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Like-charge attraction between metal nanoparticles in a 1:1 electrolyte solution

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We calculate the force between two spherical *metal* nanoparticles of charge Q_1 and Q_2 in a dilute 1:1 electrolyte solution. Numerically solving the non-linear Poisson-Boltzmann equation, we find that metal nanoparticles with the same sign of charge can attract one another. This is fundamentally different from what is found for like-charged, non-polarizable, colloidal particles, the two body interaction potential for which is always repulsive inside a dilute 1:1 electrolyte. Furthermore, existence of like-charge attraction between spherical metal nanoparticles is even more surprising in view of the result that such attraction is impossible between parallel metal slabs, showing the fundamental importance of curvature. To overcome a slow convergence of the numerical solution of the full non-linear Poisson-Boltzmann equation, we developed a modified Derjaguin approximation which allows us to accurately and rapidly calculate the interaction potential between two metal nanoparticles, or between a metal nanoparticle and a phospholipid membrane.

Metal nanoparticles suspended in an electrolyte solution have attracted a lot of attention for various applications^{1–10}. Because of their strong affinity for biological surfaces and compatibility with immune system¹¹, gold nanoparticles are being used for cancer treatment and drug delivery^{12–14}. They have also found applications in catalysis^{15,16} and optics^{17,18}. Unfortunately our theoretical understanding of the interactions between metal nanoparticles inside an electrolyte solution is rather limited. Gold nanoparticles are often synthesized using citrate as a stabilizing agent^{19,20}, resulting in a polydisperse suspension of negatively charged nanoparticles at pH 7. When such particles are in vicinity of one another, in addition to the direct Coulomb force between the two particles, there is an additional interaction arising from the induced charge on the metal cores. The induced charge is non-uniformly distributed over the metal cores, but its net amount is zero for each particle. As the two nanoparticles approach one another, both the surface charge distribution and the electrostatic potential on each particle change with the distance of separation. Most theoretical works on colloidal suspensions ignore the effects of polarizability and treat the particle surface charge distribution as fixed and uniform²¹. There are, however, some recent works which explore effects of charge regulation²² and patchiness^{22–26} on the interaction between planar surfaces, the physics behind such systems, however, is quite different from the polarizability effects that we will be interested to explore in the present Letter. Recent computational methods try to mimic the behavior of metallic materials using parametrized Lennard-Jones particles^{9,27}. With the exception of metal planar surfaces^{6,28}, the direct implementation of proper electrostatic boundary conditions in simulations using Green function methods is very complicated, requiring the use of computationally very demanding boundary elements

methods in order to account for polarization effects^{29,30}.

It is well known that like-charged colloidal particles can attract one another if suspension contains multivalent counterions^{21,31–42}. This attraction results from the electrostatic correlations between the double layers of condensed *multivalent* counterions²¹. On the other hand, it is also believed that no such attraction is possible in electrolyte solutions with only 1:1 electrolyte^{43,44} for which correlation effects are negligible and the mean-field Poisson-Boltzmann (PB) equation is almost exact²¹. Absence of like-charge attraction for non-polarizable colloidal particles has been confirmed using explicit Monte-Carlo simulations⁴⁵. Furthermore, it can be shown explicitly that like-charged parallel metal slabs inside a dilute 1:1 electrolyte always repel one another. Contrary to all of the above, in this Letter we will show that two *spherical* like-charged *metal* nanoparticles can attract one another in a dilute 1:1 electrolyte solution. The surprising attraction is a consequence of the polarization of the metal cores and is similar to the attraction between charged conducting spheres in vacuum^{46,47}. The polarization induced like-charge attraction should be very important for the interaction between charged gold particles and phospholipid membranes – a situation of great practical importance in medical applications^{48,49}.

We start by considering the interaction between two parallel infinite metal slabs of width d and total surface charge densities $2\sigma_1$ and $2\sigma_2$, separated by a surface-to-surface distance L , as shown in Fig. 1(a). Both faces of the metal slabs are charged. The charge on each face will adjust itself so as to minimize the total free energy of the system. When $L \rightarrow \infty$, both faces of slab 1 will have the same surface charge density σ_1 , and of slab 2, σ_2 .

For dilute 1:1 electrolyte solutions, electrostatic correlations between the ions are negligible and the mean field PB equation is quasi exact. To calculate the force between two metal slabs separated by the surface-to-surface distance L we must solve the non-linear PB equation

$$\epsilon \nabla^2 \phi = 8\pi q \rho_S \sinh[-\beta q \phi], \quad (1)$$

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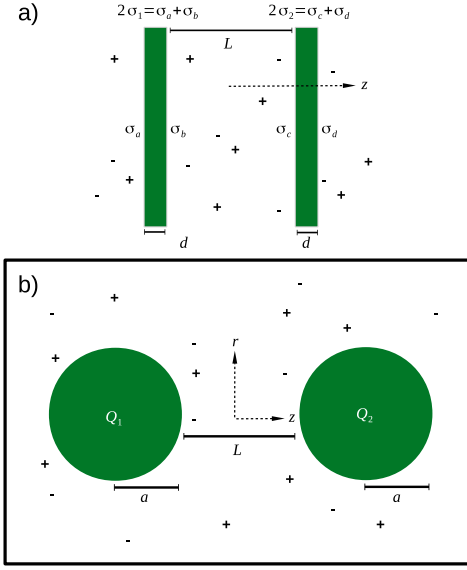


FIG. 1. (a) Two infinite metal slabs of width d and total charge density $2\sigma_1$ and $2\sigma_2$, respectively. $\sigma_{a,b,c,d}$ represent the surface charge densities on the faces of the two slabs. The values of $\sigma_{a,b,c,d}$ change depending on the separation between the slabs, while the total charge density on each slab remains fixed. (b) Two like-charged spherical metal nanoparticles of charge Q_1 and Q_2 and radius a , separated by a surface-to-surface distance L , in an electrolyte solution of concentration ρ_S .

where ϕ is the electrostatic potential, q is the elementary charge, ϵ is the dielectric constant of water, and $\beta = 1/k_B T$. The Bjerrum length is defined as $\lambda_B = \beta q^2 / \epsilon = 7.2 \text{ \AA}$, the value for water at room temperature. Inside the metal, the electric field must vanish, so that each slab is an equipotential volume. This means that the contact density of ions on both faces of a slab is identical and the kinetic contribution to the disjoining pressure P must vanish. The pressure is then determined only by the electric stress

$$\beta P(L) = \beta \epsilon E_{out}(L)^2 / 8\pi - \beta \epsilon E_{in}(L)^2 / 8\pi, \quad (2)$$

where E_{in} and E_{out} are the electric fields at the interior and exterior surfaces of a slab. By the superposition, for two like-charged metal slabs $|E_{out}| > |E_{in}|$, so that the pressure will always be repulsive. This is demonstrated in Fig. 2, where we have numerically solved the PB equation using using 4th order Runge-Kutta and explicitly calculated the pressure between various like-charged metal slabs.

We next consider two metal nanoparticles depicted in Fig. 1(b) inside a 1:1 electrolyte solution of concentration ρ_S . Both particles have radius a and charge Q_1 and Q_2 , respectively. The surface-to-surface separation is again L . To solve Eq. 1 we now use a relaxation method in cylindrical coordinate system and define the following boundary conditions: $\phi(\infty, z) = \phi(r, \pm\infty) = \phi'(0, z) =$

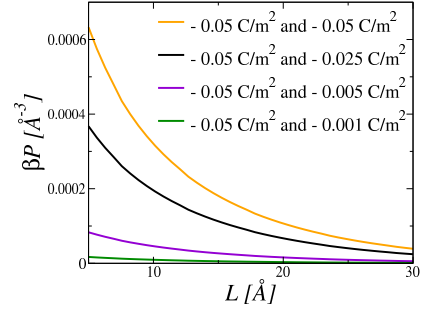


FIG. 2. The pressure between different like-charged metal slabs of width $d = 10 \text{ \AA}$, and the charge indicated in the figure, separated by a distance L . The pressure is always repulsive, independent of the charge on each slab. The salt concentration is 100 mM.

0, $\phi|_{S_1} = \phi_1$ and $\phi|_{S_2} = \phi_2$ where ϕ_1 and ϕ_2 are *a priori* unknown electrostatic potentials inside the nanoparticles 1 and 2, respectively. Starting from an initial guess for the values of ϕ_1 and ϕ_2 , our algorithm performs a search for the potentials ϕ_1 and ϕ_2 until the charge on each nanoparticle — calculated using the Gauss law, $Q = -\frac{\epsilon}{4\pi} \oint_{S'} \mathbf{E} \cdot d\mathbf{S}'$, where $\mathbf{E} = -\nabla\phi(r, z)$ is the electric field and S' is the nanoparticle surface — agrees with the initially specified value of Q_1 and Q_2 . The electrostatic-entropic force per unit volume is $\mathbf{f} = \nabla \cdot \mathbf{\Pi}$, where $\mathbf{\Pi}$ is the entropic-electromagnetic stress tensor

$$\Pi_{ij} = -p(r, z)\delta_{ij} + \frac{\epsilon}{4\pi} \left[E_i(r, z)E_j(r, z) - \frac{1}{2}E^2(r, z)\delta_{ij} \right]. \quad (3)$$

The kinetic pressure is $p(r, z) = k_B T \rho_S (e^{-\beta q \phi(r, z)} + e^{\beta q \phi(r, z)})$, and $E(r, z)$ and $E_i(r, z)$ are the modulus and the components of the electric field, respectively. The force can be expressed in terms of an integral of the stress tensor over an arbitrary surface enclosing one of the particles, $F = \oint \hat{\mathbf{z}} \cdot \mathbf{\Pi} \cdot \hat{\mathbf{n}} dA$. Choosing the boundary surface to be a cylinder of radius a and length $2a$ we obtain

$$\begin{aligned} \beta F = 2\pi \int_0^a dr \, r \left[\rho_S e^{-\beta q \phi(r, L/2)} + \rho_S e^{\beta q \phi(r, L/2)} - \right. \\ \left. \rho_S e^{-\beta q \phi(r, L/2+2a)} - \rho_S e^{\beta q \phi(r, L/2+2a)} + \right. \\ \left. \frac{\beta \epsilon}{8\pi} \left[E_r^2(r, L/2) - E_z^2(r, L/2) + \right. \right. \\ \left. \left. E_z^2(r, L/2+2a) - E_r^2(r, L/2+2a) \right] \right] + \\ \left. 2\pi a \int_{L/2}^{L/2+2a} dz \, \frac{\beta \epsilon}{4\pi} E_r(a, z) E_z(a, z) \right], \quad (4) \end{aligned}$$

where the positive sign of the force signifies repulsion between the nanoparticles. The results of the numerical integration are shown as symbols in Fig. 3(a). We find that the interaction between two like-charged spherical *metal nanoparticles* inside a 1:1 electrolyte solution

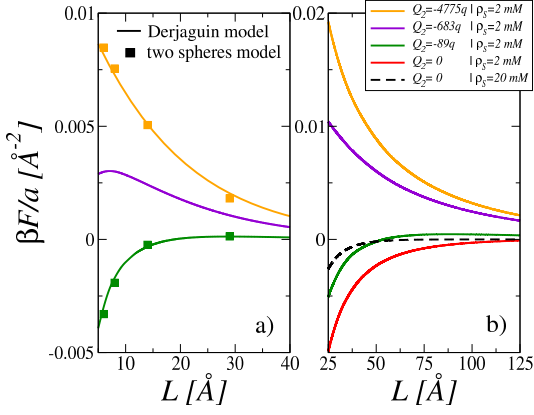


FIG. 3. (a) Electrostatic-entropic force between two like-charged metal nanoparticles of radius $a = 50 \text{ \AA}$ and charge $Q_1 = -67q$ and $Q_2 = -67q, -31q$ and $-6q$ — orange, violet and green curves, respectively — in electrolyte at 40 mM. Positive force is repulsive and negative is attractive. The squares are forces calculated numerically using PB equation in cylindrical coordinates and Eq. 4, the lines are calculated using the modified Derjaguin approximation, Eq. 6. (b) Electrostatic-entropic force — calculated using the modified Derjaguin approximation, Eq. 6 — between two like-charged metallic nanoparticles of radius $a = 200 \text{ \AA}$ and charges $Q_1 = -4775q$ and various values of Q_2 . Salt concentrations as indicated in the figure.

can be either attractive or repulsive, depending on their relative charge and electrolyte concentration! This is quite surprising in view of our previous result showing that like-charge attraction is impossible between parallel metal slabs. The curvature of nanoparticles, therefore, plays a fundamental role for existence of like-charge attraction.

Unfortunately the relaxation method that we developed to calculate the interaction force between two metal nanoparticles is quite expensive of CPU time. To obtain accurate results requires a very fine mesh, which makes the convergence very slow, in particular for large particles and low salt concentrations. Furthermore if one of the charged objects is non metal, such as say a phospholipid membrane, significant modifications to the algorithm must be made, since in this case the surface of such object will no longer be equipotential. In order to overcome these difficulties we have developed a modified Derjaguin approximation, which allows us to efficiently calculate the interaction potential between two metal nanoparticles or between a nanoparticle and a charged planar surface.

Derjaguin approximation allows one to calculate the interaction force between spherical particles, if the corresponding expressions are known for the interaction between planar objects. Consider two infinite metal slabs of width d and total surface charge densities $2\sigma_1$ and $2\sigma_2$, separated by a surface-to-surface distance L , as depicted in Fig. 1(a). Both faces of each metal slab are

charged, with the surface charge on each face depending on the separation between the slabs, while the *total* surface charge on each slab is fixed. The values of $\sigma_{1,2}$ are not precisely the surface charge densities on the corresponding spherical nanoparticles. The nanoparticle surface charge density must be renormalized in order to account for the curvature effects. This is done by demanding that for large $L \rightarrow \infty$, the electrostatic potential of a metal slab should be the same as for the corresponding nanoparticle. This renormalized surface charge will then produce the same electric field in the vicinity of a slab as exists near a spherical nanoparticle. The surface potential ϕ_{sp} of an isolated spherical particle with a surface charge density σ_{sp} can be easily calculated by numerically solving the PB equation in spherical coordinates. Once this is known, the corresponding surface charge density on each face of an isolated slab σ_{sl} , can be calculated using the analytical solution of PB equation for a charged plane⁵⁰,

$$\sigma_{sl} = \sqrt{\frac{2\rho_S\epsilon}{\pi\beta}} \sinh\left(\frac{\beta q\phi_{sp}}{2}\right). \quad (5)$$

This provides a mapping between the surface charge densities of spherical nanoparticles and of metal slabs, $\sigma_{1,2}$, used in Derjaguin construction.

In the spirit of Derjaguin approximation, we now discretize the spherical surfaces of each nanoparticle into parallel planar slabs. If the disjoining pressure $P(l)$ between the slabs separated by a surface-to-surface distance l is known, the total force between spherical nanoparticles can be calculated as⁵⁰,

$$\beta F = \pi a \int_L^\infty P(l) dl. \quad (6)$$

The expression for $P(l)$ is the same as in Eq.(2). The validity of Derjaguin approximation is restricted to, $L/a \ll 1$ and $\kappa a \gg 1$, where $\kappa = \sqrt{8\pi\lambda_B\rho_S}$ is the inverse Debye length⁵¹. For metal nanoparticles there is an additional complication since the slabs belonging to the same nanoparticle must be equipotential. However, we do not know *a priori* what this potential is, since it depends on the separation between the nanoparticles. However, we do know that the total charge on each nanoparticle is fixed, independent of separation, which means that the total charge on the slabs that compose a nanoparticle must also be conserved. This results in two constraints which determine the electrostatic potentials of metal slabs when the nanoparticles are at surface-to-surface separation L ,

$$\begin{aligned} \int_L^{L+2a} [\sigma_a(l) + \sigma_b(l) - 2\sigma_1] dl &= 0, \\ \int_L^{L+2a} [\sigma_c(l) + \sigma_d(l) - 2\sigma_2] dl &= 0. \end{aligned} \quad (7)$$

Note that each slab of our modified Derjaguin approximation has a different surface charge, while all the slabs

corresponding to the same nanoparticle have the same electrostatic potential, which changes with L . To calculate the disjoining pressure, we first guess the value of the electrostatic potential on each slab, ϕ_1^{guess} and ϕ_2^{guess} . Since the electric field inside the metal slabs is zero, the surface charge on the two external faces, see Fig. 1(a), can be calculated analytically from the exact solution of the PB equation⁵⁰,

$$\sigma_{a,d} = \sqrt{\frac{2\rho_S\epsilon}{\pi\beta}} \sinh\left(\frac{\beta q\phi_{1,2}^{guess}}{2}\right). \quad (8)$$

To calculate the charge on the interior faces, we numerically integrate the one dimensional PB equation using 4th order Runge-Kutta. The surface charges $\sigma_{b,c}$ can then be obtained using the electric field and the Gauss law. The values of ϕ_1^{guess} and ϕ_2^{guess} are then adjusted until the constraints given by Eqs. 7 are satisfied. In practice, this is done using the Newton-Raphson or some alternative root-finding algorithm.

In Fig. 3(a) the forces calculated using Eq. 4 and Eq. 6 are compared. The agreement is very good, showing that the modified Derjaguin approach provides an excellent approximation for calculating the force between metal nanoparticles, with a significant gain in CPU time. It is now possible to explore the parameter space to see the precise conditions which lead to like-charge attraction, Fig. 3(b). The attraction is a consequence of the non-uniform surface charge induced on the metal cores of the nanoparticles. However, since the total force contains both electrostatic and entropic contributions, there is no simple criterion that one can use to determine the specific conditions for which like-charge attraction will manifest itself. In Fig. 3(b), we use the modified Derjaguin approximation to calculate the force between large nanoparticles of radii $a = 200$ Å, in dilute electrolyte solution — conditions for which a direct integration of the non-linear PB equation is very time consuming. Once again for sufficiently different values of Q_1 and Q_2 , like-charge attraction manifests itself. Furthermore, we observe that for low salt concentrations, attraction can extend to very large distances.

The modified Derjaguin approach introduced in this Letter can also be used to study adsorption of metal nanoparticles with charge Q to a charged phospholipid membrane with surface charge density σ , see Fig. 4. Within the Derjaguin approximation the electric field just outside the membrane is directly determined by the Gauss law, $E(0) = 4\pi\sigma/\epsilon$, which allows us to easily integrate the 1d PB equation using 4th order Runge-Kutta. The potential on the metal slabs is once again determined using the charge conservation condition,

$$\int_L^{L+2a} [\sigma_a(l) + \sigma_b - 2\sigma_n] dl = 0, \quad (9)$$

where $2\sigma_n$ is the renormalized total surface charge on the metal slab, calculated using Eq. 5. The electrostatic-entropic force between the membrane and the nanoparticle can be calculated using Eq. 6, replacing the prefactor

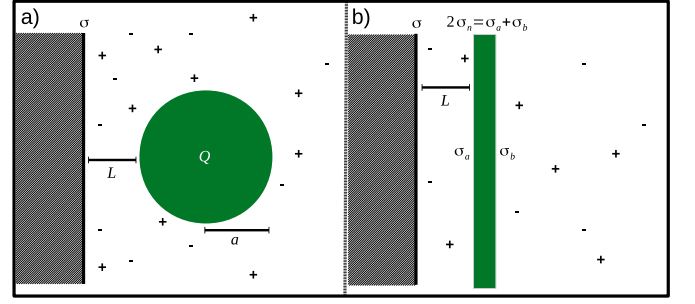


FIG. 4. (a) A metal nanoparticle of charge Q and radius a , at surface-to-surface distance L from a charged planar membrane, inside an electrolyte solution. (b) Representation of the modified Derjaguin approximation for this system.

πa by $2\pi a$, valid for the interaction of a sphere with a planar surface⁵⁰. The interaction potential can be obtained by integrating the force as a function of separation. To quantitatively study the adsorption of metal nanoparticles to the membrane one must also take into account the dispersion interaction⁵²

$$U_v = -\frac{A}{12} \left[\frac{2a}{L} + \frac{1}{(1 + L/2a)} + 2 \log\left(\frac{L/2a}{1 + L/2a}\right) \right], \quad (10)$$

where $A \approx 8.9 k_B T$ is the Hamaker constant characteristic of decane-gold in water at room temperature⁵³.

We now explore the interaction between gold nanoparticles of radius $a = 200$ Å and negative charge Q , with a like-charged phospholipid membrane of surface charge density $\sigma = -0.26$ C/m², in a dilute electrolyte solution of 2 mM. We see that strongly charged nanoparticles are repelled from the surface. However when the modulus of

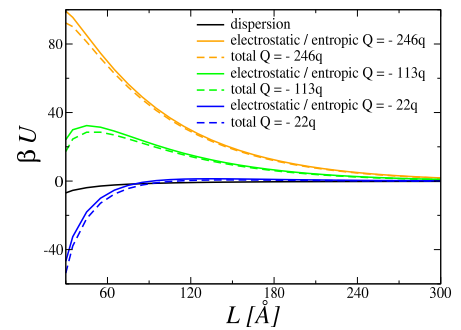


FIG. 5. Interaction potentials between a spherical metal nanoparticle of radius $a = 200$ Å and charge Q , indicated in the figure, and a membrane of charge density $\sigma = -0.26$ C/m². The electrolyte concentration is 2 mM. Solid curves are the electrostatic-entropic potentials for different nanoparticle charges, while the dashed curves are the total interaction potentials, which also include the van der Waals dispersion interaction. The membrane was modeled as a decane, with Hamaker constant $A \approx 8.9 k_B T$.

Q is not too large the interaction becomes attractive at sufficiently short separations, see Fig. 5. As the modulus of the charge decreases, the range of like-charge attraction increases. Fig. 5 also shows that for these low salt concentrations, the total particle-membrane interaction potential is dominated by the electrostatic-entropic contribution, with the dispersion potential being negligible. If salt concentration is increased, the electrostatic contribution will become screened and the total potential will be dominated by the dispersion interaction. Knowledge of the interaction potential between the metal nanoparticles and a phospholipid membrane allows us to easily calculate the adsorption isotherms. This will be explored in the future work.

In this Letter we have explored like-charge attraction between spherical metal nanoparticles inside a monovalent electrolyte solution. Existence of such attraction is particularly surprising considering that two like-charged parallel metal slabs always repel one another, demonstrating the importance of curvature for this counterintuitive result. We have used two methods to explore interaction between nanoparticles – a direct numerical integration of the full non-linear PB equation in cylindrical coordinates, and a newly introduced modified Derjaguin approximation. Both approaches provide identical results, but the modified Derjaguin approximation leads to orders of magnitude gain in CPU time. We have also used the modified Derjaguin approximation to study the adsorption of charged metal nanoparticles to biological membranes. The new theory provides an efficient way to calculate the adsorption isotherms important in various medical applications. It can also be used to study stability of dispersions and to explore heterogeneous coagulation of suspensions of metal nanoparticles.

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