Effective potential between two spheres in a suspension of adhesive rods

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Analytic treatment and Monte Carlo simulations are used to study the effective potential between two spheres in a suspension of rods whose ends can adhere to the surface of the spheres. When only one end of each rod is adhesive the effective potential changes from being attractive to repulsive with enhancing the adherence, but when both ends of each rod are adhesive the effective potential is not a monotonic function of the distance between the two spheres for strong adherence. As the adhesive strength is fixed, the range of the effective potential will increase with increasing the length of the rods. When the adhesive range is much smaller than the diameter of the spheres, its influence on single end adhesion is approximately linear and on two end adhesion is about quadratic. Our results are qualitatively consistent with a recent experimental work.

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I. INTRODUCTION

Mixtures of colloids have attracted wide interest for their practical applications (food, paints, drugs) as well as fundamental physics (diversity of structure and phase behavior). Besides the interactions between the particles, the entropy plays an important role in phase transitions and structure formations of mixtures. For an asymmetric binary mixture, the aggregation of large particles will provide more free volume for small particles and then increase the entropy of the system. If the entropy contributes the dominant part of the free energy in the mixture, aggregation will take place. The tendency of the aggregation due to the entropy is equivalent to an effective potential (EP) between any two large particles. The EP induced by the entropy is called the depletion potential and the pioneering work of the depletion interaction was executed by Asakura and Oosawa [1].

For a binary mixture composed of large spheres and thin rods, the depletion interaction between two spheres induced by rods has been studied through the theoretical analyses [2–4], numerical calculations [5–7], and experiments [8,9]. The phase behavior and structure of this mixture have also been studied by different methods [10–14]. Though simulations [10,12] and theoretical analyses [10–12] have indicated that there are gas-liquid and also fluid-solid phase separations in this mixture, only the latter was confirmed by the experiment [14]. Despite the lack of the gas-liquid separation, complex microphase separations [13] have been found in such mixtures. These results have shown richness and complexity in mixtures of rods and spheres.

In Ref. [8], the experimental measurements confirmed that the EP between colloidal spheres induced by the rodlike fd bacteriophage viruses changes from being attractive to repulsive or harmonic through adding salt into the suspension. At low salt concentrations, the interactions between spheres and rods are due to the excluded-volume effect, so the EP is the attractive depletion potential. At high salt concentrations it was speculated that when one end (two ends) of each rod can stick to the surface of spheres, the EP will be repulsive (nonmonotonic). The influence of adherence to the EP was also validated in another study of colloidal interactions and self-assembly through DNA hybridization [15]. At high temperatures there is no hybridization between grafted strands and linker strands, so the EP is repulsive, which stems from the steric exclusion between spheres and grafted strands. However, at low temperatures the hybridization is stable so two spheres can link each other through their grafted strands hybridized with a same linker strand which offers attraction to the EP.

The above experiments inspire us to study the EP between spheres in a suspension of adhesive rods. The paper is organized as follows. In Sec. II we present the model, in which the rods and spheres interact via the excluded-volume and attractive square-well potentials and give a simplified formulation for the EP. In Sec. III the model is used to study the influences of the adhesive strength, the adhesive range, and the length of rods to the EP by the Monte Carlo simulations. In Sec. IV a brief summary and some concluding remarks are given.

II. MODEL AND FORMULATION

For a suspension of thin hard rods, there is a phase transition from the isotropic fluid to the nematic liquid crystal between the concentrations $3.3/(L^2D)$ and $4.2/(L^2D)$ from the Onsager theory [16], where L is the length of a rod and D is its diameter. If the concentration is far lower than the Onsager concentration $3.3/(L^2D)$, the excluded-volume interaction between rods can be ignored, because its contribution to the free energy is the second order in the rod concentration [2]. For fd viruses, $L/D>100$ and its concentration used in Ref. [8] is very dilute, so we consider here the infinitely thin rods to model the fd viruses and neglect their mutual interactions. In our model the interaction between a rod and a sphere has two parts. The first part is the excluded-volume interaction that is infinite when the rod overlaps with the sphere. The second part is the short range adhesive interaction between the ends of the rod and the surface of the sphere. The latter can be modeled by a square-well potential with the depth ϵ and breadth d, so ϵ is the adhesive strength and d the adhesive range.

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We consider a container with a volume V in which there are N rods and two spheres separated by a distance H. The configurational partition function of this system is

$$Z(H) = \int_V \exp[-\beta U(\boldsymbol{r}^N, \boldsymbol{\omega}^N, H)] d\boldsymbol{r}^N \, d\boldsymbol{\omega}^N, \tag{1}$$

where $\beta=(k_B T)^{-1}$, k_B is Boltzmann's constant, and T is the temperature, $U(\boldsymbol{r}^N, \boldsymbol{\omega}^N, H)$ is the total potential energy of the system from all rods, $\boldsymbol{r}$ and $\boldsymbol{\omega}$ are the translational and orientational coordinates of a rod, respectively. In the approximation of infinitely thin rods, the total potential energy can be expressed by the sum of the potential energies of all single rods, then $Z(H)$ can be written as

$$Z(H) = \left(\int_V \exp[-\beta U(\boldsymbol{r}, \boldsymbol{\omega}, H)] d\boldsymbol{r} \, d\boldsymbol{\omega} \right)^N, \tag{2}$$

where $U(\boldsymbol{r}, \boldsymbol{\omega}, H)$ is the potential energy of a single rod. For convenience, the arguments in U will be omitted in the following.

According to the relationship between the free energy and partition function $F=-k_B T \ln Z$, we can obtain the free energy difference between the present mixture and the ideal solution of rods without any spheres; it reads

$$\beta[F(H) - F_0] = -N \ln \frac{\int_V \exp(-\beta U) d\boldsymbol{r} \, d\boldsymbol{\omega}}{\int_V d\boldsymbol{r} \, d\boldsymbol{\omega}}, \tag{3}$$

where $F(H)$ and F_0 are the free energies of the mixture and the ideal solution, respectively. For a solution of rods with a given concentration, adding two spheres into the solution will change the concentration, but this influence can be ignored when the volume of the solution is much larger than that of the spheres. In the thermodynamic limit, i.e., N and V both tend to the infinity, but N/V keeps constant, Eq. (3) can be simplified to

$$\begin{aligned} \beta[F(H) - F_0] &= -N \ln \left(1 + \frac{\int_V [\exp(-\beta U) - 1] d\boldsymbol{r} \, d\boldsymbol{\omega}}{V} \right) \\ &= -\frac{N}{4\pi V} \left(\int_V \exp(-\beta U) d\boldsymbol{r} \, d\boldsymbol{\omega} - 4\pi V \right), \end{aligned} \tag{4}$$

by considering that $\int_V [\exp(-\beta U) - 1] d\boldsymbol{r} \, d\boldsymbol{\omega}/V$ is infinitesimal because $\exp(-\beta U) - 1$ is nonzero only in a finite region, so the logarithm in Eq. (4) can be expanded in a power series and only the first two terms are kept.

The volume of the container can be divided into three parts, V_o, V_a, and V_f, as shown in Fig. 1. V_o is the volume occupied by the spheres, V_f is the volume in which rods can rotate freely, and V_a is the volume which can contain the center of rods but restrict the orientation of the rods through overlapping or adherence with spheres. It is noted that the part of the integral in V_f counteracts the counterpart of the ideal system, and the part of the integral in V_o is zero, therefore only the integral in V_a should be considered and V_a is a function of H. As usual, only the relative value of the free energy has meaning to the effective potential, so F_0 can be discarded. Based on these considerations, Eq. (4)is rewritten as

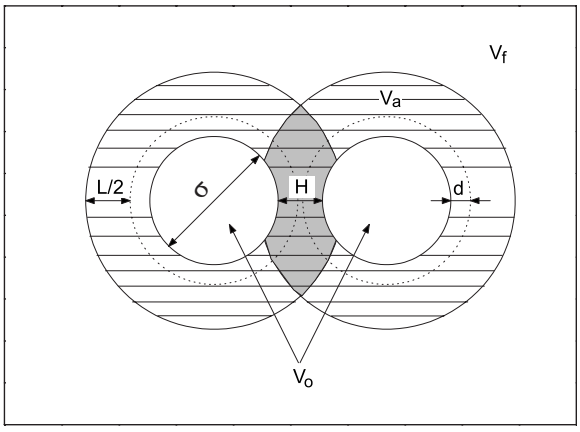

FIG. 1. Schematic drawing of the configuration of two spheres in a suspension of thin rods. σ is the diameter of the spheres, L is the length of the rods, H is the distance between the two spheres' surfaces, and d is the breadth of the square potential well. V_o is the volume occupied by the spheres, V_a is the volume in which the orientation of the rods is affected by the spheres, V_f is the free volume for the rods.

$$\frac{\beta V}{N} F(H) = V_o - \frac{1}{4\pi} \left(\int_{V_a} \exp(-\beta U) d\boldsymbol{r} \, d\boldsymbol{\omega} - 4\pi V_a \right). \tag{5}$$

If there are only excluded-volume interactions between the rods and spheres, the integral in Eq. (5) can be calculated through the Yaman-Jeppesen-Marques (YJM) model directly [5]. However, the YJM model cannot be used to deal with the finite interaction effectively. Here we shall use the Monte Carlo simulations to calculate the free energy and for this purpose Eq. (5) is rewritten in the form of an ensemble average. Discarding the constant V_o, we obtain

$$\begin{aligned} \frac{\beta}{\rho_N} F(H) &= V_a \left(1 - \frac{\int_{V_a} \exp(-\beta U) \exp(-\beta U_0) d\boldsymbol{r} \, d\boldsymbol{\omega}}{\int_{V_a} \exp(-\beta U_0) d\boldsymbol{r} \, d\boldsymbol{\omega}} \right) \\ &= V_a [1 - \langle \exp(-\beta U) \rangle_{V_a,0}], \end{aligned} \tag{6}$$

where $\rho_N=N/V$ is the number density of the rods, U_0 is the energy of a rod in the ideal system and is just zero. The angular bracket denotes to calculate the ensemble average of the expression in it. Furthermore, the average process over the position and orientation can be changed into the integral with the variable U, then Eq. (6) is written as

$$\frac{\beta}{\rho_N} F(H) = V_a \left(1 - \int_{-\infty}^{+\infty} f(U,H) \exp(-\beta U) dU \right), \tag{7}$$

where $f(U,H)$ is the normalized probability of the configuration whose potential energy is equal to U.

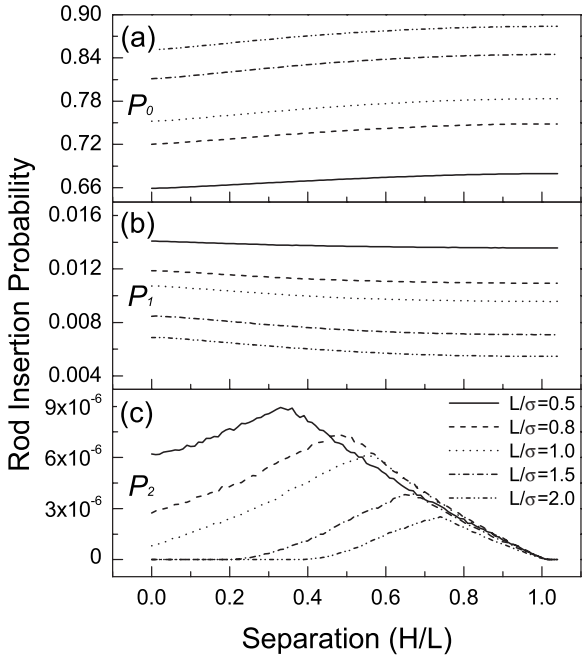

FIG. 2. P_0, P_1, and P_2 vs H are illustrated in (a)–(c) for various values of L and $d=0.01L$.

It is reasonable to assume that the adhesive interaction between a rod and a sphere can be modeled by a square-well potential, then the number of possible values of U is finite. When only one end of a rod is adhesive, according to the relative position between the rod and the two spheres, there are three possible values, i.e., 0, ϵ, and ∞, for U. When both ends of a rod are adhesive, there is one more possible value, that is 2ϵ, for U. When $U=\infty$, the corresponding configuration has no contribution to the free energy. So the integral in Eq. (7) can be replaced by the summation as

$$F(H) = \frac{\rho_N^*}{\beta} V_a^* \left(1 - \sum_{i=0}^{2} f_i(H) \exp(-\beta U_i) \right), \tag{8}$$

where $i=0,1,2$ correspond to $U=0,\epsilon,2\epsilon$, respectively. $\rho_N^* = \rho_N \sigma^3$ and $V_a^* = V_a/\sigma^3$ are reduced quantities, where σ is the diameter of the spheres as shown in Fig. 1.

There is one specific configuration which should be indicated. When $H<2d$, the surface potential wells of the two spheres will overlap, an adhesive end of a rod may adhere to the two spheres at the same time, therefore U of this kind of configuration seems to be 2ϵ, and this brings a singular attractive interaction to the EP. Actually, in experiments the EP between two spheres is repulsive at very short distance, because of the finite diameter of rods and the steric or electric repulsive interaction between spheres, so the singularity can be avoided. In contrast to experimental realization, we define $U=\epsilon$ for this kind of configuration appearing in calculations.

The important quantity to know is the normalized probabilities $f_i(H)$ which will be obtained by the Monte Carlo simulations as follows. For a given H, the center of a rod is inserted randomly in V_a and the orientation of the rod is random too. We take the total times of the insertion M_t as 8.0×10^8. All the configurations without overlapping between the rod and two spheres are divided into three kinds, S_0, S_1, and S_2, through distinguishing the positions of the two ends of the rod. We name the part of V_a occupied by the potential wells as the adhesive shells which are demarcated by the dotted lines in Fig. 1. For a configuration of the inserting rod, if none of the ends of the rod is in an adhesive shell it belongs to S_0, if only one end of the rod is in the adhesive shells it belongs to S_1, and if both ends are in the adhesive shells it belongs to S_2. The numbers of the configurations belonged to S_0, S_1, and S_2 are denoted by $M_0(H)$, $M_1(H)$, and $M_2(H)$, respectively. We define the rod insertion probabilities $P_0(H)$, $P_1(H)$, and $P_2(H)$ as

$$P_0(H) = \frac{M_0(H)}{M_t}, \quad P_1(H) = \frac{M_1(H)}{M_t}, \quad P_2(H) = \frac{M_2(H)}{M_t}.$$

When the both ends of the rod are adhesive the relationships between $f_i(H)$ and $P_i(H)$ are

$$f_0(H) = P_0(H), \quad f_1(H) = P_1(H), \quad f_2(H) = P_2(H).$$

On the other hand, when only one end of the rod is adhesive the relationships are changed to

$$f_0(H) = P_0(H) + P_1(H)/2,$$

$$f_1(H) = P_2(H) + P_1(H)/2,$$

$$f_2(H) = 0,$$

because for a configuration belonging to S_1 the end in the adhesive shells has half the chance to be the adhesive one.

As pointed out before, the EP is in fact the difference of two free energies and we can set $H=L+2d$ as the reference point, so EP equals $F(H)-F(L+2d)$.

III. NUMERICAL RESULTS AND DISCUSSIONS

The numerical results of the probabilities $P_i(H)$ $(i=0,1,2)$ are shown in Fig. 2 as functions of H with $L=0.5\sigma$, 0.8σ, 1.0σ, 1.5σ, 2.0σ, and $d=0.01L$. Volume V_a can be further divided into the common part and the self-part. The common part of V_a is the gray area in Fig. 1 in which the orientation of a rod is affected by the two spheres at the same time and the self-part is the rest. The ends of the rod have more opportunities in the adhesive shells when the rod is in the common part than in the self-part. Increasing H will increase the ratio of the self-part to the common part, so $P_0(H)$ increases and $P_1(H)$ decreases with this change as shown in Figs. 2(a) and 2(b). $P_2(H)$ is not a monotonic function and it first increases and then decreases with the increase of H as shown in Fig. 2(c). Increasing the length of the rod will decrease the ratio of V_o to V_a and weaken the influence of the spheres to the configuration of the rods in V_a. Therefore $P_1(H)$ and $P_2(H)$ will decrease but $P_0(H)$ will increase with the increase of L. The maximum of $P_2(H)$ moves to larger H/L with increasing L, because for the longer rod there is less probability to bridge two spheres at smaller H. From Fig. 2 it is found that $P_0(H) \gg P_1(H) \gg P_2(H)$, so the relationships between $f_i(H)$ and $P_i(H)$ for only one end of a rod being adhesive can be simplified as

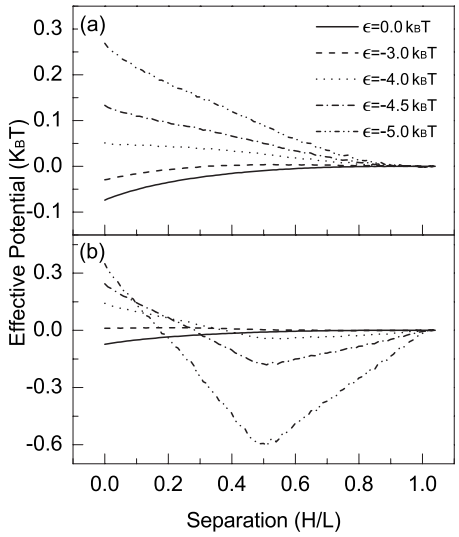

FIG. 3. Effective potential between the two spheres vs H for $L=0.8\sigma$, $d=0.01L$, and various values of ϵ. (a) Only one end of each rod is adhesive. (b) Both ends of each rod are adhesive.

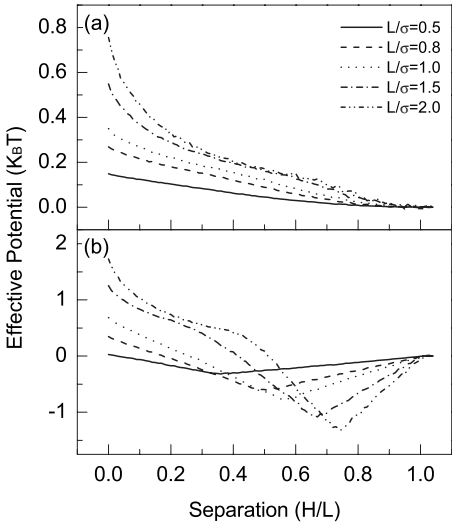

FIG. 4. Effective potential between the two spheres vs H for various values of L and $d=0.01L$ when $\epsilon=-5.0k_BT$. (a) Only one end of each rod is adhesive. (b) Both ends of each rod are adhesive.

$$f_0(H) \simeq P_0(H), \quad f_1(H) \simeq P_1(H)/2, \quad f_2(H) = 0.$$

The influence of the adhesive strength to the EP is studied with $L=0.8\sigma$ and $d=0.01L$. The results are illustrated in Fig. 3 with $\rho_N^*=1$. When the configurational entropy is the dominant factor compared with the adhesive interaction, the EP between the two spheres is similar to the depletion potential. Contrarily, if the adhesive interaction is the more important one, the EP will deviate from the depletion potential obviously. Specifically, with only one end of a rod being adhesive, the spheres will be covered by rods which prevent the approaching between the spheres, so the EP is repulsive as shown in Fig. 3(a); with both ends of a rod being adhesive, the two ends of each rod can stick two spheres at the same time and this bridging interaction induces an nonmonotonic potential as shown in Fig. 3(b). The concentration of fd viruses corresponding to the Y and Z lines in Fig. 3 of Ref. [8] is 0.2 mg/ml and the diameter of the silica particles used there is 1.0 μm. Using the molecular weight of the fd virus 16.4×10^6 g/mol, we can obtain that the ρ_N^* corresponding to 0.2 mg/ml is about 7.3. Taking this value into our calculations, the EP with $L=0.8\sigma$, $d=0.01L$, and $\epsilon=-4.5k_BT$ is qualitatively consistent with the experiments.

From Eq. (8) we can see that the EP is affected by V_a and $f_i(H)$, simultaneously. For a certain H, V_a and $f_i(H)$ are then determined by the length of the rods. From Fig. 2 it can be seen that increasing L will weaken the influence of the spheres to the orientation of the rods in V_a and result in the decrease of $P_1(H)$ and $P_2(H)$. On the other hand, increasing L will obviously increase the value of V_a. The combined influence of L to the EP is shown in Fig. 4 with $d=0.01L$, $\epsilon=-5.0k_BT$, and $\rho_N^*=1$. When only one end of each rod is adhesive, the strength of the EP increases with increasing L as shown in Fig. 4(a). When both ends of each rod are adhesive, increasing L will enhance the EP and move its minimum to larger H/L. This minimum is corresponding to the maximum of $P_2(H)$ in Fig. 2(c).

There are two adjustable parameters for a square potential well. One is the depth ϵ and the other the breadth d. We have shown the influence of the former on the EP in Fig. 3 and will study the influence of the latter hereinafter. The probabilities $P_i(H)$ for $L=1.0\sigma$ and $d=0.005L$, $0.01L$, $0.02L$ are calculated, the results are shown in Fig. 5. When $d \ll \sigma$, the volume of the adhesive shells is approximately proportional to the breadth d, so $P_1(H)$ is almost a linear function of d. From Fig. 5 it can be found that the ratio $P_1(H)$ is about 1:2:4 with the value of d in the sequence of $0.005L$, $0.01L$, and $0.02L$ for the whole range of H. The relationship between $P_2(H)$ and d is a little more complex and affected by the distance H apparently. $P_2(H)$ behaves like a quadratic function of d only when H is in the vicinity of the maximum of $P_2(H)$. The EP vs H with $d=0.005L$, $0.01L$, $0.02L$ is calculated when $L=1.0\sigma$ and $\epsilon=-5.0k_BT$. The results are illustrated in Fig. 6 with $\rho_N^*=1$. When d/L increases from 0.005 to 0.02, the maximum of the repulsive potential induced by the single end adhesion increases about eight times and the minimum of the attractive potential induced by the two end adhesion increases about 26 times. So the adhesive range has strong influence on the EP especially for the attractive potential which stems from the bridging interaction of rods.

IV. SUMMARY

We have studied the EP between two spheres in a suspension of infinitely thin rods with their one end or two ends of each rod adhesive to the surface of the spheres. We have simplified the expression of the free energy of the mixture and associated it with the distribution of the ends of the rods, then determined the distribution by the Monte Carlo simulations. When only one end of each rod is adhesive, enhancing the adherence will increase the number of rods adhering to the surface of the spheres and prevent the spheres from approaching each other, so the EP between the spheres are repulsive. When both ends of each rod are adhesive, enhancing the adherence will enhance the bridging of the rods and provide an attractive interaction between the spheres, but at

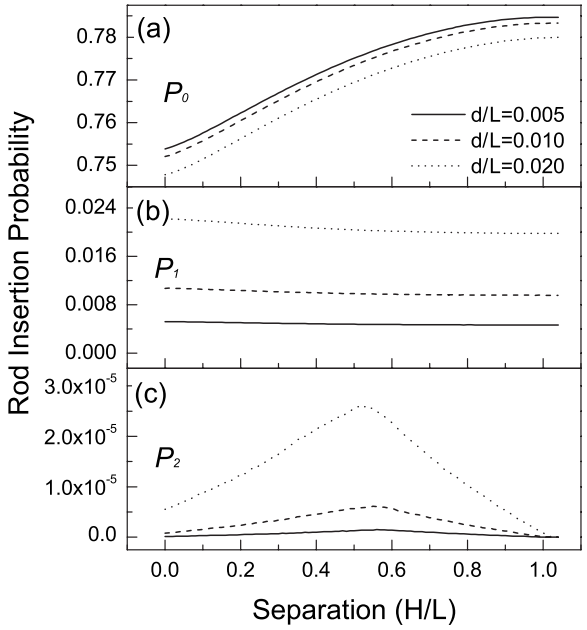

FIG. 5. P_0, P_1, and P_2 vs H are illustrated in (a)–(c) for $L=1.0\sigma$ and various values of d.

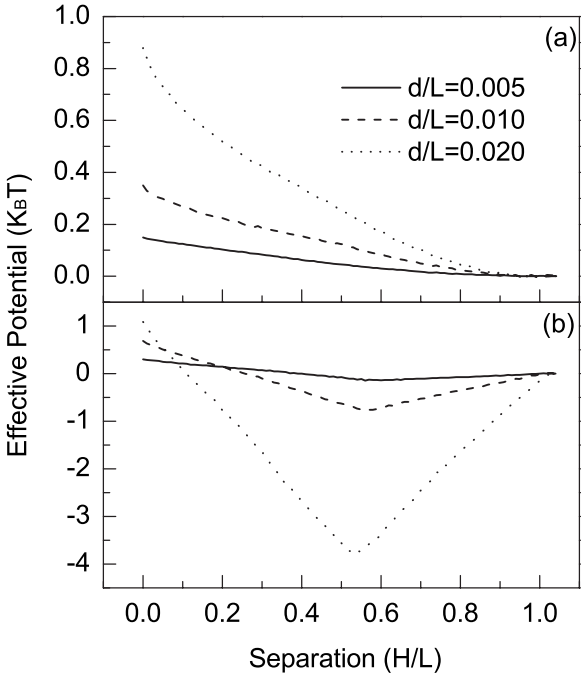

FIG. 6. Effective potential between the two spheres vs H for $L=1.0\sigma$, $\epsilon=-5.0k_BT$, and various values of d. (a) Only one end of each rod is adhesive. (b) Both ends of each rod are adhesive.

the close distance the excluded-volume interaction is dominant. With a certain adhesive strength, increasing the length of the rods will enhance the EP, because the longer the rods are, the larger the affected area is. The adhesive range has strong influence on the EP for the two kinds of adhesion, especially for the two end adhesion. Our results are qualitatively consistent with the previous experimental measurements.

It is instructive to point out that there is a limitation for the method used here due to the neglect of mutual interactions between rods, so it cannot be applied to calculate the effective potential in dense solutions. Still, this method can deal with the finite short range interaction between particles and rods without any restriction on the particles' shape or the form of interactions. If the finite short range interaction is not the square well but with a complex form, the free energy of the system can be calculated by Eq. (6) directly.

ACKNOWLEDGMENTS

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