# Computer simulation on the collision-sticking dynamics of two colloidal particles in an optical trap 

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#### Abstract

Collisions of a particle pair induced by optical tweezers have been employed to study colloidal stability. In order to deepen insights regarding the collision-sticking dynamics of a particle pair in the optical trap that were observed in experimental approaches at the particle level, the authors carry out a Brownian dynamics simulation. In the simulation, various contributing factors, including the Derjaguin-Landau-Verwey-Overbeek interaction of particles, hydrodynamic interactions, optical trapping forces on the two particles, and the Brownian motion, were all taken into account. The simulation reproduces the tendencies of the accumulated sticking probability during the trapping duration for the trapped particle pair described in our previous study and provides an explanation for why the two entangled particles in the trap experience two different statuses. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712183]


## I. INTRODUCTION

A microscopic approach to evaluate the colloidal stability by means of artificially induced particle collisions with the aid of optical tweezers has been developed. ${ }^{1,2}$ In such a method, after two particles are trapped by optical tweezers for a short time (the trapping duration), they are released to monitor whether they will stick together or separate. Then, all the trapped pairs $n$ and the aggregated pairs $n_{c}$ are counted to obtain the statistically averaged "accumulated sticking probability" $P\left(=n_{c} / n\right)$ during the trapping duration $\tau$. The key problem is how to achieve the commonly referred "sticking probability" or "collision efficiency" $p,{ }^{3,4}$ namely, the probability that a collision of two particles leads to permanent doublets, through the accumulated sticking probability $P(\tau)$. To make the conversion from $P(\tau)$ to $p$ possible, a physical model has been proposed based on the experimental observation of a particle pair trapped for a short time. ${ }^{1,2,5}$

Experiments show an exponential increase of the accumulated sticking probability $P$ with $\tau$ following a rapid initial increase. The explanation for this special behavior as described in Refs. 1 and 5 is that the two particles in optical tweezers experience two different statuses: the "compact status" at the beginning and the subsequent "relaxed status." In the compact status, the collision frequency of the two particles is much larger than that in the relaxed status. The sticking probabilities $p$ obtained by treating the experimental data of $P$ according to the above physical model are consistent with those from the turbidity measurements.

However, it is difficult to disclose further information about the real motion and interaction of the trapped particle pair by direct observation, especially because the two particles are lined up in the $z$ direction (the direction of the laser beam) after being trapped by the optical tweezers. That is, from the observer's line of sight, one particle is hidden be-

[^0]hind the other and therefore becomes difficult to view. In this case, computer simulation provides a possible alternative to help understand the associated physical picture behind the model of the two statuses. In order to do so, a complete Brownian dynamics simulation considering both laser produced potential and interactions between particles [including Derjaguin-Landau-Verwey-Overbeck (DLVO) interactions and hydrodynamic interactions] is desirable.

The Brownian dynamics simulation of hydrodynamically interacting particles has been discussed by Ermak and McCammon. ${ }^{6}$ Therefore, the major difficulty in carrying out the simulation is how to express the force of the optical field exerted on two particles during the trapping process. This is schematically shown in Fig. 1, where $z$ is the beam propagation direction. Figures 1(a) and 1(b) show the relative positions of particles 1 and 2, respectively, before and after particle 2 is captured by optical tweezers. From Fig. 1(b) we can see that when two particles are simultaneously held by the optical tweezers, the laser beam reaches the upper particle after passing through the lower one due to the two particles lining up along the beam direction. Therefore, the trapping potential should be very different from the case of a single


FIG. 1. Schematic side view of the trapping process of two particles. $z$ is the propagation direction of the laser beam. (a) The second particle is not trapped yet. (b) Both particles are trapped by optical tweezers.
particle system. This problem becomes even more challenging due to the uncertainty of positions of two particles undergoing the Brownian motion, especially during the transition from the state shown in Fig. 1(a) to the one in Fig. 1(b), because the position of each particle will affect the trapping forces exerted on the other particle as well as on itself.

In this study, an interaction mode is proposed by taking all of the above considerations into account and a Brownian dynamics simulation is carried out based on the interaction mode. The corresponding simulation has reproduced the relevant feature of the $P \sim \tau$ curve found in the previous experiments. ${ }^{1}$ The simulation demonstrates that the assumption of the two statuses proposed in Refs. 1 and 5 is likely to be associated with the different interaction modes during the transition from (a) and (b) in Fig. 1.

## II. BROWNIAN DYNAMICS SIMULATION OF HYDRODYNAMICALLY INTERACTING PARTICLES

Physically, the solvent flow induced by one particle must have an effect through frictional forces on others, which is the reason for the hydrodynamic interactions between particles. This effect will retard the diffusion of particles when particles are closer together and should be considered in the Brownian dynamics simulation. The Langevin equation for the system of $N$ Brownian particles with hydrodynamic interactions is

$$
\begin{equation*}
m_{i} \dot{v}_{i}=-\sum_{j} \zeta_{i j} v_{j}+F_{i}+\sum_{j} \alpha_{i j} f_{j}, \tag{1}
\end{equation*}
$$

where $i$ and $j$ represent components $(1<=i, j<=3 N)$, and $v$ and $m$ represent the velocity and mass of particles, respectively. $F$ is a systematic force due to the interaction potential energy between particles plus any external force. $\Sigma_{j} \alpha_{i j} f_{j}$ represents the randomly fluctuating force exerted on a particle by the surrounding fluid resulting from random collisions of solvent molecules with the particle. $-\sum_{j} \zeta_{i j} v_{j}$ represents the friction force due to systematic collisions with the solvent molecules as the particle moves, which tends to decrease the particle velocity. The coefficients $\zeta_{i j}$ are the hydrodynamic friction tensor. The $f_{j}$ have Gaussian distribution with the mean and covariance

$$
\left\langle f_{i}\right\rangle=0,
$$

$$
\begin{equation*}
\left\langle f_{i}(t) f_{j}(t)\right\rangle=2 \delta_{i j} \delta\left(t-t^{\prime}\right) \tag{2}
\end{equation*}
$$

The coefficients $\alpha_{i j}$ are related to the hydrodynamic friction tensor by

$$
\begin{equation*}
\zeta_{i j}=\frac{1}{k_{B} T} \sum_{l} \alpha_{i l} \alpha_{j l} \tag{3}
\end{equation*}
$$

where $k_{B}$ is the Boltzmann constant and $T$ is the temperature.
Ermak and McCammon and Elimetech et al. have given the equations for Brownian dynamics simulation of the positions of particles from the Langevin equation (1) as ${ }^{6,7}$

$$
\begin{equation*}
r_{i}=r_{i}^{0}+\sum_{j} \frac{\partial D_{i j}^{0}}{\partial r_{j}} \Delta t+\sum_{j} \frac{D_{i j}^{0} F_{j}^{0}}{k_{B} T} \Delta t+R_{i}(\Delta t) \tag{4}
\end{equation*}
$$

where the superscript " 0 " indicates that the relevant variable takes its value before each subsequent update of the simulation. The displacement $R_{i}(\Delta t)$ is a random displacement with a Gaussian distribution function whose average value is zero and variance-covariance is $\left\langle R_{i}(\Delta t) R_{j}(\Delta t)\right\rangle=2 D_{i j}^{0} \Delta t$. Here $D_{i j}$ is the diffusion tensor related to $\zeta_{i j}$ by

$$
\begin{equation*}
\sum_{j} \zeta_{i j} D_{j l}=\sum_{j} D_{i j} \zeta_{j l}=k_{B} T \delta_{i l} \tag{5}
\end{equation*}
$$

When the hydrodynamic interactions are ignored, the diffusion tensor $D_{i j}$ is a constant matrix; otherwise, it will be a configuration-dependent matrix. In this paper, we use the Rotne-Prager diffusion tensor given by

$$
\begin{align*}
D_{i j}= & \frac{k_{B} T}{6 \pi \eta R} \delta_{i j} \quad i, j \text { on the same particle } \\
D_{i j}= & \frac{k_{B} T}{8 \pi \eta r_{i j}}\left[\left(\mathbf{I}+\frac{\mathbf{r}_{i j} \mathbf{r}_{i j}}{r_{i j}^{2}}\right)+\frac{2 R^{2}}{r_{i j}^{2}}\left(\frac{1}{3} \mathbf{I}\right.\right. \\
& \left.\left.-\frac{\mathbf{r}_{i j} \mathbf{r}_{i j}}{r_{i j}^{2}}\right)\right] \quad i, j \text { on different particles. } \tag{6}
\end{align*}
$$

Here $\eta$ is the solvent viscosity, $R$ is the sphere radius, $\delta_{i j}$ is the Kronecker delta, $\mathbf{r}_{i j}$ is the vector from the center of sphere $i$ to the center of sphere $j$, and $\mathbf{I}$ is the unit tensor. As the Rotne-Prager diffusion tensor has the property

$$
\begin{equation*}
\sum_{j} \frac{\partial D_{i j}}{\partial r_{j}} \equiv 0 \tag{7}
\end{equation*}
$$

this term can be dropped from Eq. (4). The simulation equation becomes

$$
\begin{equation*}
r_{l}=r_{i}^{0}+\sum_{j} \frac{D_{i j}^{0} F_{j}^{0}}{k_{B} T} \Delta t+R_{i}(\Delta t) \tag{8}
\end{equation*}
$$

The time step $\Delta t$ is taken to be $10^{-6} \mathrm{~s}$ in this study.
In general, the Brownian dynamics simulation is time consuming if the particle number $N$ is large. This is due to the calculation of the Brownian displacement $R_{i}(\Delta t)$ from the large variance-convariance matrix $\left\langle R_{i}(\Delta t) R_{j}(\Delta t)\right\rangle=2 D_{i j}^{0} \Delta t$. In this paper, however, since only two particles are involved, the determination of $R_{i}(\Delta t)$ becomes much simpler.

## III. EXTERNAL FORCES ON PARTICLES

## A. DLVO interaction

For two particles caught by optical tweezers, the $F$ in Eq. (8) includes two parts the interaction force of the two particles and the forces exerted by the optical tweezers. In the simulation, the DLVO potential ${ }^{7-9}$ is used to express interactions between two trapped particles. In the DLVO theory, the attraction potential between two particles of the same radius due to the van der Waals attraction can be approximately expressed as ${ }^{9}$

$$
\begin{equation*}
U_{A}=-\frac{A R}{12 H}=-\frac{A^{\prime}}{H}, \tag{9}
\end{equation*}
$$

where $A^{\prime}=-A R / 12, A$ is the Hamaker constant, $R$ is the particle radius, and $H$ is the distance between the surfaces of the two particles. The repulsive potential due to the electrical double layer is usually expressed by the following equation: ${ }^{9}$

$$
\begin{equation*}
U_{R}=B \exp (-\kappa H) \tag{10}
\end{equation*}
$$

where $\kappa$ is the Debye-Hückel parameter, which is related to the ion concentration and the electrovalence of ions. $B$ is a parameter related to surface potential, $\kappa$, and the ion concentration. Given the parameters $A, B$, and $\kappa$, the interaction potential and the interaction force between particles can be determined.

## B. The force exerted by optical tweezers

For a single particle trapped by optical tweezers, the trapping force, that is, the force that the optical tweezers exert on the particle, has been extensively investigated. It is known that the trapping force near the trapping position approximates a spring force. ${ }^{10}$ This approximation should work reasonably well until the trapping force reaches its maximum. When the particle is further away from the position of the maximum trapping force, the trapping force will begin to decrease and finally vanish. A parameter named "tweezers stiffness" is usually used to identify the spring force near the trapping position. With a good approximation, the stiffness is isotropic along the transverse directions (namely, to be perpendicular to the $z$ direction, which is the longitudinal direction along the beam propagation of optical tweezers), but not along the $z$ direction. ${ }^{10,11}$

However, for two particles trapped by optical tweezers, the trapping forces are much more complicated than that for one trapped particle. For single particle trapping, the trapping force depends only on the position of the particle. For trapping two particles, the position change of one particle will result in a relevant change in the incident optical field on the other particle. Therefore, the position of each particle not only affects the force exerted on the particle itself but also affects the force on the other particle. Xu et al. ${ }^{12}$ have calculated the axial trapping forces for two particles based on ray optics approximation. However, the calculation used in the ray optics model is not suitable for the particles discussed in this study. Furthermore, their discussion only considered the particles moving along the $z$ axis with no transverse displacement.

Considering that two entangled particles trapped by an optical tweezers can appear to influence one another simultaneously, we divide the force on each particle into two components. The first component is just like the trapping forces for a single trapped particle, so the forces can be considered a spring force near the trapping position. The other component is connected with the relative position of the two particles by considering that the position of each particle will influence the forces exerted on the other.

Before the discussion of the trapping forces, the coordinates should first be established. At the beginning of the simulation, the first particle is assumed to be at its equilib-


FIG. 2. Different types of DLVO interactions used in the simulation. (a) $A^{\prime}=2 \times 10^{-30} \mathrm{~J} \mathrm{~m}, B=4 \times 10^{-20} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$. (b) $A^{\prime}=1 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B$ $=4 \times 10^{-20} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$. (c) $A^{\prime}=5 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B=1 \times 10^{-19} \mathrm{~J}, \kappa=5$ $\times 10^{7} \mathrm{~m}^{-1}$.
rium trapping position, as shown in Fig. 1(a). We set this position to be the coordinate origin in the following discussion. The $x$ and $z$ directions are shown in Fig. 1.

For the convenience of further discussion, some symbols will be used to represent different quantities. In this paper, the same symbol will always stand for the same quantity and the subscript will identify which particle is being referred to. For example, $x, y, z$ are used to denote the instantaneous position of each particle, while $x_{i}, y_{i}, z_{i}$ are used to denote the instantaneous position of particle $i$.

To determine the first component of the trapping force that is considered a spring force near the trapping position, we need to determine the particles' trapping positions where this component of the optical trapping force on each particle is equal to zero. Since the laser beam will be partially refracted by the lower particle before it meets the upper particle, the lower particle will act somewhat as a convex lens. This "convex lens," in turn, converges the beam and causes significant change in the optical field, making the $z$ coordinate of the trapping position of the upper particle larger than 0 (i.e., the original trapping position). On the other hand, the reflected beam from the upper particle will also influence the optical field acting on the lower one, which may make the $z$ coordinate of the trapping position of the lower particle smaller than 0 .

The transverse distance $R_{x y}=\sqrt{\left(x_{1}-x_{2}\right)^{2}+\left(y_{1}-y_{2}\right)^{2}}$ is related to the portion of the beam refracted by the lower particle before hitting the upper particle and therefore related to the degree of correlation between two particles by laser beam. When $R_{x y}$ is close to zero, a great portion of the laser beam that hits the upper particle comes through the lower particle and therefore causes the two particles to become highly correlated. In this case, each of the particles has its own equilibrium position. When $R_{x y}$ is larger than some value, the refraction of the beams will be assumed to have no influence on the trapping positions, so that they should have the same equilibrium position or trapping position. We assume that the difference between the $z$ coordinates of the trapping positions of the two particles to be $R_{I}$ when $R_{x y}=0$, and it becomes smaller than $R_{I}$ when $R_{x y}$ is larger, so we express the $z$ coordinates of the trapping positions as the following equation:

$$
z_{0}= \begin{cases}0, & R_{x y} \geqslant 0.5 R  \tag{11}\\ \pm \sqrt{1-\left[R_{x y} /(0.5 R)\right]^{2}} * R_{I} / 2, & R_{x y}<0.5 R\end{cases}
$$

Because the laser beam is propagated along the $z$ axis, we assume that the $x$ and $y$ coordinates of the trapping positions (namely, $x_{0}$ and $y_{0}$ ) are not influenced by the refraction of the beams by the lower particle, so that $x_{0,1}=x_{0,2}$ and $y_{0,1}=y_{0,2}$. This assumption is also supported by our experimental observation that the two particles distribute along the $z$ axis when both are trapped.

Following the experimental procedure described in Ref. 1, we begin the simulation with one particle in the trapping position while the other is a distance away from the first particle. The initial position of the second particle is set up to be $(2.2 R, 0,0)$, which is beyond the trapping range of the optical tweezers. In the simulation, the optical tweezers are moved, together with the first trapped particle, to approach and catch the second particle. Without loss of generality, we take the moving direction of the optical tweezers to be along the $x$ axis with a speed of $v_{x}=10 \mu \mathrm{~m} / \mathrm{s}$, which matches the actual speed in experiment. After the second particle is trapped, namely, the two particles enter a trapping status, the optical tweezers cease to move and we set the trapping duration $\tau$ to be zero for this moment. Therefore, the values of $x_{0}$ and $y_{0}$ in the simulation are

$$
\begin{align*}
& x_{0,1}=x_{0,2}= \begin{cases}n v_{x} \Delta t, & \tau<0 \\
x_{0}(\tau=0), & \tau \geqslant 0\end{cases} \\
& y_{0,1}=y_{0,2}=0 \tag{12}
\end{align*}
$$

where $n$ is the number of steps and $\Delta t$ is the time step in the simulation.

For one particle trapped by optical tweezers, the trapping force near the trapping position is approximately a spring force ${ }^{10}$ and reaches maximum when the displacement of the particle from the trapping position is approximately equal to the particle radius $R .{ }^{13}$ Therefore, the first component of the trapping force can be expressed as

$$
\begin{align*}
& F_{\mathrm{optx}}=\left\{\begin{array}{l}
-k_{x} d_{x y}\left[\left(x-x_{0}\right) / d_{x y}\right], \quad d_{x y}<R \\
-k_{x}\left(2 * R-d_{x y}\right)\left[\left(x-x_{0}\right) / d_{x y}\right], \quad R<d_{x y}<2 R \\
0, \quad d_{x y}>2 R,
\end{array}\right. \\
& F_{\text {opty }}=\left\{\begin{array}{l}
-k_{y} d_{x y}\left[\left(y-y_{0}\right) / d_{x y}\right], \quad d_{x y}<R \\
-k_{y}\left(2 * R-d_{x y}\right)\left[\left(y-y_{0}\right) / d_{x y}\right], \quad R<d_{x y}<2 R \\
0, \quad d_{x y}>2 R,
\end{array}\right. \\
& F_{\text {opt } z}=\left\{\begin{array}{l}
-k_{z}\left(z-z_{0}\right), \quad\left|z-z_{0}\right|<R \\
-k_{z}\left(2 * R-\left|z-z_{0}\right|\right)\left[\left(z-z_{0}\right) /\left|z-z_{0}\right|\right], \\
R<\left|z-z_{0}\right|<2 R
\end{array}\right.  \tag{13}\\
& 0, \quad\left|z-z_{0}\right|>2 R,
\end{align*}
$$

where $x_{0}, y_{0}, z_{0}$ is the trapping position, $x, y, z$ is the instantaneous position of the particle, and $d_{x y}$ is the transverse displacement which is equal to $\sqrt{\left(x-x_{0}\right)^{2}+\left(y-y_{0}\right)^{2}} . F_{\mathrm{opt} x}$, $F_{\text {opty }}$, and $F_{\text {optz }}$ represent the first component of trapping force along the $x, y$, and $z$ directions, respectively. In Eq. (13), we assume that the transverse trapping force is zero when the transverse displacement is larger than $2 R$, which is the same for the longitudinal trapping force. The reason to adopt the above expression is based on the theoretically calculated force of optical tweezers for single particle trapping. ${ }^{13,14}$

Similar to Ref. 10 , we take $k_{x}$ equal to $k_{y}$ and the longitudinal stiffness $k_{z 0}=k_{x} / 5$ when the particle is along the beam axis, that is, $d_{x y}=0$. However, when $d_{x y}$ is very large, not only the transverse trapping force but also the longitudinal force will become zero. Therefore, the $k_{z}$ will change from zero to $k_{z 0}$ as $d_{x y}$ decreases from infinity to zero. As indicated by Eq. (13), the $F_{\text {opt }}$ and $F_{\text {opty }}$ become zero when $d_{x y}>2 R$, and we assume that the $F_{\text {optx }}$ also becomes zero in this case. Therefore, to meet this requirement, $k_{z}$ can be expressed by the following equation:

$$
k_{z}= \begin{cases}k_{z 0}\left(1-d_{x y} / 2 R\right), & d_{x y}<2 R  \tag{14}\\ 0, & d_{x y} \geqslant 2 R\end{cases}
$$

The other component of the trapping force depends on the relative position of the two particles. We assume that
when $R_{x y}<2 R$, a part of light passing through the lower particle may be reflected back and forth between the two particles. These multiple reflections would induce a repulsion force between the two particles due to the momentum change
of the laser beam. This force becomes larger when the particles are closer and vanishes when the particles' distance is greater than a certain value, say, $R_{l}$. Therefore, we express this component of trapping forces (repulsive forces) as

$$
\begin{align*}
& F_{r x, i}= \begin{cases}C k_{x}\left(R_{l}-R_{12}\right) *\left(x_{i}-x_{j}\right) / R_{12}, & R_{12} \leqslant R_{l} \\
0, & R_{12}>R_{l},\end{cases} \\
& F_{r y, i}=\left\{\begin{array}{ll}
C k_{y}\left(R_{l}-R_{12}\right) *\left(y_{i}-y_{j}\right) / R_{12}, & R_{12} \leqslant R_{l} \\
0, & R_{12}>R_{l},
\end{array} \quad i, j=1,2, \quad i \neq j,\right.  \tag{15}\\
& F_{r z, i}= \begin{cases}C k_{z 0}\left(R_{l}-R_{12}\right) *\left(z_{i}-z_{j}\right) / R_{12}, & R_{12} \leqslant R_{l} \\
0, & R_{12}>R_{l},\end{cases}
\end{align*}
$$

when $R_{x y}<2 R$. Here $R_{12}$ is the center-to-center distance between the two particles, and $C$ is a constant to determine the intensity of the repulsion, which is taken to be 5 in the simulation. $F_{r x}, F_{r y}$, and $F_{r z}$ are used to represent this component of trapping force along the $x, y$, and $z$ directions, respectively. $R_{l}$ is equal to $R_{I}$ in Eq. (11), which is set to be $2.2 R$ in the simulation. The final trapping forces in the simulation are determined by summing the two components calculated from Eqs. (13) and (15).

After the determination of DLVO interactions and the optical trapping forces, the accumulated sticking probability $P(\tau)$ during trapping duration $\tau$ is determined from Brownian dynamics simulation. For simplicity, we assume that the two particles aggregate once they come in contact in the simulation. This can be confirmed by checking if the center-to-center distance is smaller than the diameter. For each trapping duration $\tau$ and specified DLVO interaction for each particle pair, more than 1000 simulation runs were performed to obtain average results.

## IV. RESULTS AND DISCUSSION

The accumulated sticking probabilities for different trapping durations of the two particles are simulated for different DLVO interactions with different parameters. The expression for the DLVO interactions used in this paper is

$$
\begin{equation*}
U=C^{\prime}\left(-\frac{A^{\prime}}{H}+B \exp (-\kappa H)\right) \tag{16}
\end{equation*}
$$

where $A^{\prime}, B$, and $\kappa$ determine the shape of the DLVO interaction potential, and $C^{\prime}$ is used to adjust the potential barrier, which is directly related to the sticking probability $p$. Three shapes of the DLVO potential are depicted in Fig. 2. In Fig. $2(\mathrm{a}), A^{\prime}=2 \times 10^{-30} \mathrm{~J} \mathrm{~m}, B=4 \times 10^{-20} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$, and $C^{\prime}$ is taken to be $0.6,0.9$, and 1.2, respectively. In Fig. 2(b), the parameters are $A^{\prime}=2 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B=4 \times 10^{-20} \mathrm{~J}, \kappa=5$ $\times 10^{7} \mathrm{~m}^{-1}$, with $C^{\prime}=1,2$, and 3, respectively. In Fig. 2(c), $A^{\prime}=5 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B=1 \times 10^{-19} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$, with $C^{\prime}$ $=1,1.5$, and 2.5 , respectively. These figures show different configurations of the interaction potential. The potentials in

Fig. 2(a) have almost no second minimum, while in Fig. 2(c) there are obvious second minima.

Figure 3 shows the accumulated sticking probabilities $P(\tau)$ obtained from our simulation for different trapping durations $\tau$ with different DLVO potentials and tweezers stiffnesses. The DLVO potentials used in Fig. 3 are corresponding to those shown in Fig. 2. From Fig. 3, we can see that the accumulated sticking probability $P(\tau)$ increases as $\tau$ increases. Previous experiments show that there is a jump at the beginning of the collision induced by optical tweezers and $P(\tau)$ exhibits an exponential increase with $\tau^{1}$. In other words, the plot of $\ln (1-P(\tau))$ against $\tau$ should be a straight line without passing through the origin. ${ }^{1,5}$

Our simulation (see Fig. 4 using the same data from Fig. 3) shows the same behavior as our experiment: $\ln (1-P(\tau))$ is linearly related to $\tau$ with negative intercepts. For collisions of a particle pair induced by optical tweezers as described in Refs. 1, 2, and 5, the sticking probability $p$ (or the stability ratio $W$ ) is determined by the intercept $\ln (1-p)$. Concerning the influence of the trapping force on the results, Fig. 4 shows that increasing $k_{x}$ by four times (i.e., $k_{x}=1 \mathrm{pN} / \mu \mathrm{m}$ is changed to $4 \mathrm{pN} / \mu \mathrm{m}$ ) causes only small shifts in the value of the intercept. This implies that the stiffness of the tweezers, which determines the strength of the trapping force, has only little influence on the sticking probability $p$, which has been supported by experimental evidence. ${ }^{1}$

Figure 4 also shows that $\ln (1-P(\tau=0.2 \mathrm{~s}))$ is a good approximation to the intercept $\ln (1-p)$ for all the simulated results with different DLVO interactions and tweezers stiffnesses $k_{x}$. This result indicates that $P(\tau=0.2 \mathrm{~s})$ is a good approximation for $p$, which further confirms the validity of the improved experimental approach proposed in Ref. 2.

The simulation results for the three different types of DLVO interactions also indicate that the method of using optical tweezers to measure sticking probability $p$ is applicable to different kinds of interaction potential such as the DLVO interactions used in the simulation, regardless of whether a second minimum of the potential exists.

The main features reflected in Figs. 3 and 4 are associated with the presence of two different statuses experienced


FIG. 3. Simulated results of $P(\tau)$ for different trapping durations $\tau$ with different DLVO interactions and tweezers stiffnesses $k_{x}$. The DLVO interactions are (a) $A^{\prime}=2 \times 10^{-30} \mathrm{~J} \mathrm{~m}, B=4 \times 10^{-20} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$; (b) $A^{\prime}=1$ $\times 10^{-28} \mathrm{~J} \mathrm{~m}, B=4 \times 10^{-20} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1} ;$ (c) $A^{\prime}=5 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B=1$ $\times 10^{-19} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$.
by the trapped particle pair. ${ }^{1,2,5}$ The $\ln (1-P(\tau))-\tau$ curve is a straight line related to the so called relaxed status, and the intercept is linked with particle aggregation in the compact status. The intercept is $\ln (1-p)$, where $p$ is the sticking probability and the reciprocal of the stability ratio $W$. The Brown-


FIG. 4. Simulated results of $\ln (1-P(\tau))$ for different trapping durations $\tau$ with different DLVO interactions and tweezers stiffnesses $k_{x}$. The data can be fitted linearly. The DLVO interactions are (a) $A^{\prime}=2 \times 10^{-30} \mathrm{~J} \mathrm{~m}, B=4$ $\times 10^{-20} \mathrm{~J}, \quad \kappa=5 \times 10^{7} \mathrm{~m}^{-1} ; ~(\mathrm{~b}) \quad A^{\prime}=1 \times 10^{-28} \mathrm{~J} \mathrm{~m}, \quad B=4 \times 10^{-20} \mathrm{~J}, \quad \kappa=5$ $\times 10^{7} \mathrm{~m}^{-1}$; (c) $A^{\prime}=5 \times 10^{-28} \mathrm{~J} \mathrm{~m}, B=1 \times 10^{-19} \mathrm{~J}, \kappa=5 \times 10^{7} \mathrm{~m}^{-1}$.
ian dynamics simulation can help explain why and how the transition from compact status to relaxed status takes place.

For studying the difference between the two statuses, the simulated results of $P(\tau=0)$ are compared with the $p$ estimated from Fig. 4, showing that $P(\tau=0)$ is equal to $p$ for
each of the DLVO interactions within the error range. Therefore, $\tau=0$ is the moment to distinguish the two different statuses. By analyzing the different conditions before and after $\tau=0$, the reason for the different statuses can be explained explicitly.

To catch the second particle, the optical tweezers (with the first particle trapped) are moved to approach the second particle. The period for the compact status is considered to be from the moment that the second particle feels the attractive force to the moment that both particles are trapped. During this period, there is observable transverse distance $R_{x y}$ between two particles although this distance keeps reducing. Because the $R_{x y}$ is large, the separation of the trapping positions of the two particles is smaller than that in the relaxed status, especially when $R_{x y}>0.5 R$, i.e., the trapping positions of the two particles actually coincide as shown by Eq. (11). Therefore, both moving speed and trapping force of the optical tweezers help two particles to approach each other and fall into the compact status.

In the relaxed status, the two particles stay along the $z$ axis, as shown in Fig. 1(b). Therefore, the transverse distance $R_{x y}$ should be around zero and therefore the trapping positions for two particles become separated according to Eq. (11). It implies that the collision frequency in the relaxed status should be much less than that in the compact status. As the two particles are steadily trapped in the relaxed status, the value of $\Delta P(\tau) /(1-P(\tau))$ is proportional to time interval $\Delta \tau$. This will lead to the relationship that $\ln (1-P(\tau))$ is proportional to $\tau$, as have been deduced by Refs. 1 and 5 .

## V. CONCLUSION

In this study, the accumulated sticking probability $P(\tau)$ for different time durations $\tau$ that the two particles stay in the optical tweezers is simulated by Brownian dynamics simulation. Various contributing factors, including the DLVO interaction of particles, hydrodynamic interactions, optical trapping forces on the two particles, and the Brownian motion, are considered in the simulation. The simulation results have reproduced the relevant features of the $\ln (1-P)-\tau$ curve found in the previous experiments.

The simulation demonstrates that the method for measuring the stability ratio by optical tweezers proposed in Refs. 1 and 2 is applicable to different types of DLVO interactions, no matter if there is obvious second minimum or not. In addition, the tweezers stiffness has little influence on the obtained value of $p$.

This study provides an explanation for the transition from the compact status to the relaxed status. It reveals that this transition is associated with the change in mutual positions of two particles related to the laser beam direction. The relaxed status corresponds to that one particle is behind the other along the laser beam direction and the compact status denotes the process from the second particle being attracted to the optical tweezers to both particles being lined up along the laser beam direction. In the relaxed status, two particles stay in separated equilibrium positions (trapping positions) and therefore have much lower collision frequency than those in the compact status.

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    ${ }^{2}$ Z. W. Sun, S. H. Xu, J. Liu, Y. M. Li, L. R. Lou, and J. C. Xie, J. Chem. Phys. 122, 184904 (2005).
    ${ }^{3}$ N. Fuchs, Z. Phys. 89, 736 (1934).
    ${ }^{4}$ M. Y. Han and H. K. Lee, Colloids Surf., A 202, 23 (2002).
    ${ }^{5}$ S. H. Xu, L. R. Lou, Y. M. Li, and Z. W. Sun, Colloids Surf., A 225, 159 (2005).
    ${ }^{6}$ D. L. Ermak and J. A. McCammon, J. Chem. Phys. 69, 1352 (1978).
    ${ }^{7}$ M. Elimelech, J. Gregory, X. Jia, and R. A. Williams, Particle Deposition and Aggregation (Butterworth-Heinemann, Oxford, 1995).
    ${ }^{8}$ E. J. W. Verwey and J. Th. G. Overbeek, Theory of the Stability of Lyophobic Colloids (Elsevier, Amsterdam, 1948).
    ${ }^{9}$ P. C. Hiemenz, Principles of Colloid and Surface Chemistry (Dekker, New York, 1986).
    ${ }^{10}$ M. Capitano, G. Romano, R. Ballerini, M. Giuntini, D. Dunlap, and L. Finzi, Rev. Sci. Instrum. 73, 1687 (2002).
    ${ }^{11}$ A. Rohrbach and E. H. K. Stelzer, Appl. Opt. 41, 2494 (2002).
    ${ }_{13}^{12}$ S. H. Xu, Y. M. Li, and L. R. Lou, Appl. Opt. 44, 2667 (2005).
    ${ }^{13}$ A. Ashkin, Biophys. J. 61, 569 (1992).
    ${ }^{14}$ S. H. Xu, Y. M. Li, and L. R. Lou, Chin. Phys. 15, 1391 (2006).

