Dynamics for dense packing of colloids*

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Abstract

Colloidal packing by evaporation is a process that particles are packed by Stokes' forces. As particles are far from each other, interactions among them are too weak to be taken into account and it's the Stokes' force on free particles that is in charge of packing. However, when they are close to some extent, the force is countered by particle interactions. Here, with the aid of force balance model, we demonstrate that the further packing is achieved by all drag forces of particles in the upstream.

Introduction

Particles at micro/nano-meter scales can be packed into bulk materials of interests from sciences to applications [1-2], such as, photonics, electronics, sensors, energy storage, catalysis, and coatings. Packing colloidal particles by evaporation is a ubiquitous way to make such materials [3-7]. Obviously, properties of such a material are directly related to its micro-structure, which is decided by the packing history, particularly in the sol-gel transition regime where close particles are being packed to the final structure. The packing drive should be the viscous drag of fluid flow on particles. In the beginning, particles are far away from each other in liquid such that there is no any action between them and they can be regarded as free ones. When particles are close to some extents, their Brownian motions could lead to frequent collision of particles, and the denser they are, the higher the frequency, and the stronger the collusive strength. This collision makes them tend to move back to the dilute regime, leading to a backward diffusion of particles in the sol-gel transition regime. At the moment, the viscous drag has to counter the trend of diffusion while it is packing particles closer. To undertake both tasks, the drag has to rise but the rise is limited. Here, we demonstrate numerically that packing a dense structure of particles is not achieved by Stokes force on one particle, and a particle is pushed towards a dense structure before it with the aid of drags of other particles in the upstream.

Numerical Method

Molecular dynamics is the most straight to solve packing particles, where the mechanical balance on each particle is solved on the basis of the Newton law. The results are tempo-spatial positions of particles and corresponding velocities during the course of calculation. But it is slow and costly for dense packing. The convective-diffusion model is usually used to simulate the packing process of colloids where the diffusion coefficient is a fitted parameter of experiments of colloidal packing,

under conditions of particle sizes, volume fractions, and inter-particle actions. In other words, all of these effects on packing, whether known well or not, have been contained in the coefficients. Here we want to see an individual effect explicitly, so the balance model is proper. In the mode, the convection and diffusion are considered in terms of forces on particles, such as Stokes' force and osmotic force. In essence, it is another form of the convective diffusion model. To study the extra drive for packing, we choose the simplest case, that is, the unidirectional drying of colloids. Because the structure is random, we assume that packed particles in the case can be represented by a line of particles. Because the drying is slow, the packing is assumed to be quasi-equilibrium. Under these conditions, the balance of forces on a particle should be

$$F_s + F_{\phi,1} + F_{DLVO,1} = F_{\phi,2} + F_{DLVO,2} \ . \tag{1}$$

Where F_s is the Stokes' force, $F_{\phi,1}, F_{\phi,2}$ are forward and backward osmotic forces, and forward

and backward DLVO actions are $F_{DLVO,1}, F_{DLVO,2}$.

The osmotic forces DLVO actions in the equation will be changed once a new particle is appended to the line and accordingly, their spacing distances change, reflecting the variation in volume fraction of particles. These forces are defined in the following.

Stokes' force. For a free particle, the Stokes' force can be estimated as $F_{PD} = 6\pi\mu a \cdot u$, where μ

is the solvent viscosity and u is the fluid velocity relative to the particle. When particles are close, the net area for fluid flow is decreased, raising the viscous drag. On average, the drag is estimated with the Darcy law for the porous medium. For the case of one dimension (1D), the pressure drop over a length L is $\Delta P = u \dfrac{\mu}{k} L$. Here, u is the volumetric flow rate per sectional area, and μ the

viscosity of water. $k = \dfrac{2a^2}{9} \dfrac{(1-\phi)^3}{\phi^2}$ is the permeability dependent of ϕ that is the volume fraction

of particles. Thus, the drag for a particle can be estimated as

$$F_{PD} = -\frac{\Delta P}{L} \cdot (2a) \cdot \pi a^2 = -u\frac{\mu}{k} \cdot 2\pi a^3 \ . \tag{2}$$

where a is the radius of particles, h is the distance between particles on average.

Osmotic force. In mechanical terms, the diffusion of particles can be solved by osmotic force. For non-interacting particles, the osmotic force on a particle has been proposed as $F = \nabla e'$ (Russel and Routh 1998), e' is a change in energy as one particle replaces water molecules in the space, and its gradient is

$$\nabla e^{'} = k_B T \frac{1}{\phi} \frac{d(\phi Z(\phi))}{d\phi} \nabla \phi \ . \tag{3}$$

where $Z(\phi)$ is the compressibility factor,

$$Z(\phi) = \frac{1 + a_1\phi + a_2\phi^2 + a_3\phi^3 + a_4\phi^4}{1 - \phi/\phi_p} \tag{4}$$

$a_1 = 4 - 1/\phi_p$, $a_2 = 10 - 4/\phi_p$, $a_3 = 18 - 10/\phi_p$, $a_4 = \alpha/\phi_p^5 - 18/\phi_p$, $\alpha \approx 1.5, \phi_p = 0.64$.

So, the motion of a particle in close packing regime is decided by the balance between the Stokes' force and the osmotic force. For charged particles, a third action has to be considered, which involves the electrostatic interaction and is called as DLVO action (Derjaguin, Landau, Verwey, and Overbeek action).

DLVO action. In a suspension, its charged particles are actually sustained by the force as described below

$$F(h) = \frac{64 n_0 \pi a \Gamma^2 k_B T}{\kappa} e^{-\kappa h} - \frac{aA}{12h^2} \tag{5}$$

where a is the radius of particle and h is the average separation between two particle surfaces, $A = 1.3 \times 10^{-20} J$, is the Hamacker constant; n_0 is the number of salt molecules per cubic meters and κ^{-1} is the Debye screen length. Γ is defined as $\Gamma = \tanh(e\zeta/4k_B T)$, where $\zeta \approx -50\text{mV}$ is the potential near the particle surface .

Micro-structure. In these forces, the volume fraction ϕ is a key parameter, which depends on the micro-structure. In order to relate ϕ to the particle separation, we assume that it is a regular tetrahedron before paerticles are fully packed, as shown in Figure 1. In this simple structure, the volume fraction can be determined as $\phi = 4V/V_t$ in a tetrahedron cell of volume V_t, $V_t = \sqrt{2}/12(h+2a)^3$, and V is the volume of a particle intercepted by the cell as calculated as $V = 0.0439(3\pi a^3/4)$. So, the local volume fraction can be evaluated once we know the average distance of local particles.
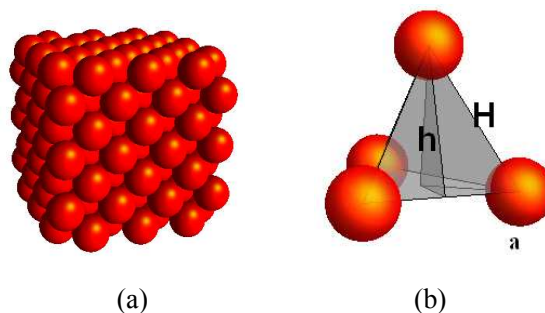

(a)   (b)

Figure 1 The assumed particle structure

(a)regular matrix of particles, (b) one unit

As stated above, a unidirectional packing case is represented by a chain of nodes. To determine the local volume fraction, regular tetrahedrons are added to each node. As indicated in Figure 2(a,b), two tetrahedrons share one colored node while between tow nodes, two tetrahedrons share one bottom. The calculation is conducted on the colored particles as shown in Figure 2(c). During calculation, the first particle is fixed at the evaporating end while the other ones are being packed

towards it along the line driven by their Stokes' forces. That is, the calculation starts with the last node at rear end when a new particle is added. The same procedure proceeds until the volume fraction at the evaporating end is about 0.74. When being added to the end, the new particle is first located at the initial separation to the last particle. The initial distance of two particles results from the initial volume fraction of colloids before evaporation.
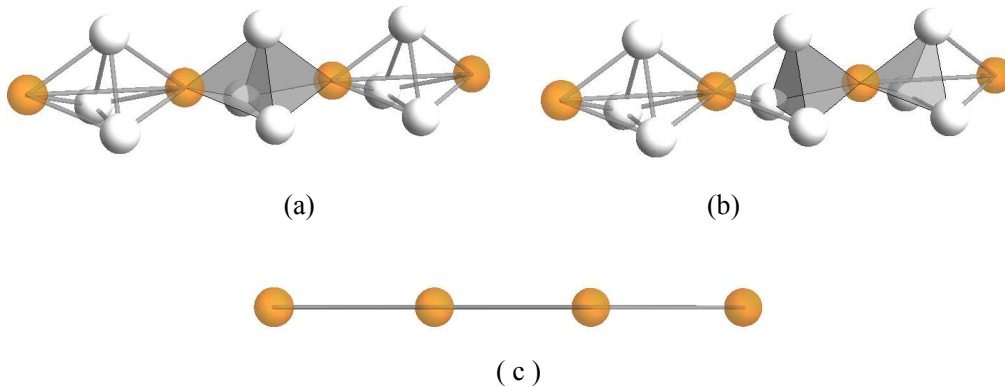
(a)   (b)

(c)

Figure 2   The simplified macro-structure based on micro-structure of particles
(a) structures between two nodes, (b) structures besides a node, (c)nodes for calculation.

  This assumed structure actually cannot fill the space completely, but the hexagonal structure does. Our assumption here is simply for the convenience of calculation and the results are modified to account for the difference. The approximation does not affect out conclusion.

Results and Discussion

  The values of the Stokes' force and The DLVO force. The modified Stokes' force is larger than the Stokes' force on a free particle, so it can pack particles closer than the latter. As shown in Figure 3(a) where the modified Stokes' force is plotted against particle separation, when particles are close to some distance, the Stokes force reaches it maximum and it is impossible for the force to pack particles to 0.64. For charged particles, the DLVO actions will let the balance occur at a larger distance, as seen in Figure.3(c). But in reality, the particles are indeed packed to 0.64. As shown below, the extra drive comes from the the accumulation of Stokes forces of particles in the upstream.
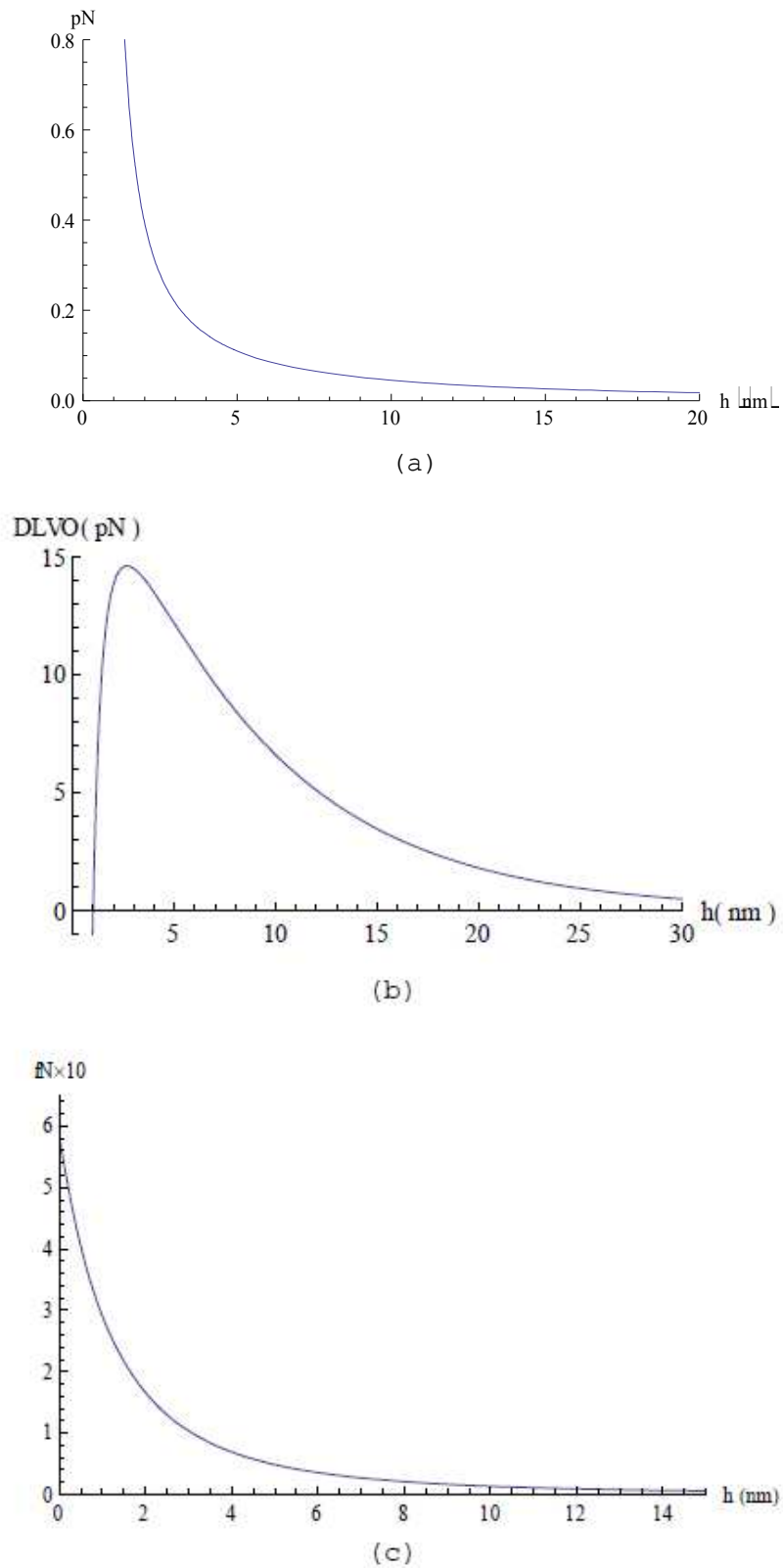
(a)

(b)

(c)

Figure 3 Forces on particles.

(a) Stokes force, (b) DLVO force, (c) Osmotic force. In the three plots, the horizontal axis is the distance of two particles

The packing process. We start our calculation from the initial separation of two particles with regard to the initial volume fraction of particles 0.4, and we obtain the distribution of volume fraction in the transition when the volume fraction at the free surface is at 0.74. In calculation, the

fluid flow is at 1 um/s For particles of 30nm in radius, the distribution in volume fraction is plotted against packing length in Figure.4. We can see that the 3000th particle is just added to the line when the calculation stops. The transition size is about 3000 nm long. The curvilinear demonstrates that the interaction among particles is increasing with the reduction in particles distance. The extra force to achieve this packing can only come from the Stokes force in the up stream. The curve is similar to the diffusion curve, so it is why the packing is usually treated as a diffusion process.
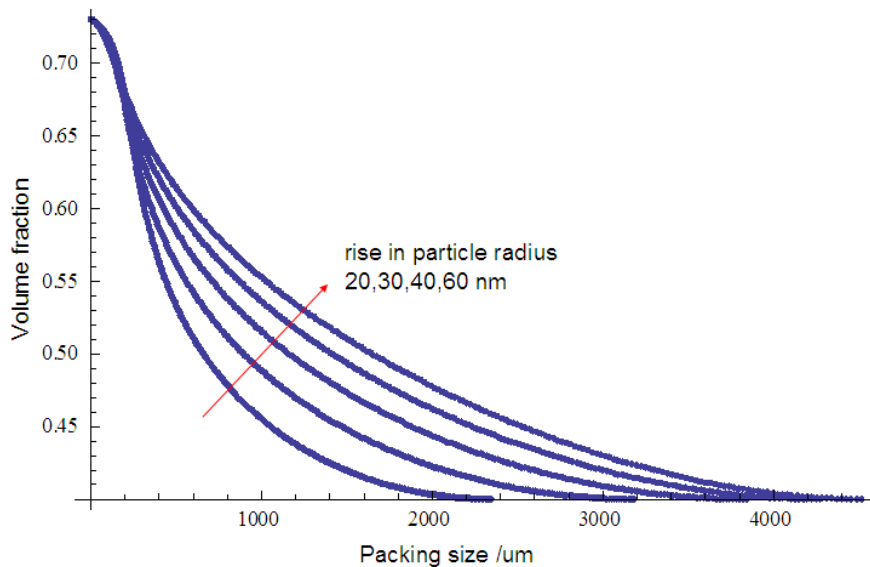
(b)

Figure.4 The calculated packing process

The particles of 20,30,40,60 nm in radius

The process will give different responses to particle sizes. As seen in Figure.4, with increasing size of particles, the transition size is reduced, meaning that the DLVO action is more sensitive to size than the Stokes force.

Recently, it was found that in the case of gravitational or centrifugal sediment of dilute charged particles, an electrical field would be set up as the small counter ions in the solvent were diffusing against the sediment. The induced electrical field in turn would lift the packed charged particles to some degrees. This finding was also extended into the case of evaporation-driven packing of charged particles. Here, we show by numerical calculation that it is impossible for the internal electrical field to be set up by ions, because the $Pe > 1$ during drying.

Conclusion

Numerically, we prove that evaporation-driven packing from loose to dense is achieved by accumulating the Stokes forces on particles in the upstream, other than proposed hydrodynamic interaction among packed particles. The transition from loose to dense structure depends on the particles size significantly.

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