Dependence of Collision Frequency on Distance between Two Hard-sphere Particles Estimated by Computer Simulation[*]

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Abstract   A Monte Carlo simulation is performed to study the dependence of collision frequency on interparticle distance for a system composed of two hard-sphere particles. The simulation quantitatively shows that the collision frequency drops down sharply as the distance between two particles increases. This characteristic provides a useful evidence for the collision-reaction dynamics of aggregation process for the two-particle system described in Ref. [1].

Keywords: Collision frequency,   Simulation,   Colloid

Colloidal stability and aggregation are controlled by collisions and interactions of particles that constitute the colloidal system. We proposed a novel approach [1-2] to the investigation of colloidal aggregation in experiments performed at microscopic particle levels. In this approach optical tweezers [3-6] are used to bring two particles into the region near the focusing plane of the microscope so we can watch what happens to them. Since the two particles are confined in a small volume, they have a high probability for collisions. We can perform a series of tests at a microscopic level to study the collision-reaction dynamics for this system of two particles. For each test, we observe the collisions of two particles and the outcome of the collisions (namely, adhere or separate after the collisions). We call this procedure artificially induced collision. This procedure makes it possible to statistically evaluate the sticking probability by testing many particle pairs. The sticking probabilities (p) are estimated by dividing the number (n) of collisions leading to permanent doublets by the total number (n_c) of particle collisions [7-11] (namely, $p = n/n_c$). In our experiment, the collisions were induced in the following procedure. First we used optical tweezers to catch one particle and then the second. After holding this pair of particles together in the optical trap for certain duration for their collisions, we released them from the trap and traced them to check if they remained together or separated. A special physical model of the collision-reaction dynamics for two particles held in the optical trap is suggested in Ref. [1].

According to this model a particle pair in the trap would experience two different status. The first one is called "compact status"; that is, at the beginning when the second particle is pulled into the trap, the head-on impact makes the particle pair stay closer. The second is called the "relaxed status" in which after the impact speed dampens down, the particle pair become relaxed and stay in an extended room. It is assumed that when two particles in the compact status, they would have a much higher collision frequency than that in the relaxed status. However, this is only a reasonable presumption, has not been verified yet. For a two-particle system how rapidly their collision frequency changes as their separation varies is an important issue to better understand the collision-reaction dynamics for this system. Commonly used methods to estimate the collision frequency are appropriate for a colloidal system having huge number of monodispersed particles according to the following equation:

$$\mathrm{d}n/\mathrm{d}t = -4\pi(2a)Dn^2 \qquad (1)$$

where n is the particle concentration, D is the relative diffusion coefficient, and a is particle radius in consideration. This equation corresponds to a bimolecular chemical reaction, if every collision makes two particles disappear. But this equation is not directly applicable to the two-particle system we described above. In this study we present a Monte Carlo simulation to quantitatively estimate how the collision frequencies are related to separations between particles for a two hard-sphere particle system.

1   Simulation

In the simulation for colloidal suspensions we adopted the hard sphere model in which the interaction of the particles has the functional form:

$$V_{ij} = \begin{cases} 0 & (r_{ij} > a) \\ \infty & (r_{ij} \leq a) \end{cases} \qquad (2)$$

where V_{ij} is the potential between particle i and j; r_{ij} is the distance between particle i and j. Hard spheres are quite simple for the definition for collision of two particles in the simulation and yet represent a good approximation for monodispersed spheres with repulsions of range short relative to the radius and negligible van der Waals attraction. The hard sphere model has been used to study packing in colloidal systems [12].

In the Monte Carlo simulation [13] the center of one particle is fixed at the origin as shown in Fig. 1 and the second particle is assigned to undergo a random walk with a spherical Gaussian distribution, and its mean-square displacement (Δ^2) is $6D\tau$, where τ is the time step. According to the Stokes-Einstein equation, the diffusion coefficient for an isolated sphere is

$$D = k_B T / 6\pi \eta a \qquad (3)$$

where a is the radius of a particle, k_B is the Boltzmman constant, T is temperature and η is the viscosity of the liquid. Actually, it can be seen from the basic algorithm described above that our simulation is a special case of the so-called Brownian dynamics simulation [14-15].

To match the experimental situation in Ref. [1], in our simulation $a = 0.497 \ \mu m$. The initial distance between two particles is d_1 (that is, the center-to-center distance between two particles is $2a + d_1$). During the simulation, all positions of the second particles are measured at each time step (or increment). When-
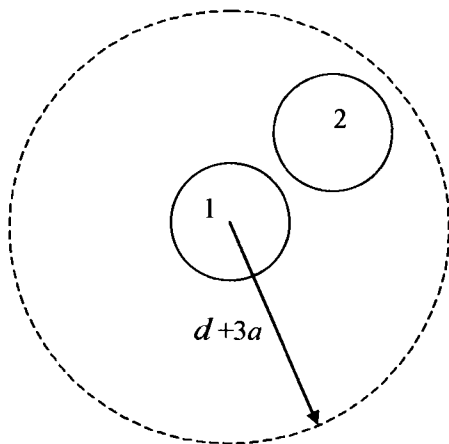

Fig. 1   The simulation model of the two hard spheres in an optical trap

The location of sphere 1 is fixed, and the sphere 2 is assigned to undergo a random walk within a spherical volume having a radius of ($d + 3a$)
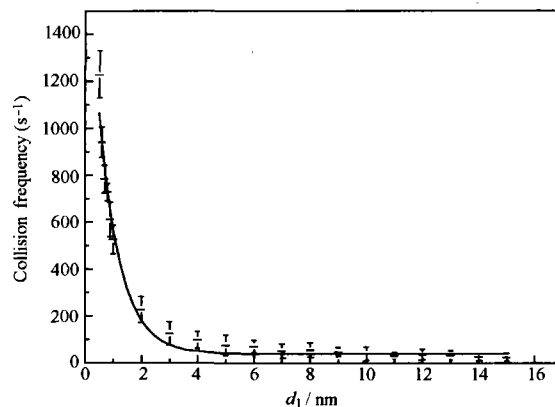

Fig. 2   The simulation result of collision frequency versus the separation between two particles

ever the distance between two particles (from their centers) is less or equal to $2a$, they are considered to collide and then the second particle will be move back to the starting point to do the diffusion motion over again. And also, whenever the distance between two particles is greater than d, the particle 2 bounces back(namely, d is the maximum allowed distance between two particles). So the particle 2 is confined within a spherical volume having a radius of ($d + 3a$). In the simulation, the time step is taken to be 5×10^{-10} s and for each calculation the particle moves 4×10^8 steps. In the simulation we took d to be 15 nm. For each initial distance d_1, 15 independent calculations are carried out and the collision frequency for each distance is averaged over the 15 calculations.

Fig. 2 shows how the collision frequency is related to the separation between two particles. We can see that when two particles are close, the collision frequency is very high and then dramatically drops down as the distance between two particles increases.

2   Conclusion

The changing tendency obtained from our computer simulation proves that the collision frequency drops down dramatically when the system described above is transferred from the compact status to the relaxed one. Therefore our simulation not only offers a quantitative relation of the collision frequency to particles' separation but also provides a direct evidence to support the collision-reaction dynamics of the system in consideration of Ref. [1].

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刚球粒子碰撞频率和距离关系的计算机模拟 *

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摘要   用 Monte Carlo 方法模拟了由两个刚球粒子组成的体系, 得到了碰撞频率和粒子间距的定量关系. 模拟结果显示, 碰撞频率随着粒子间距的增大急剧下降. 这一特性为文献[1]中描述的两个粒子体系的聚集过程的碰撞反应动力学提供了有用的旁证.

关键词: 碰撞频率,   模拟,   胶体
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