

# The influence of bond rigidity and cluster diffusion on the self-diffusion of hard spheres with square well interaction

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Hard spheres interacting through a square well potential were simulated by using two different methods: Brownian cluster dynamics (BCD) and event driven Brownian dynamics (EDBD). The structure of the equilibrium states obtained by both methods was compared and found to be almost identical. Self-diffusion coefficients ( $D$ ) were determined as a function of the interaction strength. The same values were found by using BCD or EDBD. Contrary to EDBD, BCD allows one to study the effect of bond rigidity and hydrodynamic interaction within the clusters. When the bonds are flexible, the effect of attraction on  $D$  is relatively weak compared to systems with rigid bonds.  $D$  increases first with increasing attraction strength, and then decreases for stronger interaction. Introducing intracluster hydrodynamic interaction weakly increases  $D$  for a given interaction strength. Introducing bond rigidity causes a strong decrease in  $D$  which no longer shows a maximum as function of the attraction strength. © 2008 American Institute of Physics.

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## I. INTRODUCTION

Suspensions of particles with attraction exhibit equilibrium states as well as nonequilibrium states such as gels or glasses that evolve very slowly.<sup>1-4</sup> Numerical simulations were found to be useful for the understanding of the structure and the dynamics of such systems.<sup>3,5</sup> The advantage of simulations is that large scale phenomena may be related to the microscopic trajectories of the particles. In recent years, computer simulations have yielded valuable insight not only into equilibrium properties such as cluster size distributions and structure factors but also into the evolution of the system during phase separation<sup>6-8</sup> and gelation.<sup>9-13</sup>

Often Monte Carlo methods are used to study structural properties at equilibrium and molecular dynamics to study dynamics and kinetics.<sup>14,15</sup> Monte Carlo methods allow one to study relatively large systems and generally require less computer time to obtain equilibrium states. A main drawback of classical Monte Carlo methods is that the definition of time is usually unphysical so that the evolution of the system toward equilibrium cannot be compared to that of real systems. Molecular dynamics simulate the particle displacement more realistically, but the system size and time scales that can be simulated with the current generation of computers are still relatively small.

The simplest model of interacting fluids is an ensemble of hard spheres that interact through a square well potential. Here, we compare two different methods to simulate this model system: Brownian cluster dynamics (BCD) and event driven Brownian dynamics (EDBD).<sup>16</sup> With BCD, clusters are constructed by forming bonds between spheres within

each others interaction range with a given probability. With this method, it is possible to account for hydrodynamic interaction within the clusters, although not between the clusters. It is also possible to study the influence of bond rigidity on the dynamics. This is important because in real systems, bonds may be more or less rigid. With EDBD, hydrodynamic interaction is ignored and the bonds are inherently completely flexible. We will show here that for reversibly aggregating systems, bond rigidity has no influence on the structure of the steady state, but has a huge effect on the dynamics.

In the following, we will first describe the two simulation methods. Then, we compare the structure factors and the cluster size distributions of homogeneous equilibrium states. We will show that almost the same structures are obtained at steady state with both methods. The main part of the paper deals with the self-diffusion coefficient as a function of the interaction strength. We compare the results obtained by the two simulation methods and discuss the influence of bond flexibility and intracluster hydrodynamic interaction.

## II. SIMULATION METHOD

We simulate hard spheres interacting through a square well potential characterized by a well depth  $u < 0$  and a well width  $\epsilon$  by using BCD and EDBD. Both simulation methods start with an ensemble of  $N_{\text{tot}}$  randomly distributed spheres with diameter equal to unity in a box of size  $L$  so that the volume fraction is defined as  $\phi = (\pi/6) N_{\text{tot}}/L^3$ . The box sizes used in this paper range from  $L=50$  for low volume fractions down to  $L=10$  for  $\phi=0.49$ . For the results shown here, there was no finite size effect. Both methods use periodic boundary conditions.

*Event driven Brownian dynamics.* This method was de-

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scribed in detail in literature<sup>16</sup> and we only resume here the principal features. Initially, a random velocity is assigned to each sphere from a Gaussian distribution with average squared velocity  $\langle v^2 \rangle = 3kT/M$ , where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $M$  is the mass of the particle. Events are defined as occurrences when the sphere is at a distance unity or  $1 + \epsilon$  from another sphere, i.e., when spheres touch or cross the interaction range. All spheres are moved over a distance  $r = v\Delta t$ , where  $\Delta t$  is sufficiently small so that the motion is Brownian over the relevant length scales, i.e., the interaction range and the average distance between the nearest neighbors.

The velocity of the spheres involved in the event is changed while conserving the energy and the momentum. When the event is a collision, the spheres will elastically bounce in opposite directions. When the sphere enters a well, its velocity is increased because the potential energy is decreased. When the sphere tries to leave a well, it either bounces back elastically or it exits with a lower velocity. The change in the velocity and the probability to exit the well depend on  $u$ .

The mean squared displacement of a single sphere is given by  $\langle r^2 \rangle = n(\Delta t)^2 \langle v^2 \rangle$ , where  $n$  is the number of simulation steps and  $\Delta t$  is equal to the maximum time step. If time is defined as  $t \equiv n\Delta t$ , then the free diffusion coefficient of a single sphere is equal to  $D_0 = kT\Delta t / (2M)$ . We note that in literature, often  $u$  is fixed and  $T$  is varied.

*Brownian cluster dynamics.* Spheres are considered to be in contact when they are within each others interaction range, i.e., when the center to center distance is smaller than  $1 + \epsilon$ .  $\nu$  is the total number of contacts in the system. In the so-called cluster formation step, spheres in contact are bound with probability  $P$ . Alternatively, bonds are formed with probability  $\alpha$  and broken with probability  $\beta$ , so that the  $P = \alpha / (\alpha + \beta)$ . In the latter case, one can vary the kinetics of the aggregation from diffusion limited ( $\alpha = 1$ ) to reaction limited ( $\alpha \rightarrow 0$ ) with the same  $P$  and thus the same degree of reversibility. Clusters are defined as collections of bound spheres, and monomers are clusters of size 1. After this procedure,  $N_c$  clusters are formed. We mention that more complex interaction potentials can be simulated by making  $P$  a function of the distance between two spheres.

The ratio of the number of bound ( $\nu_b$ ) to free contacts ( $\nu - \nu_b$ ) is given by the Boltzmann distribution  $\nu_b / (\nu - \nu_b) = \exp[-\Delta H / (kT)]$ , where  $\Delta H$  is the enthalpy difference between bound and free contacts. The formation of  $\nu_b$  randomly distributed bonds over  $\nu$  contacts leads to a decrease in the free energy equal to  $u$  per contact. This decrease may be written as the sum of the decrease in the enthalpy and the gain of the entropy:  $\nu u = \nu_b \Delta H - T \Delta S$ . The latter is determined by the number of ways  $\nu_b$  bonds can distributed over  $\nu$  contacts:  $T \Delta S = kT \ln(\nu! / (\nu_b! (\nu - \nu_b)!))$ . Noticing that  $P = \nu_b / \nu$ , we can express  $P$  in terms of  $u$ :

$$P = 1 - \exp\left[-\frac{u}{kT}\right]. \quad (1)$$

The cluster construction step is followed by one of the three different movement steps that each simulates a different type of cluster dynamics.

*BCD1.*  $N_{\text{tot}}$  times a sphere is randomly selected and for each selected sphere, a single attempt is made to move it a distance  $s$  in a random direction. The movement is accepted if it does not lead to overlap with any other sphere in the system and if it does not lead to the separation of bound spheres beyond the interaction range. Again, it is important to choose the step size  $s$  sufficiently small so that the motion is Brownian over the relevant length scales. We have found that the results on the equilibrium structure were independent of the step size if  $s$  was at least five times smaller than the interaction range and at least three times smaller than the average distance between nearest neighbors.<sup>8,17</sup>

The mean squared displacement of a single sphere is given by  $\langle r^2 \rangle = ns^2$ , where  $n$  is again the number of simulation steps. Time was defined as  $t \equiv ns^2$ , so that the free diffusion coefficient of single spheres is equal to  $D_0 = 1/6$ .

*BCD2.*  $N_c$  times a cluster is randomly selected and for each selected cluster, a single attempt is made to move the cluster over a distance  $s/\sqrt{d}$  in a random direction with  $d$  the diameter of the cluster. By definition, this cooperative movement never leads to bond breaking. The movement is refused if it leads to overlap of any of the spheres in the clusters with other spheres in the system. The free diffusion coefficient of single spheres is thus still  $1/6$ , but the free diffusion coefficient of clusters is  $1/(6d)$ .

*BCD3.* This movement step is a combination of the previous two. First, the movement step BCD1 is executed and the displacement of the centers of mass of each cluster is calculated. Then, each cluster is given an additional displacement in the same direction so that the total displacement of the center of mass is the same as would be obtained by the movement step of BCD2. Again, displacements are refused if they lead to overlap. As for movement step BCD2, the free diffusion coefficient of single spheres is  $1/6$  and that of larger clusters is  $1/(6d)$ . A lower degree of flexibility can be simulated by performing movement step BCD1 with a lower frequency than movement step BCD2.

The methods EDBD, BCD1, and BCD3 simulate systems with flexible bonds, while BCD2 simulates systems with rigid bonds. Using EDBD and BCD1, the effective friction coefficient of clusters is proportional to their aggregation number (so-called Rouse dynamics),<sup>18</sup> while for BCD2 and BCD3, it is proportional to their radius (so-called Zimm dynamics).<sup>19</sup> It is, of course, straightforward to modify BCD2 to simulate systems with rigid bonds in which the friction coefficient is proportional to their aggregation number. This has not been done here, because in reality hydrodynamic interaction causes the free diffusion coefficient of clusters in solution to be inversely proportional to their radius.<sup>20</sup> The movement steps of EDBD and BCD1 are similar and one expects that diffusion coefficients obtained by these methods are close.

BCD may be considered a Monte Carlo type simulation, but if one is interested only in the structural properties at equilibrium, it is more efficient to use other Monte Carlo techniques that do not yield realistic kinetics or dynamics. BCD does not fulfill the condition of detailed balance, but does lead to a steady state independent of the starting configuration, which shows that it fulfills the condition of

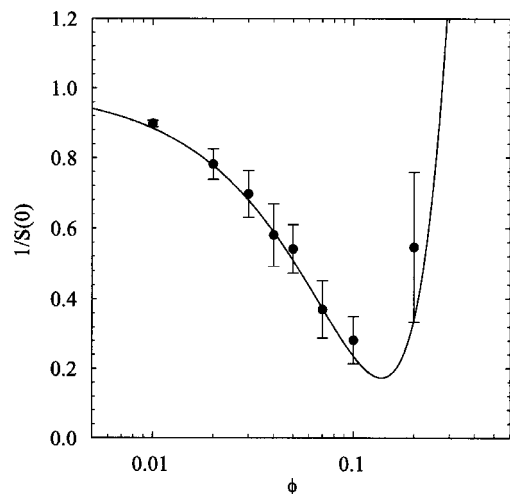


FIG. 1. Concentration dependence of the compressibility for equilibrium systems at  $\epsilon=0.5$  for  $B_{\text{att}}=10$  obtained by BCD. The solid line represents a calculation by using the second and third virial coefficients, see text. The error bars represent the 95% confidence based on the results of eight simulations.

balance.<sup>21</sup> The same steady state is reached for each of the three movement steps with one exception: BCD2 does not lead to crystallization. The reason is that the pathway to form crystals is extremely unlikely when the bonds are rigid. BCD2 is therefore an excellent method to explore the properties of attractive spheres while avoiding crystallization.<sup>8</sup>

### III. RESULTS AND DISCUSSION

#### A. Equilibrium structure

The strength of the attraction is determined by the well width and the well depth. However, the equilibrium structure obtained at different  $\epsilon$  is close if  $u$  is chosen such that the second virial coefficient is the same, especially if  $\epsilon$  is small.<sup>8,22</sup>  $B_2$  may be written as the sum of a repulsive (excluded volume) part and an attractive part:  $B_2=B_{\text{rep}}-B_{\text{att}}$ , with

$$B_{\text{rep}}=4,$$

$$B_{\text{att}}=\frac{4P}{1-P} \left( (1+\epsilon)^3 - 1 \right),$$

where the unit of  $B_2$  is the volume of a sphere.

As mentioned in the Introduction, strong attraction between the spheres leads to phase separation, while weak attraction leads to a homogeneous equilibrium state containing a distribution of transient clusters. All the three movement procedures of BCD lead to the same homogeneous equilibrium state, so for the structural properties, we do not differentiate between the three methods. We have characterized these states in terms of the static structure factor ( $S(q)$ ) and the cluster size distribution.

The structure factor at  $q \rightarrow 0$  is inversely proportional to the compressibility and can be expressed in terms of a virial expansion at small volume fractions:  $1/S(0)=1+2B_2\phi+3B_3\phi^2$ , with  $B_3$  the third virial coefficient. For hard spheres interacting with a square well potential,  $B_2$  and  $B_3$  have been

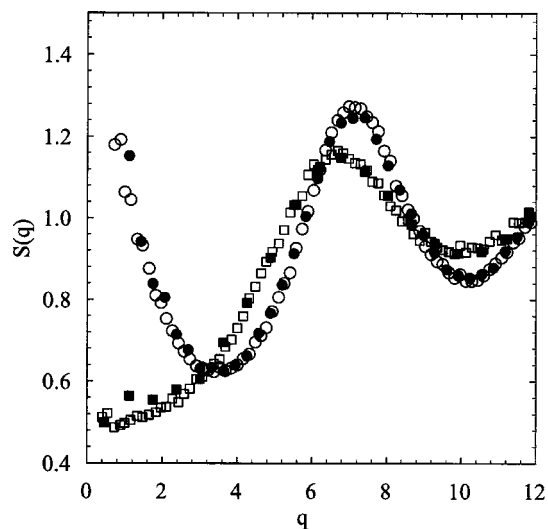


FIG. 2. Comparison of the structure factor of equilibrium systems at  $\phi=0.15$  and  $\epsilon=0.1$  obtained by BCD (filled symbols) and EDBD (open symbols) with  $B_{\text{att}}=2$  (squares) or  $B_{\text{att}}=6$  (circles).

analytically calculated.<sup>23</sup> Figure 1 shows a comparison of  $1/S(0)$  as a function of  $\phi$  obtained from BCD simulations with the values calculated by using the virial expansion. There is good agreement up to  $\phi=0.1$  beyond which higher order virial terms become important.

Figure 2 compares  $S(q)$  obtained with BCD and EDBD for  $\phi=0.15$  at two interaction strengths. Within the uncertainty range, the same structures were observed with the two methods.

The cluster size distribution represents a more precise characterization. Clusters of bound spheres can be formed by connecting spheres in contact with probability  $P=1-\exp[-u/(kT)]$  as defined above. A detailed analysis of these cluster size distributions has been reported elsewhere.<sup>8</sup> Here, we have analyzed the size distribution of clusters formed by connecting all contacts in order to facilitate comparison between BCD and EDBD. The width of the distribution increases with increasing  $u$  until at a critical value, a system spanning transient network of spheres in contact is formed. Figure 3 shows a comparison of  $N(m)$ , i.e., the average density of clusters consisting of  $m$  spheres, at  $\phi=0.15$  and  $\epsilon=0.1$  for two values of  $B_{\text{att}}$ : 2 and 4. There is a very small, but systematic difference between the cluster size distributions obtained with BCD and EDBD. Slightly larger clusters are formed with BCD. Nevertheless, we may conclude from these examples and similar comparisons at other conditions that the equilibrium structures obtained by BCD and EDBD are almost the same.

#### IV. DIFFUSION

It can be shown that random displacement with constant step size as done with BCD leads to Brownian diffusion at distances much larger than the step size.<sup>24,25</sup> For a proper comparison of the dynamic properties of BCD and EDBD simulations, one has to ensure that the time scales and the free diffusion coefficients are the same, which can be done by choosing  $\Delta t=s^2$  and  $kT\Delta t/M=1/3$ . Figure 4 shows a comparison of the average mean square displacement of hard

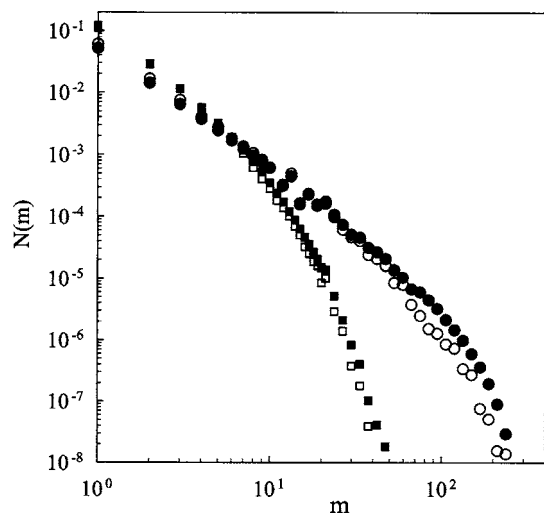


FIG. 3. Comparison of the cluster size distribution of equilibrium systems at  $\phi=0.15$  and  $\epsilon=0.1$  obtained by BCD (filled symbols) and EDBD (open symbols) with  $B_{\text{att}}=2$  (squares) or  $B_{\text{att}}=4$  (circles).

spheres obtained from BCD and EDBD at  $\phi=0.3$ . In both simulations,  $\langle r^2 \rangle$  becomes proportional to  $t$  and the diffusion coefficient can be calculated as  $D = \langle r^2 \rangle / (6t)$ . Figure 5 shows that the same  $\phi$  dependence of  $D$  is obtained by the two methods within the uncertainty of the simulations.  $D$  decreases with increasing volume fraction due to steric hindrance, and the diffusion critically slows down at the so-called glass transition, which has been the subject of intensive investigation.<sup>26,27</sup>

When we introduce attraction between the spheres, we need to consider cooperative cluster motion and bond flexibility. EDBD allows only one type of motion, but by using BCD, one can choose between different movement steps.

We have simulated the mean square displacement of spheres by using EDBD and BCD with the three different movement steps described above. In each case, diffusive motion was observed for large  $t$  and the diffusion coefficient could be determined. BCD1 and EDBD simulate the same

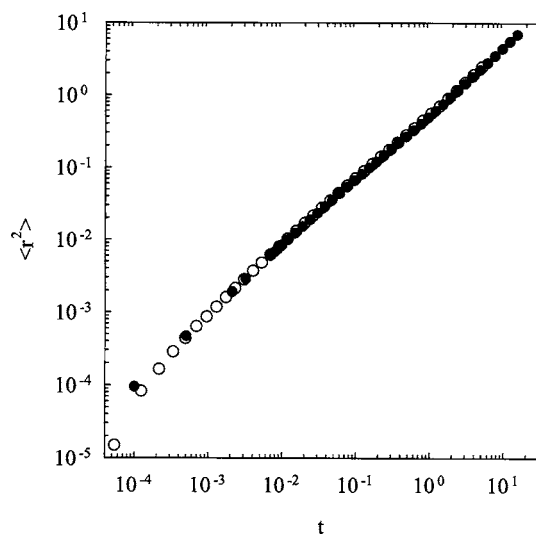


FIG. 4. Comparison of the mean square displacement of noninteracting hard spheres obtained by BCD (filled symbols) and EDBD (open symbols).

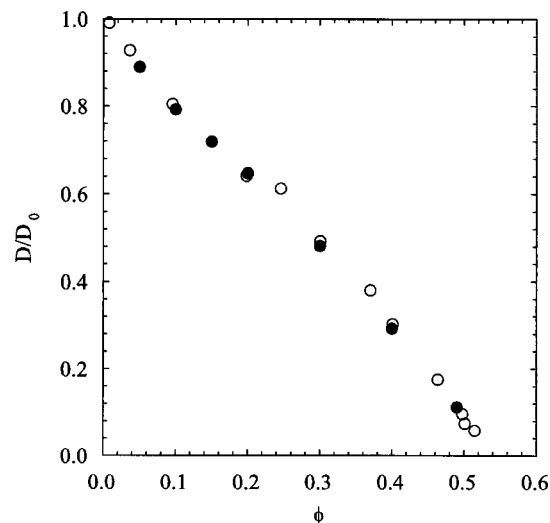


FIG. 5. Comparison of the decrease in the diffusion coefficient with increasing volume fraction for noninteracting hard spheres obtained with BCD (filled symbols) and EDBD (open symbols) (Ref. 16).

situation and therefore the results should be the same. Figure 6 shows an example of the dependence of  $D$  on the step size obtained by using BCD1. It appears that the exact value of  $D$  is more sensitive to the step size than the static structure factor or the cluster size distribution since the latter did not significantly depend on the step size for  $s < \epsilon/5$ . The value extrapolated to  $s=0$  is the same as the value found with EDBD within the simulation error. Similar results were obtained at different volume fractions and interaction strengths. The fact that these very different simulation methods lead to the same results strengthens confidence in both methods. In terms of computational efficiency, both methods are equivalent.

A comparison of the dependence of  $D$  on  $B_{\text{att}}$  obtained with BCD by using the three different movement steps is shown in Fig. 7 for two different volume fractions (0.15 and

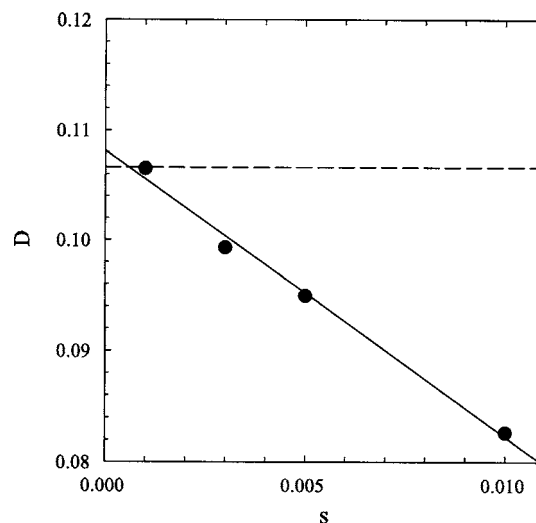


FIG. 6. Dependence of the diffusion coefficient on the step size by using BCD1 ( $\phi=0.49$ ,  $B_{\text{att}}=6$ ,  $\epsilon=0.1$ , filled symbols). The dashed line represents the result from EDBD by using the same conditions. The solid line is a linear fit through the data. We note that at  $\phi=0.49$ , the average gap between randomly distributed spheres is 0.014 (Refs. 28 and 29).

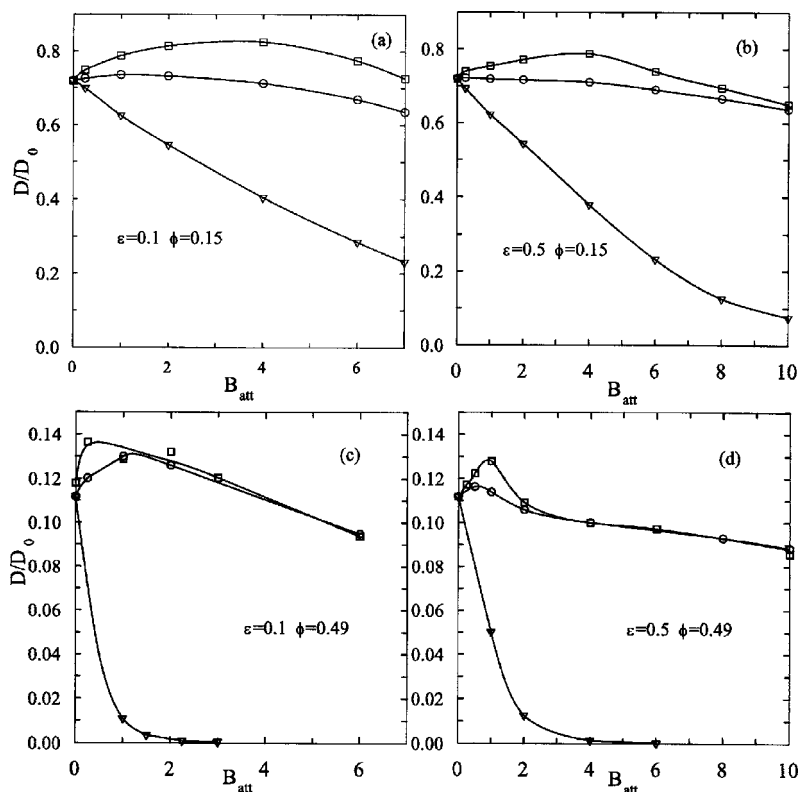


FIG. 7. Variation of the diffusion coefficient with increasing attraction obtained from BCD1 (circles), BCD2 (triangles), and BCD3 (squares) at two different volume fractions and two different interaction widths. The interaction strength is expressed in terms of the attractive part of the second virial coefficient. Solid lines are guides to the eyes.

0.49) and two different well widths (0.1 and 0.5). The range of  $B_{\text{att}}$  that can be explored is limited by the liquid-liquid or liquid-crystal phase separation that occurs at strong attraction. The values of  $D$  shown in Fig. 7 were obtained at a single value of  $s$ , but for a few examples, the effect of  $s$  was determined, which showed that they were about 10% smaller than the values extrapolated to  $s=0$ .

$D$  strongly decreases with increasing attraction when the bonds are rigid (BCD2). In this case, the displacement of bound spheres is equal to that of the center of mass of the clusters to which they belong. The size of the clusters rapidly increases with increasing attraction and beyond a critical value, a transient (bond) percolating network is formed. Spheres that are part of the network are immobile until the bonds that tie them to the network are broken. A detailed study of the diffusion coefficient of square well fluids forming rigid bonds by using BCD2 has been recently reported.<sup>30</sup> It was shown that  $D$  decreases with increasing  $B_{\text{att}}$  following a power law for large  $B_{\text{att}}$  and only becomes zero when the bonds are irreversible, i.e.,  $B_{\text{att}} \rightarrow \infty$ .

In comparison, the influence of attraction on  $D$  is weak when the bonds are flexible, i.e., using EDBD, BCD1, or BCD3. The difference between methods BCD1 (EDBD) and BCD3 is that for the latter, clusters move faster (Zimm dynamics) so that  $D$  is slightly larger. The effect increases with increasing cluster size and is expected to be maximal close to the percolation threshold. The values of  $B_{\text{att}}$  at the bond percolation thresholds are about 6 at  $\phi=0.15$  for both well widths, while at  $\phi=0.49$ , they are 0.5 and 1.2 for  $\epsilon=0.1$  and 0.5, respectively. The difference between the two methods decreases for larger  $B_{\text{att}}$  when most spheres belong to the percolating network that has no center of mass movement.

The few remaining free spheres are mostly monomers so that the movement steps BCD1 and BCD3 become equivalent.

Regardless of the method, the effect of attraction on  $D$  is qualitatively different if the bonds are flexible because in that case, bound spheres can freely move within the interaction range.  $D$  weakly increases with increasing attraction until it reaches a maximum beyond which it decreases. The relative amplitude of the increase is very small for the volume fractions studied here, but becomes important at higher volume fractions.<sup>27</sup> It is at the origin of the so-called re-entrant glass transition of interacting spheres as a function of the attraction strength.<sup>31,32</sup> The influence of attraction on the critical slowing down of hard spheres has attracted a lot of attention in the recent past and has been investigated for square well fluids by using EDBD simulations.<sup>7</sup>

The appearance of a maximum diffusion coefficient can be qualitatively understood by considering two opposing effects. On one hand, attraction causes clustering of particles so that more space is created in which monomers and clusters can freely diffuse, leading to faster diffusion of the spheres. On the other hand, bonds restrict the motion of spheres, and the long time diffusion of bound spheres is equal to the center of mass diffusion of the clusters to which they belong. The restriction becomes more important as the average bond lifetime increases.

When the attraction is weak, the average bond lifetime is still small so that the effect of restriction is weak and the effect of creating more free space dominates, leading to an increase in  $D$ . With increasing  $B_{\text{att}}$ , the clusters become larger and the average bond lifetime increases until the effect of increasing restriction of the movement becomes more important than the effect of increasing free volume so that  $D$

decreases. These features are independent of the volume fraction and the well width. The effect of attraction on the diffusion coefficient remains small in the single phase regime if the bonds are flexible at least for  $\phi < 0.5$ .

## V. SUMMARY

BCD and EDBD simulations of hard spheres interacting with a square well potential lead to steady states that have almost the same structure factor and the cluster size distribution.

EDBD assumes flexible bonds and ignores hydrodynamic interaction. The values of the self-diffusion coefficient obtained by EDBD are very close to those obtained with BCD if the same assumptions are used. A weak maximum of  $D$  is found as a function of the interaction strength caused by the opposing effects of increasing free volume and increasing bond lifetime.

The effect of intracluster hydrodynamics (Zimm dynamics) and bond rigidity can be explored with BCD. Introducing rigid bonds leads to a strong decrease in  $D$  with increasing attraction and suppresses the maximum. Introducing intracluster hydrodynamics to the system with flexible bonds weakly increases  $D$  at a given interaction strength.

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