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Strange electrostatics in physics, chemistry, and biology

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Abstract

In this paper I will briefly review some curious, and often counterintuitive, results found when the electrostatics and the many-body physics are brought together. The discussion is purely classical, with examples drawn from areas of physics, chemistry, and biology.
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1. The Thomson problem

A 100 years ago J.J. Thomson proposed an electrostatics problem which, in spite of its apparent simplicity, has not been solved up to now. After the discovery of electron, Thomson wanted to elucidate the structure of the periodic table. He conjectured that the position of a chemical element inside the periodic table depends on its electronic structure. Since proton still had to be discovered, to keep his atom neutral, Thomson postulated existence of a uniform neutralizing background. This model became known as the "plumb pudding" atom. The question was then how are

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the electrons distributed inside the atom. Specifically, what is the electronic structure of the ground state? Hundred years later this seemingly straight forward electrostatics problem still remains unsolved.

In the absence of a uniform background, the Thomson atom becomes a conductor and all the charges are expelled to the surface. The classical argument for the charge expulsion relies on the fact that the electric field inside the conductor must be zero, otherwise a current would be present. The Gauss' law then insures absence of any charge in its interior. But is this kind of macroscopic argument directly applicable to the microscopic distribution of charges? For example, suppose that there are only three electrons inside the sphere. Clearly, the ground state will be an equilateral triangle with electrons located on the surface the sphere. There is, however, another equilibrium state in which all three electrons are located co-linearly with the diameter of the sphere — two electrons on the surface and one at the center of the sphere. This charge distribution, however, is unstable and a small perturbation to the position of one of the electron can result in the expulsion of the central particle to the surface. Nevertheless, a stationary state, in which charge is present in the interior of the conductor is possible, at least in the ideal case.

The fact that there is no *stable* equilibrium configuration with electrons inside the sphere is a direct consequence of the Earnshaw's theorem [1]. The argument is very simple. Suppose that there are n electrons inside the sphere. Clearly, for small n the electrostatic repulsion will drive all of the charges to the surface. Now, suppose that we try to add an additional electron to the sphere. For its position to be stable, a generic perturbation should result in a restoring force. But Gauss law requires that the integral of the electric field over any closed surface in the interior of the sphere be zero (since there is no charge inside). Therefore, if there are some stable directions (positive contribution to the integral), they must be compensated by the unstable ones (negative contribution to the integral), and the electrostatic energy will not be minimum unless all the charges are at the surface. Thus, in the absence of a neutralizing background, the Thomson problem simplifies to finding the positions of the electrons *on the surface* of the sphere. Surprisingly, even this "surface Thomson problem" remains unsolved 100 years after its original formulation.

It is curious to ask what would happen to the charge distribution if instead of the Coulomb form, the electrostatic repulsion would follow a more general $1/r^\gamma$ law [2]. Would all charges still go to the surface or can some of them find a stable equilibrium in the interior of the sphere? Earnshaw's theorem does not apply in this case, and a different approach must be used. Too see if there is a stable position in the interior of the sphere, we compare the electrostatic energy of the configuration in which all the electrons are at the surface $E_\gamma(n)$, with a configuration in which $n-1$ particles are on the surface and one charge is at the center of the sphere [2],

$$\Delta E_\gamma(n) = E_\gamma(n-1) + \frac{q^2(n-1)}{\varepsilon a^\gamma} - E_\gamma(n) . \tag{1}$$

Clearly if $\Delta E_\gamma(n)$ is positive, the surface occupation is energetically favored, on the other hand if $\Delta E_\gamma(n) < 0$ there is a stable equilibrium position at the center of the sphere.

Unfortunately, since the surface Thomson problem does not have an explicit solution, we do not precisely know the form of $E_\gamma(n)$. Nevertheless, a simple argument based on the theory of the one component plasma (OCP), allows us to accurately estimate the electrostatic energy. We find that an analytical expression [2–4]

$$E_\gamma(n) = \frac{q^2}{2\varepsilon a^\gamma} \left[\frac{2^{1-\gamma}}{2-\gamma} n^2 - \frac{M_\gamma}{2^{\gamma-1}} n^{1+\gamma/2} \right] , \qquad (2)$$

gives a perfect fit to the ground state electrostatic energy of the surface Thomson problem as compared to the numerical minimization procedure [2], see Fig. 1. In Fig. 2, we plot $\Delta E_\gamma(n)$, for various values of γ.

From Fig. 2 it can be seen that for $\gamma \leqslant 1$, $\Delta E_\gamma(n)$ is always positive and the minimum of the electrostatic energy corresponds to all the particles residing on the surface of the sphere. The interior is unstable for any value of n. On the other hand for $\gamma > 1$ there exists a critical number of charges $n_c(\gamma)$, above which the position at the center of the sphere becomes *absolutely stable*, i.e., the global minimum of the electrostatic energy. Furthermore, even for some smaller number of charges than $n_c(\gamma)$, the center of the sphere will already be a metastable minimum, which means that any infinitesimal perturbation will result in a restoring force, even though the global minimum of the electrostatic energy will still be when all the charges are located at the surface. Curiously, the Coulomb case $\gamma = 1$ is precisely at the border between these two regimes.
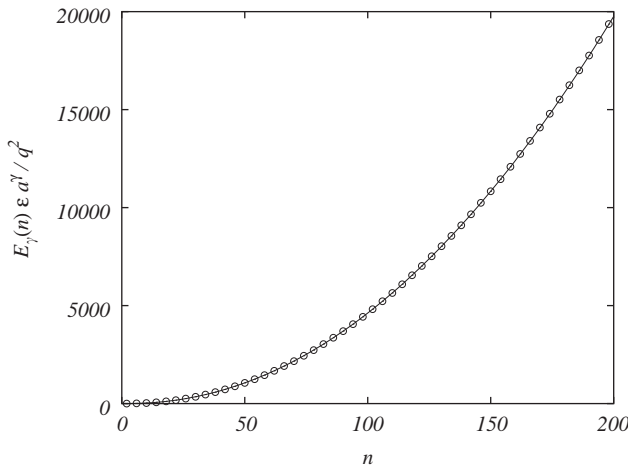

Fig. 1. Energy $E_\gamma(n)$ for $\gamma = 1.4$ as a function of the number of particles n, compared with the simulation data (points). The Madelung constant $M_\gamma \simeq 1.78$ gives a perfect fit to the data points over the whole range on n.
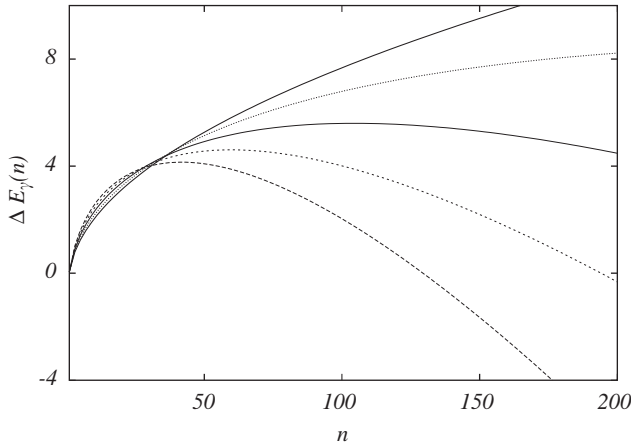
Fig. 2. The difference in energy $\Delta E_\gamma(n)$ between the configurations in which one particle is at the center of a sphere with $n-1$ particles at the surface, and the configuration in which all n charges are on the surface. The values of γ range from 1 for the topmost curve, to 1.4 for the bottommost curve, in intervals of 0.1. The topmost curve $\gamma = 1$ is a monotonically increasing function of n, while for $\gamma > 1$ the curves after reaching a maximum decline.

2. Dynamical instability of the Thomson problem

If the electrons are in motion, their interaction is no longer purely Coulombic. To order v^2/c^2, the dynamics is governed by the Darwin Lagrangian [5–7]

$$L = \frac{1}{2}\sum_i m_i v_i^2 + \frac{1}{8c^2}\sum m_i v_i^4 - \frac{1}{2}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}$$

$$+ \frac{1}{4c^2}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}}[\boldsymbol{v}_i \cdot \boldsymbol{v}_j + (\boldsymbol{v}_i \cdot \hat{\boldsymbol{r}}_{ij})(\boldsymbol{v}_j \cdot \hat{\boldsymbol{r}}_{ij})]\,, \tag{3}$$

where $\boldsymbol{v}_i$ is the velocity of electron i, and c is the speed of light. The velocity-dependent correction to the Coulomb law arises from the electromagnetic coupling between the moving particles. The Darwin Lagrangian [3] does not contain explicit time dependence, so that the Hamiltonian

$$H = \sum_i \boldsymbol{p}_i \cdot \boldsymbol{v}_i - L \tag{4}$$

with

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \boldsymbol{v}_i}\,, \tag{5}$$

is a constant of motion. Performing the Legendre transform we find

$$H = \frac{1}{2} \sum_i m_i v_i^2 + \frac{3}{8c^2} \sum m_i v_i^4 + \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$
$$+ \frac{1}{4c^2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} [\mathbf{v}_i \cdot \mathbf{v}_j + (\mathbf{v}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{v}_j \cdot \hat{\mathbf{r}}_{ij})] \,. \tag{6}$$

The ground state for n electrons on the surface of the sphere of radius a is then determined by the minimization of Eq. (4). Naively, one expects that the ground state is such that $v_i = 0$ for all i, and the electrons arrange themselves in a Wigner crystal with some topological defects. As discussed in the previous section this, indeed, what happens for a purely Coulombic interaction, since in that case the velocity dependent contribution to the Hamiltonian (kinetic energy) is always non-negative, and any particle motion results in an increase of the total energy. The Darwin Hamiltonian, however, is much more complex and our intuition fails. Specifically, we find [8] that for any sphere of radius a, there exists a critical number of electrons n_c such that for $n > n_c(a)$ a lattice arrangement is not the minimum of the electrodynamic energy [4]. Instead for $n > n_c(a)$, the electrons in the ground state are found to undergo a coherent motion. We conclude that for sufficiently high-surface charge concentrations, the Wigner lattice is dynamically unstable. A small perturbation can completely change the nature of the ground state. Fortunately, the surface charge concentration at which the Wigner lattice looses stability is many orders of magnitude larger than is normally encountered in the problems of chemistry and biology.

3. Charge reversal

One of the first thing that is learned in a course on electrostatics is that the force produced by the electric field on a charged particle is

$$\mathbf{F} = Q\mathbf{E} \,. \tag{7}$$

Therefore, a positively charged particle is expected to move in the direction of the applied field, while a negatively charged particle, will move in the direction opposite to the field. There is, however, a curious behavior that is observed in colloidal suspensions containing multivalent counterions. Under certain conditions, the electrophoretic mobility of colloidal particles can become reversed [9–15]. What can account for this surprising turn of events?

To understand the mechanism of charge reversal, we consider a simple model of a sphere with a uniform surface charge $-Zq$ in contact with an electrolyte reservoir containing $\pm q$ ions at chemical potential μ. For simplicity we restrict our attention to $T = 0$, so that the entropic effects can be ignored [16]. We would like to know how many ions will be transfered from the reservoir to the surface of the sphere once the equilibrium is established. Specifically, can the process of charge transfer result in a charge reversal of the sphere?

The amount of charge transfered is determined by the minimum of the grand potential function [16]

$$\Omega(n) = F(n) - \mu n \, , \tag{8}$$

where $F(n)$ is the electrostatic energy of the colloid with n counterions on its surface. The value of $F(n)$ can be determined simply by adding to the energy $E_1(n)$ of Eq. (2) contributions arising from the colloidal self energy and from the interaction of n counterions with the colloidal charge,

$$F(n) = \frac{Z^2 q^2}{2\varepsilon a} - \frac{Znq^2}{\varepsilon a} + E_1(N) \, . \tag{9}$$

Eq. (8) then simplifies to

$$\Omega(n) = \frac{(Z-n)^2 q^2}{2\varepsilon a} - M_1 \frac{q^2 n^{3/2}}{2\varepsilon a} - \mu n \, . \tag{10}$$

The parameter $\delta \equiv n - Z$ quantifies the extent of charge transfer. If $\delta > 0$ the sphere is overcharged while if $\delta < 0$ it stays undercharged. Minimizing Eq. (10) we find that an overcharged state is possible only if

$$Z > \left(\frac{4a\varepsilon\mu}{3M_1 q^2} \right)^2 \, . \tag{11}$$

If the ionic energy of a sodium chloride crystal is used as a measure of the characteristic chemical potential of the charge reservoir at zero temperature [16], we find that for a sphere of colloidal dimensions $a \approx 1000 \, \text{Å}$, and ions of $d \approx 1 \, \text{Å}$, the critical charge for occurrence of overcharging is $Z_\theta \approx 10^6$, which is extremely large, corresponding to one elementary charge every $10 \, \text{Å}^2$. In real colloidal suspensions, of course, the overcharging is possible with much weaker charged particles. At finite temperature, entropic effects are quite important and strongly influence the amount of counterion condensation [15].

4. Like-charge attraction

Like-charges repel and the unlike ones attract. This dictum is so famous that attempts even have been made to extend it to human relations. Yet, when the electrostatics is combined with the many body physics, the dictum looses its validity. Thus, it is found that under certain circumstances like-charged colloids inside a colloidal suspension can attract one another. The effect is still not fully understood and there is an ongoing debate about the precise mechanism causing the attraction.

One particularly important example of like-charge attraction in biological systems is the DNA condensation [15]. In aqueous solution DNA is ionized due to dissociation of its phosphate groups. This ionization results in one of the highest charge densities found in nature, one electronic charge every 1.7 Å. In spite of this huge charge concentration, over a meter DNA is packed into a nucleus of few micrometers. This efficient compaction is accomplished with the help of cationic

proteins. The bacteriophages (viruses that infect bacteria) also use multivalent cations to package their DNA. Thus, the T7 bacteriophage head is 10^{-4} times smaller than the unpacked form of its DNA [17]. Furthermore, it is found that if the multivalent polyamines, known to exist in the host bacteria, are added to an in vitro solution containing DNA, the chains condense forming toroids very similar in size and shape to the ones found in vivo [18,19]. To produce condensation, multivalent counterions must somehow induce attraction between the different parts of the DNA [20–23].

In eukaryotic cells, the cytosol is traversed by a complex network of microfilaments which are made of a protein called F-actin [24,25]. In spite of its high negative-charge density F-actin, in the presence of multivalent counterions, agglomerates forming a network of bundles [26]. Addition of monovalent salt screens the electrostatic interactions and re-dissolves the bundles [27]. What is the action of multivalent counterions which induces attraction between the like-charged macromolecules [28–43]? To understand this we can study a very simple model [33].

Consider two parallel polyions separated by a distance d inside a dilute solution containing α-valent ions [33]. The polyions will be idealized as rigid lines of charge of length $L = Zb$. Each line has Z monomers of charge $-q$ spaced uniformly along the chain. The solvent is a uniform medium of dielectric constant ε. As in the case of spherical colloids, a strong electrostatic coupling between the polyions and the microions results in the polyion charge renormalization. The precise amount of counterion condensation depends on a number of factor such as the polyion charge density, the valence of the counterions, the presence of salt, etc.

Suppose that there are n associated counterions which are free to move along the length of the polyion. The main effect of counterion condensation is the local renormalization of the monomeric charge from $-q$ to $(-1 + \alpha)q$. Lets define the occupation variables σ_{ij}, with $i = 1, 2, \ldots, Z$ and $j = 1, 2$, in such a way that $\sigma_{ij} = 1$, if a counterion is condensed at ith monomer of the jth polyion, and $\sigma_{ij} = 0$ otherwise.

The interaction energy between the two polyions is then

$$H = \frac{1}{2\varepsilon} \sum_{i,i'=1}^{Z} \sum_{j,j'=1}^{2} \frac{q^2(1 - \alpha\sigma_{ij})(1 - \alpha\sigma_{i'j'})}{r(i,j;i',j')} \,, \tag{12}$$

where the sum is restricted to $(i,j) \neq (i',j')$ and

$$r(i,j;i',j') = b\sqrt{|i - i'|^2 + (1 - \delta_{jj'})x^2} \tag{13}$$

is the distance between the monomers located at (i,j) and (i',j'), $\delta_{jj'}$ is the Kronecker delta, and $x = d/b$. The partition function is

$$Q = \sum_{\{\sigma_{ij}\}} \exp(-\beta H) \,. \tag{14}$$

The force between the two polyions is

$$F = \frac{1}{b\beta} \frac{\partial \ln Q}{\partial x} \,. \tag{15}$$

This model is so simple that for polyions with not too high values of Z, the partition function can be solved explicitly [33]. For larger $Z's$ the model can be simulated. In Fig. 3 we present the force as a function of separation for two polyions with $Z = 20$ and n condensed divalent counterions. We see that in spite of the net like-charge, the two polyion-counterion complexes can attract each other at sufficiently small separations. Furthermore, we find that a critical number $n_c = Z/2\alpha$ of condensed α-ions is necessary for the attraction to appear. For monovalent counterions the interaction is always repulsive [33].

The calculations above were presented for a very idealized model of interacting lines of charge. It is quite simple to modify the theory to account for finite polyion diameter. This modification, however, does not significantly affect the predictions of the theory. Attraction appears at small separations between the polyion surfaces—about 7 Å—after the critical number of α-ions is condensed onto the polyions [44]. We find that for macromolecules of finite diameter, less counterions are needed to induce attraction than for the two lines of equivalent charge density [44]. Furthermore, the charge–charge correlations along the polyion are of very short range [44,45], showing absence of any long-range order between the condensed counterions, contrary to the earlier speculations [29,30,34].

While the simple model presented above seems to account quite well for the like-charge attraction encountered in many biological systems, it is not sufficient to explain some of the recent experiments on attraction between confined colloidal particles. In the absence of confinement, the interaction potential between two spherical colloidal particles is found to be repulsive and completely consistent with the traditional DLVO theory [46]. However, a surprising result appears when a
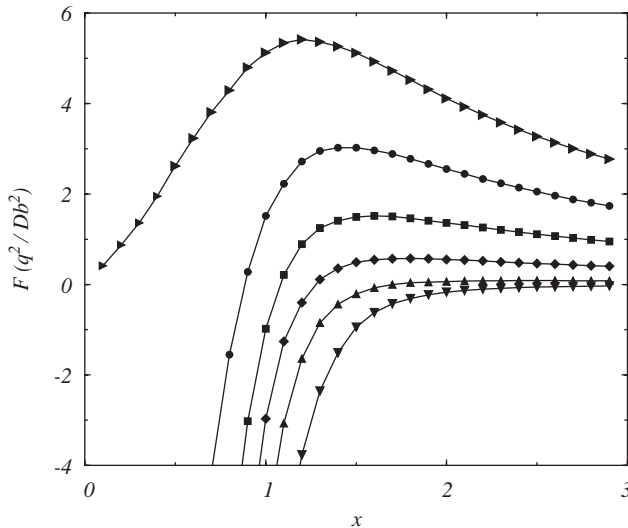

Fig. 3. Force versus distance between polyions for $Z = 20$, $\alpha = 2$, $\xi \equiv q^2/\varepsilon k_B T b = 2.283$ (corresponding to polymethacrylate) and $n = 5, \ldots, 10$ (from top to bottom) in the Monte Carlo simulation [33]. Positive force signifies repulsion between the complexes, while the negative force implies existence of attraction.

highly deionized suspension is confined between two glass plates [46–49]. For small separation between the plates, the pair potential develops a strong attractive component. The attraction is quite long ranged, comparable in its extent to the diameter of a colloidal particle, which can be as large as $1000\,\text{Å}$. Note that this is very different from the correlation induced attraction whose range is on the order of $10\,\text{Å}$. The mechanism for this long range force between the confined colloidal particles remains a mystery. A few different theories have been proposed [50] but none has proven sufficient to fully account for all the experimental results [51].

5. Conclusions

In this brief review I have presented some surprising, and often counterintuitive, results which appear when the electrostatics and the many-body physics come in contact. Some of these can be understood using quite simple models, others still remain a mystery. This is particularly the case for the long-range attraction between the confined like-charged colloids.

Relativistic corrections to the Coulomb law are found to lead to very profound modification of the ground state structure of charged systems. In the case of the surface Thomson problem, we find that for sufficiently large surface charge concentration, the ground state is no longer a Wigner lattice but is composed of electrons undergoing a coherent motion. Statistical mechanics of charged systems still has a number of surprises in store for us.

Acknowledgements

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