A study on the distribution of adsorbed nanoparticles*

LI Ding(李鼎)[1,2;1)]

1 (Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China)
2 (Graduate University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract We use Monte Carlo simulation to calculate the distributions of particles under adsorption force near planar and cylindrical surfaces, respectively. Both hard sphere interaction and repulsive Yukawa (screened coulomb) interaction are employed in our simulations. We study the influence of the inter-particle potentials. The difference between the MC simulation results and the analytical results of ideal gas model shows that the interaction between particles plays an important role in the density distribution under external fields. Moreover, the 2-dimensional constructions of particles close to the surface are studied and show relations of the interaction between particles. These results may indicate us how to improve the methods of building nanoparticle coatings and nano-scale patterns.

Key words nanoparticle, adsorption, Monte Carlo simulation, Yukawa potential

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1 Introduction

The adsorption of nanoparticles is a subject of both scientific interest and practical importance. There are several interesting phenomena such as layering and charge inversion which occur in this kind of systems[1, 2]. In applications, the method of adsorption of nanoparticles is used in creating nano-scale patterns and nanoparticle coatings to modify the physical and chemical properties of surfaces[3]. A well designed nanopatterned surface may exhibit unusual capabilities such as super-hydrophobicity and low friction[4—6]. In our previous work, it has been proved that the coverage ratio of nano-scale patterns plays a key role in changing the slip length of solid-fluid interface[7]. However the thermal motion of nanoparticles always results in a random distribution. Techniques to control the final state of adsorption process may deeply improve the methods to create nanopatterns. In this paper we find out some factors which may control the extent of adsorption and the particle distributions using computer simulations.

From the theoretical point of view, the adsorption of nanoparticles is a complex process. Generally speaking, three main factors affect the equilibrium distribution of adsorbed nanoparticles, i.e., the particle-particle interactions, the surface-particle interactions and the entropy. To study the properties of this kind of systems, computer simulation methods such as Molecular Dynamics and Monte Carlo method are the most efficient ones[1, 8]. In this paper we choose the MC method. As for the particle-particle interactions, we use both hard sphere potential and repulsive Yukawa potential which is the major part of the well known DLVO theory for colloidal systems[9]. The Van der Waals attraction in DLVO theory is neglected in our model because of its relatively short interaction range[10, 11]. Various interaction strengths and surface geometry are considered and the simulation results show that they have obvious influences on the extent of adsorption of particles. We also use the 2-dimensional Dirichlet-Voronoi constructions to study the geometry properties of the patterns fabricated by particles adsorbed on surfaces.

2 Models and methods

In simulations, we consider both adsorptive planar surface and adsorptive cylindrical surface, respectively. In the planar case, all particles making up the

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1) E-mail: hricchaya@163.com

system are confined in a $L\times L\times L$ cubic box. Here L denotes the side length of the box which is 100σ in simulation (σ is the diameter of particle). The periodic boundary conditions are applied in the (x,y) directions and the reflection boundary condition is used in the z direction which can be expressed as

$$U_{\rm rc}^{\rm flat}(z_i)=\begin{cases}\infty & z_i<0||z_i>L\\ 0 & 0\leqslant z_i\leqslant L\end{cases}, \tag{1}$$

where z_i is the z-coordinate of the ith particle. In the cylindrical case, particles are confined in a $R\times L$ cylindrical box. R is the radius of the cylindrical surface and L is the length of the box in z axis. In our simulations R is 10σ and L is 100σ. The periodic boundary condition is applied in the z direction and the reflection boundary condition is used in r direction which is expressed as

$$U_{\rm rc}^{\rm cyl}(r_i)=\begin{cases}\infty & r_i>R\\ 0 & r_i\leqslant R\end{cases}, \tag{2}$$

where r_i is the r-coordinate of the ith particle which satisfies $r_i^2=x_i^2+y_i^2$.

In both cases the total number of particles is 10^3. The total energy of the system can be written as

$$U_{\rm total}=\sum_{i,i<j}U_{\rm hs}+\sum_{i,i<j}U_{\rm Yu}+\sum_i U_{\rm ad}\,, \tag{3}$$

where $U_{\rm hs}$ is the hard sphere pair potential, $U_{\rm Yu}$ is the repulsive Yukawa pair potential and $U_{\rm ad}$ is the adsorption potential. The hard sphere potential is defined as

$$U_{\rm hs}(r_{ij})=\begin{cases}\infty & r_{ij}<\sigma\\ 0 & r_{ij}\geqslant\sigma\end{cases}, \tag{4}$$

where r_{ij} is the distance between the ith and the jth particles which satisfies $r_{ij}^2=(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2$. The repulsive Yukawa potential is defined as

$$U_{\rm Yu}(r_{ij})=\begin{cases}\dfrac{\epsilon\sigma}{r_{ij}}\exp\left[-k\sigma\left(\dfrac{r_{ij}}{\sigma}-1\right)\right] & r_{ij}\geqslant\sigma\\ 0 & r_{ij}<\sigma\end{cases}, \tag{5}$$

where ϵ is the interaction strength and k is the inverse screening length which has a complex relationship with the charge of the particle, the density and other environmental conditions such as the added salt concentration[9]. For the adsorption potential, we use a simple constant force form which is expressed as

$$U_{\rm ad}(z_i)=\begin{cases}g(l-z_i) & z_i\leqslant l\\ 0 & z_i>l\end{cases}, \tag{6}$$

in the planar surface case; and as

$$U_{\rm ad}(r_i)=\begin{cases}g(l-r_i) & r_i\leqslant l\\ 0 & r_i>l\end{cases}, \tag{7}$$

in the cylindrical surface case. Here g is the adsorption force and l denotes the range of the force. We define a quantity $U_{\rm w}\equiv g\cdot l$ as the well-depth of the adsorption potential which describes the potential strength.

The equilibrium properties of our model system are obtained by using the standard canonical MC simulations following the Metropolis scheme[12, 13]. Particle moves are considered with an acceptance ratio of 30%. In each run of simulations more than 10^4 MC steps per particle are performed. Typically, about 10^3—2×10^3 MC steps per particle are required for equilibration, and about 8×10^3 subsequent MC steps are used to accomplish the measurements.

3 Results and discussion

To testify the validity of our method, we first calculate the density profile in z-direction of adsorbed hard sphere particles. The value of l is set to 10σ for the planar surface case. The adsorption potential strength $U_{\rm w}$ increases from $0.8k_{\rm B}T$ to $4.0k_{\rm B}T$ with a step $0.8k_{\rm B}T$, here $k_{\rm B}$ is the Boltzmann constant and T is the temperature. Figs. 1(a) and (b) show the evolvement of the energy per particle and the evolvement of the quantity n_0 which is defined as the number of particles situated less than 1σ from the adsorptive surface (in the following parts of the paper we call this region as the first layer). The value of n_0 characterizes the extent of adsorption. In the figures it is obviously both the energy per particle and the value of n_0 show that the systems get equilibrium after about 10^3 MC steps per particle. Fig. 1(c) show the equilibrium density profiles in z-direction of the system. To check the results we consider the density profile of idea gas under the same external fields as in simulations. It can be expressed as

$$\rho(z)=\begin{cases}\rho_0\exp\left(-\dfrac{gz}{k_{\rm B}T}\right) & 0\leqslant z\leqslant l\\ \rho_0\exp\left(-\dfrac{gl}{k_{\rm B}T}\right) & l<z\leqslant L\end{cases}. \tag{8}$$

We can find the simulation results in Fig. 1(c) are analogous to the Eq. (8). To verify it quantificationally, we define a characteristic factor b which determines the density profile within the adsorption force range l as

$$b\equiv\frac{g\sigma}{k_{\rm B}T}\,, \tag{9}$$

and then the value of n_0 can be calculated analytically using Eq. (8) with the restriction conditions. The result is

$$n_0=\frac{N[1-\exp(-b\sigma)]}{1+(Lb-lb-1)\exp(-bl)}\,, \tag{10}$$

here N denotes the total number of particles in the system.

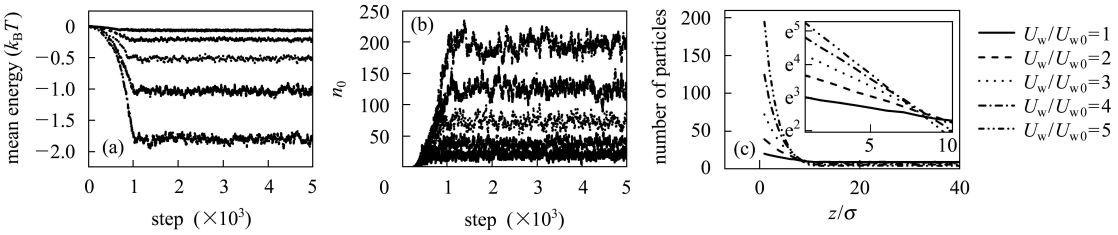

Fig. 1. Simulation results for the hard sphere particles in cubic box. (a) shows the evolvement of the mean energy per particle, (b) shows the evolvement of the value of n_0, (c) shows the density profile at the z-direction where the inset shows the results within l on linear-log coordinates. Here $U_{w0}=0.8k_BT$.

We use the simulation data to fit the values of b and n_0 and show the results in Figs. 2(a) and (b), respectively. In the Figures we find the fitting values are very close to the predictions of idea gas model. These results confirm the validity of our method. To discuss the influence of the adsorption force range, we study also systems in which $l=1\sigma$. The results are shown in Fig. 2(c). The values of n_0 are also very close to the results of Eq. (10). This exhibits that the adsorption force range has no exceptive influences on the results under our settings.

In the cylindrical surface case, due to the geometry construction, the results are different from the planar surface case. The density profile of idea gas has the form as

$$\rho(r)=\begin{cases}\rho_0\exp\left[-\dfrac{g(R-r)}{k_BT}\right] & R-l\leqslant r\leqslant R\\ \rho_0\exp\left(-\dfrac{gl}{k_BT}\right) & 0\leqslant r<R-l\end{cases}, \quad (11)$$

and the value of n_0 can be computed as

$$n_0=\frac{2N[Rb-1-(Rb-\sigma b-1)\exp(-b\sigma)]}{[(Lb-lb-1)^2+1]\exp(-b\sigma)+2(Rb-1)}. \quad (12)$$

We set $l=1\sigma$ here and the simulation results are shown in Fig. 2(d). They are well fitted to the prediction of Eq. (12).

In the next part, we show the effects of the interaction between particles on the density profile in the z-direction. As discussed before, we use $l=10\sigma$ for planar case and $l=1\sigma$ for cylindrical case. The adsorption potential strength U_w is set as $4k_BT$. The repulsive Yukawa potential has two control parameters: the interaction strength ϵ and the inverse screening length k. To understand fully their effects, we vary the values of both ϵ and k respectively in simulations. With the simulation results we fit the quantity b and n_0 in the planar case and fit the value of n_0 only in cylindrical case.

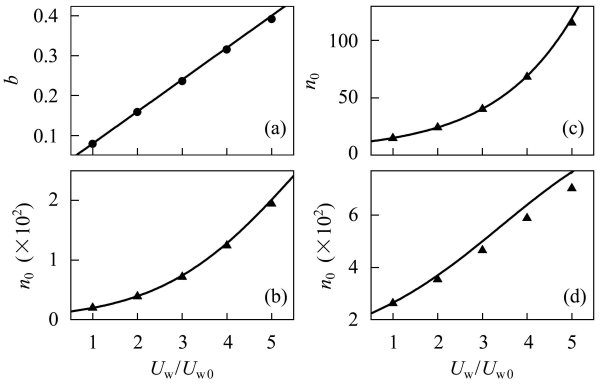

Fig. 2. The fitting results of hard sphere particles. Circles present the fitting value of b and triangles present the fitting value of n_0. The solid curves are the predictions of the ideal gas model. (a) and (b) are the planar case with $l=10\sigma$, (c) is the planar case with $l=1\sigma$, and (d) is the cylindrical case with $l=1\sigma$. Other parameters are the same as in Fig. 1.

The fitting results are shown in Fig. 3. We can see that the values of n_0 and b decrease monotonously when the value of ϵ increases or the value of k decreases in the planar case as shown in Figs. 3(a) and (b). But in the cylindrical case, a parabolic-like curve observed as in Fig. 3(c) shows that when the effective potential range increases, the extent of adsorption decreases first and then increases and there is a minimum near $k\sigma=1$. It is well known that repulsive particles tend to disperse in space. In an open system like the planar case, particles can move away without limit, so the adsorbed particles have the tendency to push others away from the surface which can be described as screening effects and it results in a monotone behavior as shown in figures. But in the confined system such as the cylindrical case, the boundary condition limits particles to move within a finite space which causes an effective force to push particles onto the surface. This confined effect will enhance the adsorption of particles. The competition between the confining effect and the screening effect

leads the parabolic-like behavior in Fig. 3(c). We can predict that the value of n_0 may increase when ϵ is large enough which is beyond the range of which shown in Fig. 3(d). Another interesting thing here is the different effect of ϵ and k. In principle, both increasing ϵ and decreasing k cause stronger effective potential strength and larger effective potential range. The difference is that the value of ϵ determines mainly its strength and the value of k characterizes primarily the potential range. As analyzed before, we know that the confined effect is a volume effect which exhibits more obviously by decreasing k than increasing ϵ.

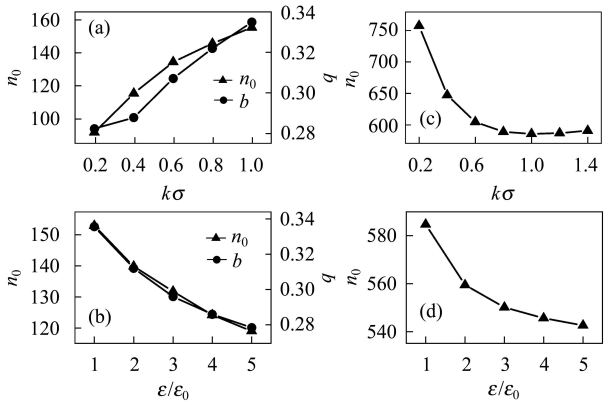

Fig. 3. Fitting results for the different hard core Yukawa particles. Triangles are the fitting values of n_0, and circles are the fitting values of b. (a) and (b) show the results for cubic case, (c) and (d) show the cylindrical case. $\epsilon_0 = 4k_BT$. $k\sigma = 1$ when ϵ varies in (b), (d) and $\epsilon = 4k_BT$ when $k\sigma$ varies in (a), (c).

Finally we analyze the geometry properties of the patterns constructed by the adsorbed particles. Due to the adsorbed particle random distribution, we compute their Dilichlet-Voronoi polygons[14] as the neighboring region for each particle within the first layer by the following method. We project the 3-dimensional position coordinates (as (x_i, y_i, z_i) for the ith particle) of all particles within the first layer onto the adsorptive surface. This treatment creates a discrete 2-dimensional point set as $\{P_i | 1 \leqslant i \leqslant n_0\}$. For the planar case $P_i = (x_i, y_i)$, and for the cylindrical case it is

$$P_i = \begin{cases} \left(R\arccos\left(\dfrac{x_i}{\sqrt{x_i^2+y_i^2}} \right), z_i \right) & y_i \geqslant 0 \\ \left(-R\arccos\left(\dfrac{x_i}{\sqrt{x_i^2+y_i^2}} \right), z_i \right) & y_i < 0 \end{cases}. \quad (13)$$

Then we construct the Dilichlet-Voronoi polygon for each point with this 2-dimensional point set. The definition of Dilichlet-Voronoi polygon C_i for the point $P_i \in \{P_i\}$ is shown as below:

$$C_i = \left\{ P | \forall_{i \neq j} \mathrm{dist}(P_i, P) \leqslant \mathrm{dist}(P_j, P) \right\}, \quad (14)$$

here dist(,) is the distance function, and P denotes all points on the surface. Fig. 4 shows a typical Dilichlet-Voronoi diagram generated by a random points set. The fluctuation of the areas of Dilichlet-Voronoi polygons is considered as a measurement of the regularity of the particle arrangement within the first layer in our paper.

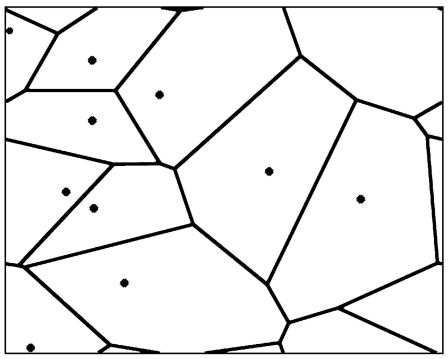

Fig. 4. Dilichlet-Voronoi polygons for 10 random points. Here periodic boundary conditions are used.

We calculate the mean area of the Dilichlet-Voronoi polygons and their relative error RE which are obtained by dividing the standard deviation by the mean area for each frame at equilibrium state. The value of RE describes the fluctuation of polygon areas. The simulation details are the same as those in the previous part. The results are shown in Fig. 5. We can find that when the value of ϵ increases or the value of k decreases, the relative errors decrease monotonously in both planar and cylindrical cases. This means that the distribution of stronger repulsive interacting particles is more regular.

In summary, we use computer simulation method to study the distributions of adsorbed hard core repulsive Yukawa particles in this paper. The extent of adsorption and the 2-dimensional profile of patterns constructed by the adsorbed particles in first layer are calculated. The results show that a stronger repulsive strength of the particle-particle interaction will results in a more regular distribution. For the extent of adsorption, the confined system gives different results to the open system.

In real systems, the interactions are far more complex than those modelled in this paper. A more precise model system may give more detailed results. However, it does not change the conclusion in this paper.

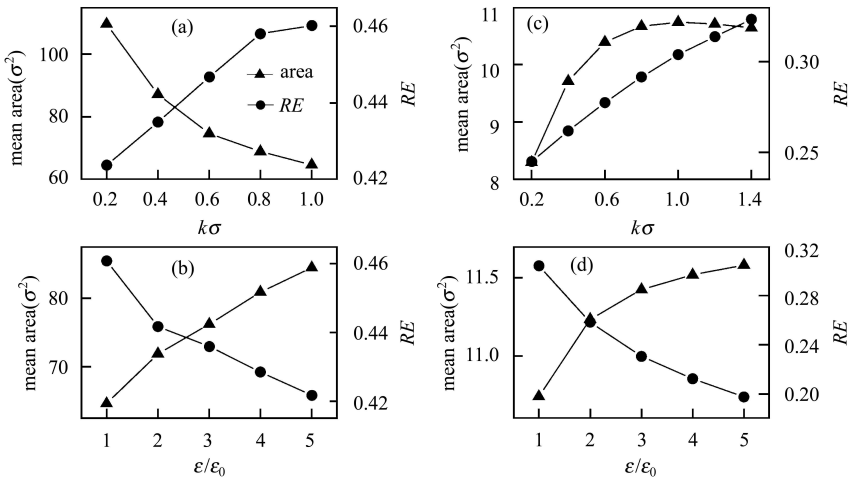

Fig. 5. Mean area and relative error for Dilichlet-Voronoi polygons with different Yukawa potentials. Triangles are the value of mean area and circles are the value of *RE*. (a) and (b) show the results of cubic case, (c) and (d) show the results of cylindrical case. Other parameters are the same as in Fig. 3.

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