The Simulation on Nanoelectrodes Arrays for Nanoscale Objects Electrostatics
Manipulation in Normal Saline

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(Dated: December 1, 2014)

We present numerical calculations of electronic free energy, based on the nonlinear Poisson-Boltzmann equation, for the case of a nanoelectrodes array in normal Saline. We focus on a pentagram-shaped planar nanoelectrodes array where the ten electrodes has the same amount of charge but the charge symbols change. We analyze the arrays’ self-free-energy’s dependence on its size and shape. We find that the free energy, though also is influenced by the electrostatic energy, is much sensitive to the term of entropic contribution, i.e., the free energy given by the rearrangement of ions. We studied the interaction between a charged nanoparticle and the array when the particle passing vertically above the arrays center. We also analyze the free energy change when two arrays centers are overlapped but separated vertically and rotate relatively to each other. This work not only provides a theoretical prediction for the nanoscale electrostatic manipulation, which is to an extent beyond the limit of optic or magnetic tweezers, but also aid in a better understand of specific binding between biomacromolecules.

I. INTRODUCTION

In live biosystems, a huge number of effective, rapid and regular interactions occur every second among intracellular micro/nanoparticles and macromolecules. People have already done plenty of research on this issue and realized that these complex process are all based on the electromagnetic interactions between biomacromolecules and the structures and charge distribution have been studied both theoretically and experimentally. On the other hand, artificial micro/nanoparticles manipulation in fluid has been focused for it theoretical, experimental and practical meaning in recent years and various methods have been presented and developed in the past decades. The interaction between charged nanoparticles in ion solution has become focused in soft matter research, which may be used in the manipulation of nanoparticles in much smaller scale. Here we discuss in detail a theoretical nanodevice which may be used in normal saline to trap and release charged nanoparticles and to some extent, mimic the interactions between biomacromolecules. By numerical simulation, we find that well-arranged nanoelectrodes arrays, such as 5-dipole array, in solution can stimulate electrostatic fields and change the thermalodynamical property of nearby solution by ions rearrangement, which may trap charged nanoparticles. We analyzed the relationship between shapes and sizes of nanoelectrodes arrays and free energy change of system, which is produced by the electrostatic field energy and entropic contribution. By solving Poisson-Boltzmann equation, we get the electrostatic potential distribution then the net charge and ions distribution can be obtained. Then Helmholtz free energy, \( F = U_e - T\delta S \), where \( U_e \) represents the electrostatic energy and \( -T\delta S \) represents the entropic contribution at constant temperature \( T \), can be solved. In this way, we analyze the dependence of free energy to the location of a charged nanoparticle if it moves vertically above the center of the nanoelectrodes array, thus the interaction between nanoparticle and arrays can be solved. Furthermore, we analyzed the free energy change when two vertically overlapped arrays rotate relatively to each other. We calculate the influence on the free energy by varying the polarity dipoles. We believe this could be a framework of a new method for particle manipulation smaller than the size of 10nm and a simple mimic of specific binding to an extent.

II. THE SIMULATION OF SINGLE PENTAGRAM SHAPED ELECTRODES ARRAY

We present the simulation of the potential distribution based on Poisson-Boltzmann theory and we complete the calculation of free energy with the considering of electrostatic energy and entropic contribution. In order to get the potential distribution, we solved the nonlinear PB equation, Eq. (1), with the appropriate boundary conditions. After getting the special distribution of electrostatic potential, \( \varphi(x, y, z) \), all the information can be got by integrating equation (1)-(6). In the system we study, the equilibrium state of the macroscopic system is corresponded to the minimum of free energy. For this incompressible system, we introduce Helmholtz free energy to evaluate the stability of system and get the relationship between Helmholtz free energy and nano-electrodes arrays shape and size. Using this method, we analyzed the interaction between a charged nanoscale particle and the array. We also present the interaction between two arrays, when their centers are overlapped but separated vertically and rotate with different angles. Meanwhile, the influence on the free energy by varying the polarities of dipoles has been calculated.
constant of vacuum and $\varepsilon$

Red spheres indicate positively charged nanospheres (+20 nm to 9.6 nm) and analyzed the corresponding distance $D$ between the center of the outer ray and of the negatively charged spheres is $D/2$. The array can also be interpreted as an array of 5 dipoles.

FIG. 1. The schematic diagram of a nanoelectrode array.

A. Electrostatic potential distribution above the array and systems free energy.

We numerically solve the potential distribution in the vicinity of the array like a pentagram in normal saline in Fig. 1, where each nanosphere electrodes diameter is 4 nm, and the properties switch one by one. Thus, it gives rise to 5 dipoles and the distance between each electrodes influenced the potential distribution and free energy.

We write the PB equation

$$\nabla^2 \phi = \frac{e}{\varepsilon_0 \varepsilon_w} \sum_i z_i c_{i0} \left[ -\exp \left( \frac{z_i e \phi}{k_B T} \right) + \exp \left( \frac{z_i e \phi}{k_B T} \right) \right]$$  (1)

where $\phi$ represents the voltage, $\varepsilon_0$ represents dielectric constant of vacuum and $\varepsilon_w = 80$ represents relative di-

Fig. 2 shows the electrostatics potential distribution on the surface where the nanospheres centers locate. Here the distance $D$ between the center of the outer electrodes and center of the array is 8 nm. We vary $D$ from 7.2 nm to 9.6 nm and analyzed the corresponding

$$F = U_{el} - T \Delta S = \frac{1}{2} \int \rho \phi dV - k_B T \int \left\{ \sum_i c_{i0} \left[ z_i \psi \exp(-z_i \psi) + \exp(-z_i \psi) - 1 \right] \right\} dV $$  (6)

free energy, which is plotted on the Fig. 3. Here, for each term, i.e., the energetic term, entropic contribution and free energy are all relative value compared to $D = 7.2$ nm case, where the electrostatic energetic term is $177k_B T$, entropic contribution is $35.8k_B T$ and free en-
The free energy is reduced. Charge and only one couple with same charge, thus the couples with opposite charge, which is the same to case 3.

When adjacent inner nanoelectrodes with same charge and 2 very close, though one has only one dipole switched, the calculate the free energy change, which is listed in Fig. 4.

FIG. 2. The potential distribution on $z = 0$, the plane where all the center of spheres locate.

FIG. 3. The dependence of electrostatic energy, entropic contribution and free energy to $D$. Here, the array is the same to that in Fig. 1. With $D$'s increasing, the free energy and entropic contribution decrease, while the electrostatic energy increases slightly. All the three energy are relative value compared to the case when $D = 7.2\text{nm}$.

Energy is $231.3k_B T$. The electrostatic energetic term includes the self-energy of the sphere, which is almost a constant when $D$ varies. With $D$'s increasing, the electrostatic energetic term increases because more and more ions get the influence of electrodes, however, since this influence will rearrange the distribution of ions and this factor is more influential, the entropic contribution will dominate and overwhelm. So, when $D$ gets larger, the free energy decreases.

Besides the shape and size, the polarities of dipoles in arrays also influence systems' free energy. It is because, for two electrodes with opposite charge, the closer they are to each other, and the lower the free energy is. We change 1 or 2 dipoles' polarities in Fig. 1, then we calculate the free energy change, which is listed in Fig. 4. We notice the free energy change in case 2 and case 3 are very close, though one has only one dipole switched, the other has two. It is because in case 2, there are 3 couples of adjacent inner nanoelectrodes with same charge and 2 couples with opposite charge, which is the same to case 3. Nevertheless, in case 4, there are 4 couples with different charge and only one couple with same charge, thus the free energy is reduced.

B. Interactions between a charged nanoparticle and the array.

After calculating the potential distribution and the nanoelectrodes arrays self-free-energy, we consider the interaction between a charged nanoparticle and the electrodes array when the nanoparticle passes vertically above the center of array. Because the size of the particle is close to the size of the electrodes and its charge distribution will influence the solid-solution system as well, it is not suitable to regard the particle as a point. We assume the particle is a sphere and the charge is evenly distributed in the volume. The system, including the electrodes array, the particle and the solution will stay equilibrium when the free energy is at the minimum. If not, the particle will get a force $\vec{F}$ to pull it to the minimum energy points, and the force can be calculated using $\vec{F}(x, y, z) = -\nabla \cdot F(x, y, z)$, where $F(x, y, z)$ represents the Helmholtz free energy of the system depended on the location of the center of the nanoparticle.

In our simulation, we assume a nanoparticle other than the electrodes has the charge of $+20e$ and 3nm large in diameter. This particle travel above the center of the array vertically. The array is the same to that in section A, and $D=8\text{nm}$. As Fig. 5 shows, the free energy will get bigger when $z$, the distance between the particles center and the center of the array, is getting larger. We use the relative value compared to $z = 0$ to depict the electrostatic energetic term, entropic contribution and free energy. When particle is in the center, the electrostatic energetic term is $203.3k_B T$, entropic contribution is $39.1k_B T$ and free energy is $242.4k_B T$. Though the electrostatic energy will be smaller if the particle moves away, the larger entropic contribution will overwhelm and make the free energy larger. Based on the Boltzmann theory, the probability density of finding particle at $z$ is $f(z)dz \propto \exp(-\frac{F(z)}{k_B T})$. As shown in Fig. 5(b), the probability of finding particle at $z = 0$ is twice as large as finding at $z = 4\text{nm}$. We analyze the free energy by second order polynomial fit, i.e., at the vicinity of $z = 0$, the system can be regarded as a harmonic oscillator and free energy $F^{(2)}(k_B T) = 0.18072z^2(\text{nm}^2)$. Thus, the elastic coefficient is $0.0015\text{N/m}$. (Fig. 5(c))
C. Interactions between two nanoelectrode arrays and the influence of changing dipoles’ polarity.

We analyze the interaction between the array in Fig. 1 and a same or differently polarized array. Considering the symmetry, there are only 8 cases which can represent all the combination. (Fig. 6) In every case, two arrays’ centers are horizontally overlapped but separated vertically. When they have relative angular replacement, because both the electrostatic energy and entropic contribution will change periodically by the angular replacement θ, the system’s free energy will oscillate. Since the arrays we study have 5-fold rotation symmetry, the period of free energy F(θ) will be 72°. We just simulate one period.

We calculate the free energy of each case with different angular replacement (Fig. 6), we find that in different cases, the energy change has different tendency through θ varying and the tendency change gradually with the dipoles polarities changing. We can also see that though relatively large energy difference exists when angular replacement θ = 0° or 72°, the energy differences when θ = 36° is very small, and less than 0.5k_BT. This indicates that if two cases have two similar angular replacement where θ = 36°, it is much easier to switch from one case to the other, compared to other angular replacement. This, to a certain extent, has some similarity with the unexpected structural change during the specific binding or other bio-chemical interactions.

For the case of two opposite nanoelectrodes arrays, i.e., two arrays with same shape and size but with opposite charge distribution, we find that the free energy of system get to its maximum when θ = 36°, and to the minimum when θ = 0° or 72°. In this process, the electrostatic energetic term and entropic contribution term vary also. However, the electrostatic energetic term gets to the minimum when θ = 36°. The dislocation of two electrodes with opposite charge will make the electrostatic energy between electrodes larger. However, because the total electrostatic energetic term is the sum of both electrodes and ions energy, the dislocation will allow the electrodes to appeal more ions and make the energy lower. In another word, the dislocation decreases the shielding effect between two opposite charged electrodes, thus lower the systems electrostatic energetic term. Nevertheless, the
FIG. 7. (a) the energy change of two opposite arrays system when the angular replacement $\theta$ varies from $0^\circ$ to $72^\circ$. Electrostatic energy, entropic contribution and the total free energy change are illustrated in relative value compared to $\theta = 0^\circ$ (b) corresponding probability density of different angular replacement in (a).

more appealing to ions will rearrange more ions, the entropic contribution will still overwhelm electrostatic energies decrease. In the situation where shielding effect is considerably strong, the electrostatic energy change given by adding a new ion is much smaller than the entropic contribution of ions rearrangement. Similar to section B's analysis, the ratio of probability density at maximum to at minimum is approximately 2.67. (Fig. 7)

Observing the results, the cases with two same or opposite arrays (case 1 and case 8) have the most drastic energy change during rotation. Here we analyze each kind of contribution to the free energy change during rotation. For the case of two opposite nanoelectrodes arrays, we find that the free energy of system gets to its minimum when $\theta = 36^\circ$, and to the maximum when $\theta = 0^\circ$ or $72^\circ$. In this process, the electrostatic energy term and entropic contribution term vary also. However, the electrostatic energetic term gets to the maximum when $\theta = 36^\circ$. The dislocation of two electrodes with same charge will make the electrostatic energy between same ions larger. Similar to the case of two opposite arrays, the entropic contribution will still overwhelm electrostatic energies decrease. The ratio of probability density at maximum to at minimum is approximately 2.5. (Fig. 8)

III. DISCUSSION

In our simulation, the influence caused by the entropic term is always significantly greater than by the electrostatic energetic term. It can be understood because adding an ion in this system with strong shielding effect leads to larger change in entropic contribution than in electrostatic energetic term. However, the free energy cannot change without the charge distribution. Hence, if we fabricate such devices manipulating particle using this method, there should be adequate charges which can give rise to enough changes in entropy.

In section IIIC we analyzed the change in free energy due to the varied polarities of dipoles. We have found that this varying only costs a little amount of energy, but it will change the angular dislocation of greatest probability density. It, to an extent, can illustrate the process
of specific binding when the biomacromolecules change the orientation of different charged groups. We also find that at some cases, the different two-array systems free energy will be very close and the switch between two cases is relatively easier. This, on a certain degree, is similar to the unexpected structural changes during biochemical reactions.

In our simulation, we have neglected the existence of Stern layer. However, we still consider that it is acceptable. Firstly, the size of the particles we simulated is large enough, so, the Stern layer can be regarded as a part of the particles, i.e., the true particles are smaller but possess more charge. Secondly, when controlling the particles artificially, normal saline is not the best choice. However, in biosystem, specific binding happens in a smaller scale, where the van der Waals interaction, hydrogen binding and other forms of electro-magnetic interactions dominate.

IV. CONCLUSION

To summarize, we have calculated potential distribution and free energy of a Pentagram-shaped nanoelectrodes array in normal saline. We have analyzed the interaction between a charged particle and the array and the influence of changing the polarity of dipoles. We have found that the entropic contribution is a dominating factor. We wish that this simulation will be a framework of charged nanoparticles’ manipulation by electrostatic force. To an extent, this could be regarded as a mimic of biomolecule interaction.

V. ACKNOWLEDGEMENTS

We are grateful to Dr. Linhui YE in the Department of Electronics, Peking University for his constructive advices and valuable discussions. This work was financially supported by NSF of China (Grants 11374016) and MOST of China (Grant 2012CB932702, 2011CB933002).

VI. AUTHOR CONTRIBUTIONS

Jingkun Guo and Zijin Lei contributed equally in this work. Jingkun Guo completed all the programming part and Zijin Lei thought out theoretical framework and deduced the formulas. Shengyong Xu designed this project and provided suggestions and funding.