -8\pi l_B \frac{Z}{v_0} \exp(-Z\Psi(x) - 2Z\mu) \\ & \times \frac{1}{l} \int_{-l/2}^{l/2} \exp(-Z\Psi(x+2s) - U(x+s)) ds. \end{aligned} \quad (9)$$

Equation (9) is valid in the region of $0 \leq x \leq D$. The boundary conditions at the charged surfaces are

$$\Psi'(x=0) = -\frac{4\pi\sigma}{l_B e_0}, \quad \Psi'(x=D) = \frac{4\pi\sigma}{l_B e_0}. \quad (10)$$

The finite size of CIs is taken into account by the distance of closest approach of the center of the CI to the charged surface ($l/2$). Equation (9) was solved numerically as described in Ref. 24.

III. RESULTS

The solution of the integrodifferential equation (9) yielded the equilibrium potential $\Psi(x)$, and the corresponding equilibrium distribution $n(x)$ and probability density $p(s|x)$.

To assess the effect of the mean field approximation, which was introduced into the theoretical description above, we carried out Monte Carlo simulations. In the simulation, the standard Monte Carlo Metropolis algorithm²⁶ with Lechner periodic boundary conditions²⁷ in the directions parallel to the charged walls was used. A system of 100–200 spheres confined between two impenetrable charged surfaces was considered. To make contact with the theory, the hard core interaction between particles and the walls was taken into account by means of the distance of the closest approach while the hard core interaction between spheres was not considered.

We will now discuss the results obtained from our theoretical analysis and Monte Carlo simulations. Figure 3 shows the free energy as a function of the distance between two negatively charged surfaces for two different surface charge densities ($\sigma = -0.033$ A s/m² and $\sigma = -0.1$ A s/m², and two different distances between the charges within a CI [$l = 2$ nm (A) and $l = 5$ nm (B)]. For comparison, the results obtained by using an approximative solution within the Debye–Hückel model²³ are shown. The obtained values of the equilibrium distance between the surfaces D_{eq} increase with increasing separation between charges l within the CI (Fig. 3, inset), which is consistent with the condition of the closest approach of the CIs. For small surface density of charge $|\sigma|$ and small separation between charges within the CI, the interaction is found to be repulsive for all distances between the charged surfaces, both within the rigorous solution of the problem as well as within the approximative solution. Large enough $|\sigma|$ and l yield a nonmonotonous behav-

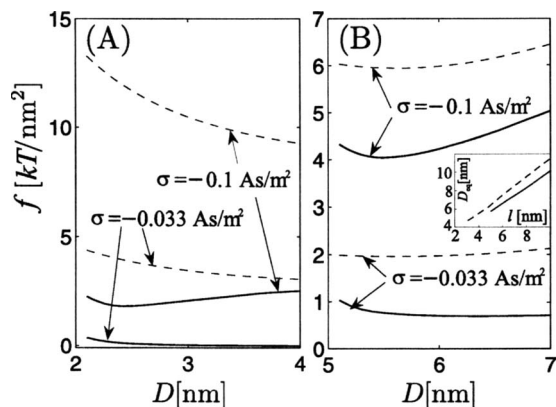


FIG. 3. The free energy f as a function of the distance between the negatively charged surfaces D for $Z=1$, two different surface charge densities: $\sigma=-0.033$ A s/m² and $\sigma=-0.1$ A s/m², and two different distances between the charges within a CI [(A) $l=2$ nm, (B) $l=5$ nm]. $l_B=0.7$ nm. Inset: the equilibrium distance between the charged surfaces D_{eq} as a function of the separation between charges l . Full lines: rigorous solution for $l_B=0.7$ nm, broken lines: approximative solution for a system containing small divalent rodlike CIs and coions²³ for Debye length $l_D=1.53$ nm.

ior of the free energy with a minimum representing the equilibrium distance between the surfaces. The effect is stronger within the rigorous solution; the minima are deeper and occur at lower $|\sigma|$ than in the approximative Debye–Huckel solution. As expected, the rigorous solution always yields lower energy than the approximative solution.

For distances between the surfaces, which are comparable to the separation of charges within the CI, the charge density profile in the solution (Fig. 4) exhibits a single peak at each side. The CIs, on the average, orient to form bridging between the charged surfaces. For somewhat larger distances between the surfaces, we see a peak in the middle which correspond to “interdigitation” of the ordered CIs. Charges of CIs of both layers contribute at $D/2$ so a central peak in the charge density is formed. For larger distances, the profile exhibits twin peaks close to both charged surfaces due to orientational ordering of CIs with one charge closest to the charged surface. An excellent agreement between the calculated density profile and the results of Monte Carlo simulations can be seen.

We also calculated the orientational order of the CIs in

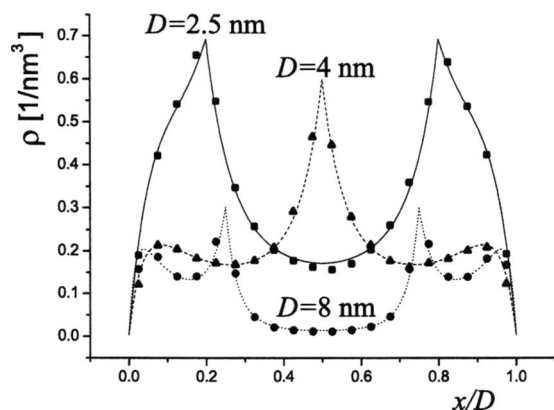


FIG. 4. The profile of the density of charge due to CIs between the charged surfaces. Lines: the solutions of the integrodifferential equation (9). Points: results of the Monte Carlo method. $Z=1$, $l=2$ nm, and $\sigma=-0.07$ A s/m².

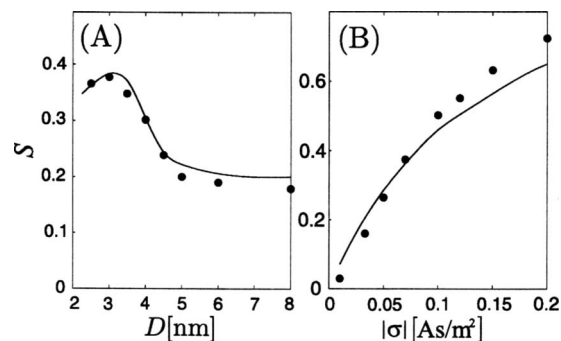


FIG. 5. The average order parameter $S=\langle(3 \cos^2 \vartheta - 1)/2\rangle$, where ϑ is measured with respect to the x -axis (A) dependent on the distance between the charged surfaces D for $Z=1$, $l=2$ nm, and $\sigma=-0.07$ A s/m² and (B) in dependent on the surface charge density $|\sigma|$ for $Z=1$, $l=2$ nm, and $D=2.5$ nm. Lines: the solutions of the integrodifferential equation (9). Points: results of the Monte Carlo method.

the system by computing its nematic order parameter S . This is shown in Fig. 5. The average orientation of the quadrupoles entrapped in spherical CIs is perpendicular to the charged surfaces, in contrast to the configuration of the rodlike CIs,²⁴ which is mostly parallel. The order parameter S is sensitive to the charge density of the surface. As larger $|\sigma|$ gives stronger field and larger gradient of the field in the vicinity of the charged surfaces, S increases with increasing $|\sigma|$. The dependence of S on D , however, exhibits a maximum close to an intercharge distance l (reflected also in Fig. 4). This is the configuration with minimum distance between the charges on CI and surfaces and maximum distance between the charges on CI themselves.

IV. DISCUSSION

The concept of free energy decrease due to orientational ordering was previously used in the determination of equilibrium shapes of phospholipid bilayers,²⁸ where it was shown that the in-plane orientational ordering of membrane constituents can decrease the free energy of a phospholipid vesicle by stabilizing shapes with larger area regions with unequal principal curvatures. The in-plane ordering was later generalized to three-dimensional ordering of ions in the electric double layer theory.^{24,29} Our results show that internal degrees of freedom (orientational and positional ordering of constrained charges) coupled with a particular form of direct interaction between charges (an imposed fixed distance within pairs of charges) contribute to the decrease in the free energy of the system of spherical CIs. Orientational ordering enables the particles to attain a configuration which is energetically the most favorable. The effect is strong enough to cause an attractive interaction between like-charged surfaces. We find that the origin of the attraction in the system of spherical particles with quadrupolar charge distribution is identical to that in the system of rodlike particles,²⁴ namely, the energetically favorable orientational ordering of the quadrupoles in the spatially varying electric field. This effect was interpreted as the bridging between the charged surfaces.²⁴ However, in the present system of spherical particles, the orientation of the quadrupoles is in effect perpendicular to the charged surfaces for all distances between the

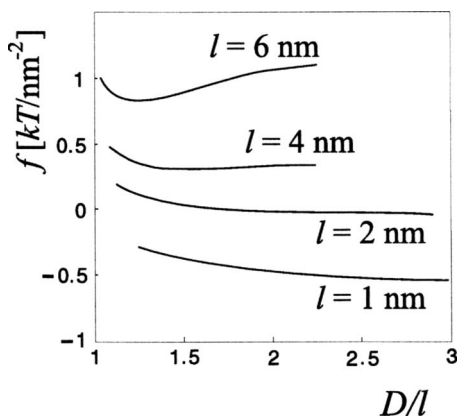


FIG. 6. The free energy f as a function of the distance between the negatively charged surfaces D for four different extensions between charges l . Other parameters are $Z=1$, $\sigma=-0.033$ A s/m², and $l_B=0.7$ nm.

charged surfaces, while in the system of rodlike particles, the orientation of the rods is in effect parallel to the charged surfaces, except for the distances D which are close to the charge separation within the rods l , where both the parallel and the perpendicular orientation are energetically favored.

It should be noted that the attractive interaction between like-charged surfaces in our model is obtained within the density functional theory which is a mean field approach (Fig. 3). This interaction vanishes when the two charges are brought toward the center of the ion, as is obtained in the standard PB theory, to which our equations reduce when the parameter l is taken as zero. Figure 6 shows that the interaction between the charged surfaces changes from attractive to repulsive as the distance between charges, in an ion l , is decreased at a fixed surface charge density σ . Thus, the attraction between the like-charged surfaces shown in Fig. 3 does not originate from the correlated interaction between CIs. Instead, attraction originates from intraparticle interactions (an imposed interionic interaction expressed by fixed distance between charges within an ion). This effect may be very important in DNA condensation by polyamines³⁰ since polyamines are water soluble linear molecules with monovalent charges separated for a distance l within nanometer range.

We show that the density functional theory and the Monte Carlo simulation show remarkably good agreement for the ion density profiles (Fig. 4) and for the average orientational order parameter (Fig. 5). We thus argue that the bridging effect arising from the orientational ordering of extended charges is sufficient for attractive interaction between like-charged surfaces as is revealed here within the mean field approach. Direct interaction between ions may give rise to additional effects which we are currently investigating in this problem.

V. SUMMARY

To summarize, we have shown that globular CIs with quadrupolar charge distribution can mediate attraction between like-charged surfaces even at low valency of the ions.

The CIs orient in such a way that both charges of the quadrupole are closest to the oppositely charged surfaces so that the electrostatic energy is the lowest. Results from the Monte Carlo simulations are shown to agree well with those obtained from the minimization of the free energy functional. A density functional theory, which is on the mean field level, is able to describe this attractive interaction between like-charged surfaces.

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