Size Polydispersity in Random Sequential Adsorption: An Integral-Equation Theory

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ABSTRACT

We have developed an algorithm for predicting the structure of monolayer films generated through the random sequential adsorption (RSA) by modifying a set of Ornstein-Zernike equations (OZ). This type of integral-equation theory has long been used to estimate the structures of equilibrium three-dimensional and two-dimensional fluids. It was then modified to compute the structures built in a non-equilibrium situation, which are that of fluids adsorbing within disordered quenched matrix. This finally leads to the successful algorithm for RSA. In this model, fluid particles are added at random onto a surface one at a time. Once it reaches the surface, if it does not overlap with previously adsorbed particles, it will irreversibly adsorbed at that position. If it overlaps, a new insertion attempt is provoked. A new cycle of adsorption continues in this fashion. Our previous work on RSA assumed that particles were spheres of the same size. However, colloidal particles and bioparticles are of various sizes by nature. In this work, we, therefore, study the effect of size polydispersity on the structures of the monolayer films by incorporating the size distribution of spherical particles along with their corresponding interaction potentials to the set of our OZ equations. The distribution could be totally at random in certain diameter range. Together with appropriate closures such as Percus-Yevick approximation, we compute for the radial distribution functions from the integral equations. The results are in good agreements with ones obtained from Monte Carlo simulation.

KEYWORDS
Ornstein-Zernike, sequential adsorption, size polydispersity, hard spheres

INTRODUCTION

For the adsorption of large molecules such as proteins (Feder and Giaever, 1980) and colloids (Onoda and Liniger, 1986) on solid surfaces, the interactions between a molecule and the surface are strong. Multiple bonds may be formed very quickly, so that desorption and surface diffusion become negligible and adsorption may be reasonably considered an irreversible process. This is often modeled by the random sequential adsorption (RSA). In this model, rigid molecules are sequentially added onto a surface at random, with the only condition that they do not overlap with one another. Once successfully inserted, a molecule is frozen in position and can neither move on the surface nor be removed. RSA gives rise to the configurations which are different from their equilibrium counterparts. The kinetics of RSA has been studied extensively and the model has also been modified to add more realistic features. Instead of random arrivals, specific transport mechanisms for the arrival of particles from the bulk to the vicinity of the surface has been considered, including ballistic deposition (Adamczyk et al., 1999) where an external field such as gravity plays a role, and diffusional deposition, where Brownian motion (Luthi et al., 1997) and hydrodynamic interactions (Bafaluy et al., 1993) are incorporated. Studies which consider interactions between adsorbates (Oberholzer et al., 1997) and of adsorbates with free particles near to (but
not adsorbed onto) the surface (Oberholzer et al., 1997), actually revert the RSA model to an equilibrium situation. Some of these studies involve desorption from the surface (Adamczyk et al., 1999), and also surface diffusion (Belardinelli et al., 1993). Among these works, we have proposed a model called sequential quenching (Wang et al., 2000), in which the surface diffusion follows the arrival of particles onto the surface. After a particle gets equilibrated with other previously quenched particles, the particle itself is quenched in place and the new addition begins. For the situations where there is no attractive interaction among particles and strong interaction between particles and the surface, the deposition of particles will grow a monolayer film. Statistical thermodynamics provides methods to obtain such structures. The three dimensional fluid structures have long been investigated by equilibrium liquid theories such as Ornstein-Zernike integral-equation theory. Subsequently, the two dimensional structures of fluid was studied and its application yield structures of monolayer film. Madden and Glandt (1988) and later Given and Stell (1992) developed the application of integral equation theories to systems where at least one of the components is not in equilibrium but quenched in an imposed configuration. The Replica Ornstein-Zernike (ROZ) integral equations (1993) have been applied to the description of fluids adsorbed within quenched disordered matrices. In a sequential quenching process each newly arriving particle samples the space on the surface within the disordered matrix formed by the already quenched ones and is thus a particular case of a quenched-annealed mixture.

In our previous work, we applied the set of integral equations (modified Ornstein-Zernike equations) to a study of the simple sequential quenching of hard particles of the same size, whose resulted structures are equivalent to ones grown through the random sequential adsorption (RSA) (Wang et al., 2000). The equivalence arises from the fact that a newly added, annealed hard particle performs a uniform sampling from the free volume of the sequentially quenched system. Therefore, it becomes irrelevant whether it is or is not allowed to undergo equilibration and the result of the addition is identical to that of a successful insertion in RSA. We also extended our work to study the effect of short-range attractive forces among particles on the final structures of the films (Danwanichakul and Glandt, 2001). Still we assumed size monodispersity in that work. However, particles in nature such as colloidal- and bio-particles are not monodisperse - their sizes vary considerably (Harnarp et al., 2001). Most work on structures of polydisperse systems are for equilibrium situations. The integral-equation theories were proposed to study Yukawa fluids (D’Aguanno and Klein, 1992), colloidal suspensions (Lado, 1996), and fluid mixtures of adhesive colloidal particles (Gazzillo and Giacometti, 2002), by using the continuous Schulz distribution for size polydispersity. Some works explain equilibrium structures of monolayer films (Lado, 1998). Influence of polydispersity on random sequential adsorption has also been investigated by kinetic equations. The structures obtained from simulations are consistent with ones from experiments (Adamczyk et al., 1997). Unlike those works, in this study we aim to apply our integral-equation theory to the random sequential adsorption of polydisperse spherical particles, together with the Percus-Yevick approximation which is often used in the study of fluid structures. The effect of polydispersity is added by simply randomizing the sizes in a specified range. This can be elaborated further by using any continuous distribution such as Gaussian or Schulz distribution in the future work. We also verify the results with Monte Carlo simulations, which has been proved very helpful before.

**THEORY**

**Modified Ornstein-Zernike Integral Equations for RSA**

We treat the sequentially quenched structure as a multi-component system, in the sense that each particle is regarded as a different species, which we label by the total density of the system, $\rho$, at the time it was added. The structure is reported through the value of the radial distribution function $g(r, \rho_1, \rho_2)$. It
is the probability of finding particle 1 at the distance $r$ away from particle 2. Therefore $g(r, \bar{\rho}_1, \bar{\rho}_2) = h(r, \bar{\rho}_1, \bar{\rho}_2) + 1$ is the correlation function between particles quenched at densities $\bar{\rho}_1$ and $\bar{\rho}_2$, respectively and $h(r, \bar{\rho}_1, \bar{\rho}_2)$ is called total correlation function which is the combination of the direct part ($c(r, \bar{\rho}_1, \bar{\rho}_2)$) and indirect part ($b(r, \bar{\rho}_1, \bar{\rho}_2)$). Note also that $g(r, \bar{\rho}_1, \bar{\rho}_2)$ is not a function of the current density $\rho$ because it is fixed once $\bar{\rho}_2$ is reached (for $\bar{\rho}_1 < \bar{\rho}_2$). Integral equations of the OZ type are based on identifying the contributions to the expansion of the total correlation function $h(r, \bar{\rho}_1, \bar{\rho}_2)$ in terms of its cluster integrals. The detail of diagrammatic expansion was thoroughly given in Refs (Morita and Hiroike, 1961, Stell, 1964, Hansen and McDonald, 1986). Madden and Glandt (1988) established that the total correlation functions consist of the sum of all topologically distinct two-rooted Mayer graphs that one-irreducible (i.e. free from articulation points) and also free of shielding sets. The latter are defined as quenched articulation sets whose removal would produce unrooted fragments containing at least one annealed particle. This condition requires that the terms in the correlation functions between quenched particles (i.e. obstacles) be free of any annealed points. In other words, the calculation of the structure of the obstacles becomes a separable problem.

In a sequentially quenched system a newly added particle experiences all previously quenched particles as obstacles. In this case, a shielding set would be any whose removal would produce unrooted fragments containing at least one particle younger (i.e. of higher $\bar{\rho}$) than every particle in the set. An equivalent definition of the allowed diagrams was provided by Given (1992). Since all individual particles are identified by the order of their arrival, identified here by $\bar{\rho}$, the diagrams can be written in terms of “uphill” or directed Mayer bonds, each of them starting at the particle of lower label and ending at the one with the higher label. In this notation, allowed diagrams are all two-rooted, irreducible graphs such that each field point is connected to one of the roots by an uphill path. Given (1992) further observed that the correlation function $h(r; \bar{\rho}_1, \bar{\rho}_2)$ can be expressed as a sum of two parts,

$$h(r; \bar{\rho}_1, \bar{\rho}_2) = \tilde{h}_1(r; \bar{\rho}_1, \bar{\rho}_2) + \tilde{h}_2(r; \bar{\rho}_1, \bar{\rho}_2).$$

The first term in the right-hand side is the sum of diagrams containing an uphill path from one root (the one with the lower $\bar{\rho}$) to the other. Thus, symmetrically, the uphill path may go from root 1 to root 2 (denoted by $\tilde{h}_1$) or vice versa (i.e. $\tilde{h}_2$). All other diagrams are collected into the remaining term. The integral equations for each term are as the following:

$$\tilde{h}_1(r; \bar{\rho}_1, \bar{\rho}_2) = c_1(r; \bar{\rho}_1, \bar{\rho}_2) + \int_{\bar{\rho}_1}^{\bar{\rho}_2} d\bar{\rho}_3 \ c_1(r; \bar{\rho}_1, \bar{\rho}_3) \otimes \tilde{h}_1(r; \bar{\rho}_3, \bar{\rho}_2)$$

$$\tilde{h}_2(r; \bar{\rho}_1, \bar{\rho}_2) = c_2(r; \bar{\rho}_1, \bar{\rho}_2) + \int_{0}^{\bar{\rho}_1} d\bar{\rho}_3 \ c_2(r; \bar{\rho}_1, \bar{\rho}_3) \otimes \tilde{h}_1(r; \bar{\rho}_3, \bar{\rho}_2) + \int_{\bar{\rho}_2}^{\bar{\rho}_1} d\bar{\rho}_3 \ c_2(r; \bar{\rho}_1, \bar{\rho}_3) \otimes \tilde{h}_1(r; \bar{\rho}_3, \bar{\rho}_2)$$

$$+ \int_{0}^{\bar{\rho}_1} d\bar{\rho}_3 \int_{0}^{\bar{\rho}_2} d\bar{\rho}_4 \ \tilde{h}_1(r; \bar{\rho}_1, \bar{\rho}_3) \otimes c_2(r; \bar{\rho}_3, \bar{\rho}_4) \otimes \tilde{h}_1(r; \bar{\rho}_4, \bar{\rho}_2)$$
The overall total correlation function $\overline{h}(r; \rho)$ is obtained by averaging over all possible values of $\rho_1$ and $\rho_2$,

$$\overline{h}(r; \rho) = \frac{2}{\rho^2} \int_0^\rho \int_0^\rho \overline{h}_1(r; \rho_1, \rho_2) + \frac{1}{\rho^2} \int_0^\rho \int_0^\rho \overline{h}_2(r; \rho_1, \rho_2)$$  \hspace{1cm} (4)

The factor of 2 in the first term takes into account the fact that the uphill path may go from root 1 to root 2 (denoted by $\overline{h}_1$) or vice versa (i.e. $\overline{h}_2$).

The sets of integral equations, Eqs. (2) and (3), have to be solved simultaneously with suitable closures. The Percus-Yevick (PY) approximation is a closure frequently used in conjunction with the Ornstein-Zernike equation. We adapted the PY closure of equilibrium situation to be used in this non-equilibrium situation as

$$\overline{h}_1(r) = f(r) + b_1(r) + f(r) \left[ \overline{h}_1(r) + b_2(r) \right]$$ \hspace{1cm} (5)

$$\overline{h}_2(r) = b_2(r).$$ \hspace{1cm} (6)

In Eqs. (5) and (6), the indirect correlation functions ($b$) were defined according to the total correlation function ($h$) which has two parts. The function $f(r)$ is the Mayer function, defined as $\frac{1}{e^{u_{12}/kT} - 1}$, where $u_{12}$ is the potential function, $k$ is the Boltzmann’s constant and $T$ is the temperature.

**NUMERICAL INTEGRATION AND SIMULATION METHOD**

**Numerical Integrations**

For computational purposes it is necessary to approximate the multi-component system by a mixture of discrete species, corresponding to the stepwise addition of finite amounts of material. The correlation functions were discretized in $\rho$-space using $\Delta \rho = 0.005$. By taking the two-dimensional Fourier transform, we obtain algebraic relations among all variables. Several numerical methods can be used in Fourier transformation, including method by Lado (1971).

The potential function used in this calculation is merely hard spheres which can be written as

$$u_{12}(r) = \begin{cases} \infty, & r \leq \frac{\sigma_1 + \sigma_2}{2} \\ 0, & r > \frac{\sigma_1 + \sigma_2}{2} \end{cases}$$ \hspace{1cm} (7)

Here, $\sigma_1$ and $\sigma_2$ are the diameters of two spheres. This means two spheres cannot overlap with each other and there is not any attractive interaction in the system. We apply size polydispersity of spheres in the systems by random selection in the range of $0.75 < \frac{\sigma}{\langle \sigma \rangle} < 1.25$, where $\langle \sigma \rangle$ is the mean diameter of spheres which is unity, so that every particle size has the same probability. The cut-off distance, at which
the correlation functions are expected to decay to unity, is chosen to be $r_{\text{cut}} = 6 \langle \sigma \rangle$. Both in real space and Fourier space, 120 increments are used in the calculations. The values of $h$ and $b$ of previous density (results of previous calculation) will be the input trials for the next density (next calculation) to solve for next $h$ and $b$. The method is simply trial and error and the results are obtained when the input trials and the solved results are in close approximation.

**Monte Carlo Simulations (MC)**

We performed simulations to verify the accuracy of the numerical results from the Ornstein-Zernike equations and to generate typical configurations for analysis. The calculation of the radial distribution function $g(r_i + \Delta r)_{\text{av}}$ is, as customary, based on a histogram for small increments of width $\Delta r$.

The averaged distribution function is then trivially obtained as the ratio between number of pairs $N_i$, collected from $n$ configurations, at the separation ranging from $r_i$ and $r_i + \Delta r$ from the average particle to the corresponding number in a system of ideal-gas or randomly placed particles.

$$ g(r_i + \frac{\Delta r}{2}) = \frac{N_i}{\pi r_i \Delta r \rho N n} \quad (8) $$

where, $N_i$ is the number of particles in the distance increment $r_i + \Delta r$, $N$ is the total number of particle in the system, and $\rho$ is the number density of the system, i.e. number of particle per unit area.

The details of the simulations are as the following. Particles were added one by one onto a $200 \langle \sigma \rangle^2$ surface. If an added particle overlapped with previously quenched particles, it was removed and a new addition is attempted until the insertion was successful. The cycle was repeated until the system reached the required density. We employed periodic boundary conditions, surrounding the primitive cell with a periodic lattice of identical cells, so that a particle interacts with all other particles in this infinite system. Our final results, averaged over 2000 realizations, are presented in the following section.

**RESULTS AND DISCUSSION**

We studied the random sequential adsorption of hard spheres of various sizes onto a square surface. The dimensionless number density of the adsorbed particles on the surface is defined as $\rho^* = \rho \langle \sigma \rangle^2$. Figure 1 shows the results at a reduced density $\rho^* = 0.4$ together with simulation results. There is rather good agreement between them, the discrepancies being attributable to the PY approximation. The discrepancies are more clearly seen in Figure 2 which shows the results for the system of reduced density of 0.5, since the PY approximation neglects some cluster integrals which are more
significant at higher densities. In both figures, there is only one obvious peak whose height is not much higher than unity showing that particles are not much correlated, resulting in disordered structures. Unlike the vertical straight line in the case of monodisperse spherical systems, the size polydispersity can be seen through the inclined line rising from the base at about $r / \langle \sigma \rangle = 0.75$, the possible smallest size, to the first peak at about $r / \langle \sigma \rangle = 1.25$, the possible largest size.

Figure 2. Results from theory (line) compared with ones from simulations (circles) for the reduced density of 0.5.

Figure 3 compares the pair correlation functions for various densities, ranging from 0.1 to 0.5 calculated from numerical integration of integral equations. The peak is higher and the curve reaches unity more slowly for higher density. This is because the entropic effects lead to more correlated structures, in spite of no attractive interactions. To predict correct correlations at high densities we need the much better closures. However, it is of interest to report the simulation results at those densities ranging from 0.5 to 0.8 in Figure 4. Even at the highest density here ($\rho^* = 0.8$), the structure shows only short-range correlation - the forming of the second peak at this density can be observed.

Particles could be adsorbed onto the surface until there is no hole with available area to accommodate one more particle. Such jamming situation is common among all irreversible adsorptions. The studies on RSA have investigated the kinetics of jamming and many researchers have reported the jamming limits of monodisperse systems for both with attractions and no attractions. The work on jamming limits is not in the scope of this study even though we noticed that for this degree of polydispersity, the systems may reach jamming around the reduced density of 0.92. The more correct value has to be derived from the corresponding kinetic law.
The pair correlation function is known to diverge logarithmically at contact in jamming limit. The theoretical results, nevertheless, do not show this behavior at the saturation density (Danwanichakul and Glandt, 2001). This finding is not surprising given that the PY approximation neglects the elementary diagrams required for the description of the close packing of annealed particles and, presumably, also of the jamming of quenched particles. Besides, the simulations may not show the divergence at contact either if the simulated system is not big enough so the size effect is non-negligible.

The onset of jamming may be seen in Figure 5, where two configurations of polydisperse systems are displayed. The left and right pictures are at reduced density of 0.4 and 0.8, respectively. Particles with various sizes are adsorbed at random sites on the surface. The adsorption of particles will become harder at higher density where fewer holes are available. However, size polydispersity should result in higher jamming surface coverage than in monodisperse case because particles with small sizes can fit in small holes. As can be seen, the final structures of the monolayer films grown through the random sequential addition are disordered, unlike equilibrium systems where particles can move so the structures can be adjusted at later times leading to more compact and ordered structures.

CONCLUSIONS

Our modified Ornstein-Zernike equations have been applied to the random sequential adsorption of spherical particles with various sizes in a specified range. The theory treats each adsorbed particles as a different component so the overall interaction comes from approximate pair-interactions among all pairs of particles. This treatment is absolutely suitable for the situation of size polydispersity. In this study, the size of each particle was chosen at random. We have shown that the theory can be successfully applied to this condition. However, more appropriate closures are needed to obtain better results at high densities where PY-approximation fails. Even so, the theory is beneficial in many applications in colloidal particle depositions. For example, we can study the sequential adsorption of polydisperse particles with different types of interactions such as electrostatic interactions from charge polydispersity. The detail of particle size distribution, such as continuous Schulz distribution, can be incorporated into the theory with little effort. In addition, with the knowledge of kinetics of the deposition, we will understand the jamming situation more clearly. The combination between statistical mechanical background as in this study and the kinetic laws could lead to valuable tools in the study of thin film formations.

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REFERENCES


Adamczyk, Z., B. Siwek, M. Zembala, and P. Weronski; "Influence of polydispersity on random sequential adsorption of spherical particles," J. Colloid and Interface Sci. 185, 236-244 (1997)


Stell, G., in "The Equilibrium Theory of Classical Fluids" (W. A. Benjamin, New York, 1964)