On Brownian Dynamics Simulation of Nanoparticle Aggregation

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Keywords
Chemical and Biological Engineering

Disciplines
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Comments
On Brownian Dynamics Simulation of Nanoparticle Aggregation

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Abstract

Accurate simulation and control of nanoparticle aggregation in chemical reactors requires that population balance equations be solved by using realistic expressions for aggregation and breakage rate kernels. Obtaining such expressions requires that atomistic simulation approaches that can account for microscopic details of particle collisions be used. In principle, molecular dynamics simulations can provide the needed microscopic information, but because of the separation in length scales between the aggregates and solvent molecules, such simulations are too costly. Brownian dynamics simulations provide an alternative to the molecular dynamics approach for simulation of particle aggregation, but there has been no systematic attempt to validate the Brownian dynamics method for this class of problems. In this work we attempt to develop a better understanding of Brownian dynamics simulations of aggregation by (1) developing convergence criteria, (2) determining criteria for aggregation to occur in BD simulations using dimensionless variables, and (3) directly comparing BD and MD simulation predictions for a model aggregation problem.

1. Introduction

In recent years, there has been an explosion of interest in the synthesis of nanoparticles because they serve as building blocks for materials with novel mechanical, optical, electric, magnetic, thermal, chemical, and biological properties. Consequently, the ability to predict and control nanoparticle aggregation in reactors used to synthesize these particles is of prime importance. The traditional approach to modeling colloidal particle aggregation at the reactor scale is to employ mean-field rate equations, also known as population balance equations (PBEs). For example, the case of irreversible aggregation in a well-stirred batch reactor can be represented by the much-studied discrete PBE

\[
\frac{dc_i}{dt} = -\frac{1}{2} \sum_{j \neq k} K_{ij}c_j - c_i \sum_{k=1}^{\infty} K_{ik}c_k
\]

where \(c_i\) is the concentration of particles with mass \(k\) and \(K_{ij}\) is a symmetric matrix of rate constants describing the aggregation of particles with masses \(i\) and \(j\). This PBE can also be formulated in continuous form, and it has been elaborated to include mechanisms such as nucleation, growth, breakage, and feed and removal. More recently, with the introduction of the direct quadrature method of moments, multivariate forms of the PBE have received increased attention, corresponding to an increased interest in predicting and controlling not only the particle size distribution but also particle morphology.

In order to solve (either analytically or numerically) equations of the type (1), the functional form of the aggregation kernel, which depends upon particle transport mechanisms and microscopic details of the particle collision events, must be specified. To this end, the aggregation kernel is often decomposed into the product of a collision efficiency, \(0 < \alpha_i \leq 1\), and a collision frequency function, \(\beta_{ij}\), such that \(K_{ij} = \alpha_i \beta_{ij}\). Approximate expressions for the collision frequency function, \(\beta_{ij}\), have been derived for certain limiting cases, such as when the motion of the aggregates can be considered to be Brownian (particle sizes smaller than the characteristic shear gradients) or for the instance in which particles are large relative to shear gradients but smaller than the Kolmogorov microscale. The derivation of these expressions, however, requires the invocation of a number of ad hoc assumptions, such as the neglect of long range particle–particle interactions and the assumption that all aggregates are spherical. Although the latter assumption can be relaxed so that particles have an arbitrary fractal dimension, \(d_f\), it is still necessary to invoke assumptions concerning the mobility (both translational and rotational) of fractal aggregates. Derivation of an analytical expression for the collision efficiency \(\alpha_i\) is even more problematic, since the probability that an aggregation event occurs upon collision of particles of sizes \(i\) and \(j\) can in general be expected to depend upon many microscopic details including the strength of particle–particle forces, and the morphology, angle of approach, and momenta of the colliding particles. Of course \(\alpha_i\) is averaged over these microscopic collision variables so that it depends explicitly only upon measurable bulk properties and on the particle size variables, \(i\) and \(j\), but in order to perform the required averaging over the microscopic collision variables, an atomistic simulation approach must be used that can generate the relevant particle configuration ensembles.

Atomistic simulation methods such as molecular dynamics (MD) can in principle provide the detailed information concerning collision, aggregation, and breakage events that is needed to derive realistic expressions for aggregation (and breakage) rate kernels, because they explicitly represent all molecules in the system (both solute and solvent) and compute the motion of these molecules using classical Newtonian mechanics. However, in order to carry out such simulations, information is required concerning the interaction forces between all of the constituent molecules. Usually, these forces are assumed to be pairwise additive so that it is only necessary to define force laws between each type of molecule (e.g., solute–solute, solute–solvent, and solvent–solvent). Typically these forces are obtained by differentiating presumed intermolecular potential energy functions (such as the well-known Lennard-Jones potential) fitted to experimental data. These presumed potential energy functions mimic the competition between near-range repulsions arising from the overlap of electronic shells and long-
range attractive Van der Waals forces. Hence, interaction potentials typically display a potential energy minima at intermediate distances that arises from the balance of the longer range attractive forces and short range repulsive forces. More recently, there have been efforts to avoid the use of presumed interaction potentials by instead using coarse-graining procedures to compute these interaction potentials using information obtained from quantum mechanical calculations.\textsuperscript{7,8}

Even when accurate pairwise interaction potentials are available, however, other problems with using the MD approach for simulation of aggregation remain. In particular, the separation in scales between the sizes of the solvent molecules (typically $10^{-10}$–$10^{-9}$ m) and nanoparticle aggregates (usually $10^{-8}$–$10^{-7}$ m) requires an enormous number of solvent molecules to be simulated, especially for dilute systems. For example, consider Figure 1, which shows the CPU time required for each simulation time step as a function of the number of molecules simulated using the MD simulation software LAMMPS.\textsuperscript{10} Results for two sets of MD simulations are shown, each carried out under identical conditions except for the solute/solvent diameter ratio used (equal solute and solvent sizes in one case, solute diameter twice that of the solvent in the other case). It is readily apparent that the CPU time scales approximately linearly with the number of molecules, but that the CPU time grows more rapidly with increasing solute/solvent size ratio. In view of the fact that realistic simulations would require solute/solvent size ratios on the order of at least $10^{-10}$–$10^{-11}$, it is evident that MD simulation of aggregation, even when using nanoscale primary particles, is computationally demanding. Furthermore, the dynamic range of the largest aggregates to the primary nanoparticles can itself be $2$–$3$ orders of magnitude in light-scattering experiments.\textsuperscript{11} Hence, to obtain a meaningful statistical distribution of aggregates, it is clear that very large systems will need to be simulated. All these factors contribute to the conclusion that MD simulation of aggregation with existing simulation packages and hardware is computationally prohibitive.

In order to circumvent the computational limitations that result from the large number of solvent molecules required in MD simulations of nanoparticle aggregation, the Brownian dynamics (BD) approach can be used. In this method, the solute–solvent interactions are incorporated into Langevin equations for solute particles, and therefore there is no need to track solvent molecules explicitly. For example, in an isotropic system if particles are sufficiently small so that they are unaffected by fluid shear, the $i$th solute particle position, $r_i$, and velocity, $v_i$, can be described by

$$\text{dr}_i = v_i \, dt$$

and

$$\text{dv}_i = -\gamma v_i \, dt + \frac{1}{m_i} F(x_i) \, dt + \sqrt{2\gamma \sigma_{i\infty}} \, dW_i$$

In the above equations, $m_i$ is the mass of particle $i$, $\gamma$ is the frictional coefficient, and $F(x_i)$ is the net force exerted on the $i$th particle due to its interactions with all other particles. The last term in eq 3 represents the random force, where $\sigma_{i\infty}$ is the equilibrium velocity variance ($=k_BT/m_i$) and $dW_i$ is a Wiener process increment.\textsuperscript{9} For cases in which the relaxation time for the particle velocities $|\gamma|$ is short compared with the relaxation time for particle position (which includes most cases of practical interest for particles suspended in liquids), the position and velocity Langevin (PVL) equations can be integrated so that only the following position Langevin (PL) equation need be evolved:\textsuperscript{12}

$$\text{dr}_i = \frac{F(x_i)}{m_i \gamma} \, dt + \sigma_{i\infty} \sqrt{\gamma} \, dW_i$$

The advantage of using BD simulations rather than MD simulations in terms of computational cost is evident in Table 1, which compares results for MD simulations (using LAMMPS) and BD simulations (of the position equation and the velocity Langevin equation implemented in an in-house code) of identical systems with an order of magnitude separation in length scales between the solute particles and solvent molecules. In particular, a comparison of the number of simulation time steps executed per second of CPU time demonstrates that there is more than 3 orders of magnitude speedup in the BD simulations as a result of the fact that individual solvent molecules are not simulated, and positions and velocities are calculated only for solute particles. This speedup is a necessity for simulating aggregation in colloidal systems, where the number of solute particles and the aggregate sizes are relatively large.

Although several investigators have employed the BD approach to simulate particle aggregation,\textsuperscript{14–19} we are not aware of any systematic effort to establish the legitimacy and accuracy of this approach with respect to aggregation. Furthermore, it has not been demonstrated that BD simulations of aggregation duplicate the predictions produced by corresponding MD simulations, nor is it understood in general how to establish correspondence between the two types of simulations. In order to address these issues, the following questions must be answered: (1) What are the minimal requirements for numerical convergence of BD simulations of aggregation? (2) Under what conditions is particle aggregation significant in BD simulations? (3) How accurate are BD simulations of aggregation? (4) How can model coefficients for BD simulations of aggregation be obtained from MD simulations or other methods? The remainder of this paper describes efforts to begin to address questions 1–3. Specifically, in section 2, we estimate requirements for convergence of BD simulations of aggregation by considering a simple model problem with a known analytical solution and by computing the deterministic and statistical contributions to the error. In section 3, we carry out a dimensional analysis in order to delineate regions in parameter space where significant aggregation occurs in BD simulations. The regions in parameter space where the PVL to PL reduction are admissible are also identified. In section 4, we consider a model problem for directly comparing predictions of MD and BD simulations of aggregation.
Table 1. Comparison of MD and Position–Velocity Langevin BD Simulation Time for 31 Nonaggregating Solute Particles

<table>
<thead>
<tr>
<th></th>
<th>molecular dynamics</th>
<th>Brownian dynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solvent</td>
<td>solute</td>
</tr>
<tr>
<td>( \sigma ) (m)</td>
<td>( 2.85 \times 10^{-10} )</td>
<td>( 4.0 \times 10^{-9} )</td>
</tr>
<tr>
<td>( m ) (kg)</td>
<td>( 1.33 \times 10^{-26} )</td>
<td>( 3.686 \times 10^{-23} )</td>
</tr>
<tr>
<td>( \epsilon ) (kg m(^2)/s(^2))</td>
<td>( 1.073 \times 10^{-21} )</td>
<td>( 1.646 \times 10^{-20} )</td>
</tr>
<tr>
<td>( N )</td>
<td>146 840</td>
<td>31</td>
</tr>
<tr>
<td>time steps/CPU s</td>
<td>0.06</td>
<td>100</td>
</tr>
<tr>
<td>(1 processor)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>time for ( 10^5 ) steps</td>
<td>115 days</td>
<td>2 h</td>
</tr>
<tr>
<td>(20 processors)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All solvent and solute particle interactions were modeled using Lennard-Jones potentials with well depth \( \epsilon \) and particle radius \( \sigma \). The time increment in both types of simulations was fixed at \( 5 \times 10^{-15} \) s.

![Figure 2. Illustration of the ramp—well potential.](image)

2. Convergence of Brownian Dynamics Simulations

The ultimate goal of performing BD or MD simulations is to extract statistics. For aggregating systems, these statistics are usually the cluster size distribution, or its moments. While the numerical convergence requirements of MD and BD simulations of equilibrium nonaggregating systems are reasonably well understood, the same is not true for aggregating systems. In order to gain an understanding of convergence criteria for BD simulations of aggregation phenomena, information is needed concerning how the error associated with evolving eqs 2 and 3 with finite integration step size \( \Delta t \) affects estimates of aggregation statistics.\(^1\) It is also necessary to determine how these estimates are affected by the averaging procedure (for example by the use of multiple independent simulations or time averaging). Following the standard approach,\(^2\) the error in any estimate can be decomposed into a deterministic and statistical part. The deterministic error is due to the finite integration step size, and it arises from the numerical approximations involved in integrating eqs 2 and 3. In contrast, the statistical error depends on the number of samples. It is important to note that in aggregating systems the number of samples is not the number of particles \( N \), but is the number of independent realizations of the \( N \)-particle system.

Calculation of the deterministic and statistical components of the error associated with using BD simulations requires that a test problem with a known analytical solution be chosen. Any such test problem will by necessity be relatively simple, and we propose one such problem here that bears similarity to the classical Kramer’s problem.\(^3\) Presently, we consider the one-dimensional motion of a single particle immersed in a fluid in the absence of fluid shear and under the influence of the ramp—well potential depicted in Figure 2 and defined by

\[
U(x) = \begin{cases} 
\infty, & x < x_a \\
-x - x_a & \frac{x}{\sigma} - x_a & x_a \leq x \leq L \\
0, & x_a \leq x \leq L \\
\infty, & x \geq L 
\end{cases}
\]

The systematic force in eq 3 (which in the present case is due only to the interaction of a single particle with the ramp—well potential rather than multiple particle—particle interactions) can be found by differentiating the above expression so that \( F_s = -\frac{dU}{dx} \). Hence, the essential feature of the ramp well potential is that it produces a constant force of attraction, in contrast to the more commonly used square well, which is everywhere zero except at the boundaries of the well where the force is singular.

Klyatskin\(^20\) has derived a separable analytical solution for the position-velocity probability density function of a multi-particle system evolving by the position—velocity Langevin equations. Here, we calculate the solution for the single particle position—velocity probability density function, \( p(x,v) \), which can be decomposed into the product \( p(x,v) = p_x p_v \) in the ramp—well test problem. The position probability distribution is given by

\[
p_x = C_x \exp \left( -\frac{U(x)}{k_B T_m} \right)
\]

The velocity probability \( p_v \) is given by the Maxwell distribution function

\[
p_v = \sqrt{\frac{m}{2\pi k_B T_m}} \exp \left( -\frac{mv^2}{2k_B T_m} \right)
\]

The constant \( C_x \) can be found by normalization, and it can subsequently be shown that the probability that the particle lies in the interval \( \sigma < x < x_a \) is given by

\[
p_a = \frac{1 - e^{-\frac{\hat{\epsilon} \left( L - x_a \right)}{\sigma - x_a}}}{1 - e^{-\frac{\hat{\epsilon} \left( L - x_a \right)}{\sigma - x_a}}}
\]

where \( \hat{\epsilon} = \epsilon/k_B T_m \). The probability \( p_a \) can in some sense be considered to be a “trapping” probability corresponding to the system being in an aggregated state. In comparing BD simulation predictions with the analytical solution given by eq 8, we have chosen the system parameters (\( \sigma, \epsilon, x_a, m, T \)) to satisfy two cases with \( p_a = 0.74 \), and \( p_a = 0.90 \). Brownian dynamics simulations were then carried out using one-dimensional versions of the position-velocity Langevin equations in the simulations, initial particle positions were chosen randomly using a uniform distribution in the interval \( \sigma < x < L \), and the initial velocity was chosen to be a Gaussian corresponding to \( T_m \).

As was discussed above, the total error associated with the BD simulations arises from at least two sources. A deterministic error, \( D_p \) is incurred due to the fact that a finite time step \( \Delta t \) must be used to integrate eqs 2 and 3. Furthermore, as a consequence of the fact that only a finite number of samples \( M \) can be computed, a statistical error \( S_p \) is also incurred. Hence, the total error is given by \( e = D_p + S_p \). In ergodic statistically stationary systems the statistical error can be reduced either by averaging over longer times in a single simulation or by carrying out multiple independent simulations. However, in an aggregation-dominated system that produces a single volume spanning cluster, the system can become trapped in a gelled state and
therefore may not sample the accessible states with the proper frequency. Hence, in order to develop convergence criteria that are applicable to general problems involving aggregation including those that produce gelled states, we carry out multiple independent simulations executed using fixed time step sizes, $\Delta t$. Each independent simulation was carried out for $2 \times 10^7$ time steps. For each independent simulation using time step $\Delta t$, the estimate for the probability $p(\tau)$ that the particle resided in the interval $\sigma \leq x < x_0$ was computed. The ensemble average for $M$ such simulations using time step $\Delta t$ is denoted $\{p\}_{\Delta t,M}$. Therefore, the total error $e$ can be decomposed as follows:

$$
e = \{p\}_{\Delta t,M} - p_a = \{p\}_{\Delta t,M} - \{p\}_{\Delta t,\infty} + \{p\}_{\Delta t,\infty} - p_a = S_p + D_p$$

In the above expression $\{p\}_{\Delta t,\infty}$ is the expected value of the trapping probability for an infinite number of independent simulations carried out using an integration time step $\Delta t$. In practice this quantity must be approximated by carrying out a finite but large number of simulations. We approximated $\{p\}_{\Delta t,\infty}$ by choosing $M = 1 \times 10^7$.

The deterministic error $D_p = \{p\}_{\Delta t,\infty} - p_a$ will depend upon the nature of the numerical integration scheme used, and for example using a first order in time method one expects that $D_p \sim \Delta t$. We have verified this prediction and we find that $D_p$ can be kept below 0.06% for $\sigma_a \Delta t/\sigma \leq 0.004$, where $\sigma$ is the particle radius. Assuming that the errors for individual simulations are normally distributed, it can be expected that the statistical error $S_p$ obeys

$$S_p = \{p\}_{\Delta t,M} - \{p\}_{\Delta t,\infty} \sim \frac{1}{\sqrt{M}}$$

Figure 3 demonstrates that this prediction is indeed fulfilled. Also it shows that even for high $p_a = 0.90$, which corresponds to the case of diffusion-limited aggregation, the statistical error magnitude remains similar to that for $p_a = 0.74$. Therefore, the statistical error of 30% for a single simulation requires that at least 100 simulations be performed in order to reduce the statistical error so that it is comparable with the deterministic error, $D_p$. Moreover, because these results were obtained for a simple one-dimensional simulation with only a single particle, the number of simulations required to converge the predictions of BD simulations of the aggregation of a large number of particles may in many cases be prohibitive or may require the development of other methods for more rapidly reducing the statistical error. Furthermore, the rate of convergence will depend on the aggregation statistic that one seeks to extract from the BD simulations, with higher moments of the cluster size distribution converging more slowly. This analysis also demonstrates that calculations from a single BD simulation of an aggregation process are likely not converged statistically.

### Table 2. Characteristic Length, Time, and Velocity Scales in BD Simulations\(^a\)

<table>
<thead>
<tr>
<th>parameter</th>
<th>dimension</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>length</td>
<td>particle size</td>
</tr>
<tr>
<td>$r_c$</td>
<td>length</td>
<td>interaction potential cutoff distance</td>
</tr>
<tr>
<td>$1/\gamma$</td>
<td>time</td>
<td>time for force relaxation</td>
</tr>
<tr>
<td>$\tau = \alpha \sqrt{mk_BT_m}$</td>
<td>time</td>
<td>force time scale</td>
</tr>
<tr>
<td>$\sqrt{\left(k_BT_m/m\right)}$</td>
<td>velocity</td>
<td>velocity standard deviation</td>
</tr>
</tbody>
</table>

\(^a\) The parameter $\epsilon$ represents the intermolecular potential energy minimum, or well depth.

### 3. Aggregation Regime

In principle, given sufficient computational power and memory, converged BD simulations of aggregation can be executed if pairwise particle interaction potentials are known. However, it is not necessarily the case that significant aggregation will always occur in these systems, depending upon several system parameters. In this section we develop two important nondimensional parameters and use them to characterize clustering outcomes and thereby delineate a criterion for aggregation to occur in BD simulations.

Table 2 lists several relevant characteristic scales for BD simulations of interacting particles in the absence of fluid shear, and selecting from among these we identify the dimensionless reduced potential well depth and diffusivity

$$\hat{\xi} = \frac{\epsilon}{k_BT_m}$$

$$\hat{D}_\infty = \frac{D_\infty}{\sigma \sqrt{k_BT_m}}$$

where the infinite dilution diffusivity is $D_\infty = k_BT/m\gamma$. The particle volume fraction is also an important dimensionless parameter that is likely to influence clustering outcomes, but we will consider only cases of low particle loading (<1% by volume) so that variations in this parameter can be neglected. The product $\hat{\xi} \hat{D}_\infty$ can be interpreted as the ratio of the frictional and systematic force time scales. [Although there are three terms in the BD velocity evolution in eq 3, the coefficient of the noise term is related to that of the frictional term by the fluctuation–dissipation theorem. Therefore, there are only two independent timescales in that equation.] Therefore, if $\hat{\xi} \hat{D}_\infty \ll 1$ (as is the case for nanoparticles suspended in liquids) there is sufficient separation in time scales such that the BD simulations can be carried out using a position-only Langevin scheme obtained by integrating eq 3:\(^12\)

In order to quantify the clustering of particles, we calculate the extent of aggregation, $0 \leq \xi < 1$, defined as

$$\xi = 1 - \frac{M(t)}{M(0)}$$

where $M_0$ is the zeroth moment or total concentration of clusters. Hence $\xi$ is an aggregation progress variable that approaches unity as the system mass accumulates in a single cluster. Three-dimensional Brownian dynamics simulations were carried out using our in-house BD code to evolve 10000 primary particles.
Table 3. Simulation Parameters Used to Produce Figure 4

<table>
<thead>
<tr>
<th>parameter</th>
<th>description</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>no. of particles</td>
<td>10 000</td>
</tr>
<tr>
<td>$f_r$</td>
<td>particle vol fraction</td>
<td>0.005</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>particle diameter</td>
<td>3.4 x 10^{-10} m</td>
</tr>
<tr>
<td>$T$</td>
<td>temp</td>
<td>121 K</td>
</tr>
<tr>
<td>$\alpha_f/\alpha_m$</td>
<td>dimensionless friction coeff</td>
<td>1.31</td>
</tr>
</tbody>
</table>

* Particle interactions were modeled using Lennard-Jones potentials, and simulations were carried out using an in-house BD code.

Figure 4. Clustering index (see color legend) as a function of reduced interaction potential well depth, $\xi$ and reduced diffusivity, $D^\infty$. Each curve represents constant $\hat{D}$. The region bounded by $\hat{D}^\infty < 1$ represents the regime of validity of the position and velocity Langevin to PL reduction.

with random non-overlapping initial positions. Particle–particle interactions were modeled by Lennard-Jones potentials, and simulations were continued until the clustering index $\xi$ approached steady state. Other simulation details are provided in Table 3. Simulations were carried out for several fixed values of $\hat{D}^\infty$, and the results are shown in Figure 4. It is evident that the extent of aggregation depends on the value of the reduced interaction potential well depth, $\hat{D}$, and in fact $\hat{D} > 2$ is a necessary condition for significant aggregation to occur. Hence, for sufficiently small values of $\hat{D}$ corresponding to high temperatures or shallow interaction potential well depths, colliding particles have low probability of sticking because thermal fluctuations are large enough for the particles to overcome the potential energy barrier that otherwise would keep them together. Therefore, $\hat{D}$ controls how “sticky” the particles are and it must play a major role in determining the collision efficiency function, $\alpha_m$. In contrast, $\xi$ is insensitive to the value of the reduced diffusivity. This latter observation is consistent with the fact that the Gibbs stationary solution of the Fokker–Planck equation corresponding to eqs 2 and 3 yields a Boltzmann distribution of particle coordinates independent of diffusivity.

4. Simulation Accuracy

Although the Brownian dynamics method has been used by many investigators to simulate aggregation processes, little consideration has been given to the accuracy of such simulations even if statistically converged results can be obtained. Here we use the word “accuracy” in reference to how well the BD simulation predictions of aggregation reproduce those obtained from corresponding MD simulations, since the BD technique is essentially a reduction of the MD method. Because this reduction is obtained by eliminating the explicit representation of solvent molecules and replacing solvent–solute interactions with a mathematical model consisting of a stochastic fluctuating force and a deterministic frictional term, any discrepancies between predictions of the two methods are likely due to breakdowns in the assumptions and approximations implicit in these terms.

The accuracy of BD simulations for dilute nonaggregating systems has previously been considered by Giro et al. These investigators considered the situation in which the solute particles are identical to the solvent molecules, and they showed that the BD simulations closely reproduce the equilibrium solute–solute radial distribution function, $g(r)$. However, they also found that the BD-computed solute diffusivities are larger than those predicted by the MD method, and they attributed this discrepancy to the fact that the frictional coefficient $\gamma$ in the Langevin eq 3 is assumed to be constant, whereas a more realistic description (particularly for liquids) requires that the frictional coefficient be replaced by a time-dependent memory function. The fact that the BD method can accurately compute the equilibrium solute–solute radial distribution function and yet incur noticeable error in the calculation of diffusivity is perhaps to be expected for reasons mentioned in the previous section—namely that the stationary solution of the Fokker–Planck equation is independent of the diffusivity. Hence, one expects that in general, BD predictions of system dynamics will not match the predictions of corresponding MD simulations, but that equilibrium quantities can be well-predicted by BD simulations. If follows, therefore, that BD simulations of the early stages of an aggregation process far from equilibrium may differ substantially from corresponding MD calculations. In spite of this observation (and the fact that MD simulation of systems with large aggregate–solvent size scale separation is not feasible), we have endeavored to perform MD simulations with sufficiently large numbers of solute particles such that a particle size distribution can be computed (at least during the early stages of aggregation) with the aim of directly comparing these MD predictions with corresponding BD calculations.

We seek a computationally tractable model system of aggregation appropriate for comparison of BD and MD methods, within the limitations discussed above. Consequently, we follow Giro’s example and carry out simulations using equal-diameter Lennard-Jones solute and solvent particles. However, in contrast with the work of Giro, the solute–solute interaction potential well depth, $\hat{\epsilon}$, was chosen such that solute aggregation was favored (as was discussed in the previous section). Additionally, the ratio of the mass of a single solute primary particle to a solvent molecule, $m_{\text{solute}}/m_{\text{solvent}} = 50$, was chosen to be relatively large to ensure that the solute particles had lower mobility than the solvent molecules, despite the fact that they have equal size. All MD simulations were carried out using LAMMPS on an IBM eServer Blue Gene which consists of 1024 dual-core PPC440 CPUs running at 700 MHz, with 512 MB of RAM per node. Each run on the Blue Gene took up to 5 h on 1024 CPUs, and other simulation details are listed in Table 4. In the case of BD simulations, the position-velocity equations were used because the position-only reduction is not applicable for this set of parameters.

In order to determine the accuracy of the BD simulations for aggregating systems, in Figure 5 we compare the extent of aggregation $\xi$ (as defined in 12) with that obtained from MD simulations for the system described in Table 4. It is clear that on the basis of the dimensionless time used to compare the two
methods, the BD calculation predicts significantly more aggregation than does the MD simulation. The large disparity between the two curves suggests that the proper time scaling to be employed in order to provide a better basis of comparison for the two simulation methods, we shall compare the predicted cluster size distributions computed using corresponding MD and BD simulation methods. Consequently, it can be concluded that the BD simulations produce different cluster size distributions than the MD simulations, independent of any difficulties in comparing them due to lack of information concerning the proper time scaling to be employed.

Figures 7 and 8 show such plots for the MD and BD cases, respectively. Despite the relatively large statistical error associated with only carrying out a small number of independent simulations, in both cases the cluster size distributions do appear to fall on universal curves when plotted using eq 13. However, comparison of Figures 7 and 8 demonstrates that the shape of the scaling functions are clearly different for the MD and BD simulations, in both cases the cluster size distributions do appear to fall on universal curves when plotted using eq 13. However, comparison of Figures 7 and 8 demonstrates that the shape of the scaling functions are clearly different for the MD and BD simulations. Consequently, it can be concluded that the BD simulations produce different cluster size distributions than the MD simulations, independent of any difficulties in comparing them due to lack of information concerning the proper time scaling to be used. In particular, we see that the MD simulations generate

\[ N_k = s^{-2}(t)\phi(k/s(t)) \]  

(13)

where \( N_k \) is the concentration of clusters containing \( k \) monomers, \( s(t) \) is the mass-averaged particle size, and \( \phi \) is a scaling function. If eq 13 is valid, then a plot of \( s^2N_k \) vs \( k/s \) should collapse the cluster size distributions for all sufficiently large values of \( t \) such that the self-preserving regime has been reached. Figures 7 and 8 show such plots for the MD and BD cases, respectively. Despite the relatively large statistical error associated with only carrying out a small number of independent simulations, in both cases the cluster size distributions do appear to fall on universal curves when plotted using eq 13. However, comparison of Figures 7 and 8 demonstrates that the shape of the scaling functions are clearly different for the MD and BD simulations. Consequently, it can be concluded that the BD simulations produce different cluster size distributions than the MD simulations, independent of any difficulties in comparing them due to lack of information concerning the proper time scaling to be used. In particular, we see that the MD simulations generate

Table 4. Simulation Parameters Used to Produce Figure 5

<table>
<thead>
<tr>
<th>parameter</th>
<th>description</th>
<th>value (MD)</th>
<th>value (BD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{solvent} )</td>
<td>no. of solvent particles</td>
<td>809 787</td>
<td>n/a</td>
</tr>
<tr>
<td>( N_{solute} )</td>
<td>no. of solute particles</td>
<td>10 000</td>
<td>10 000</td>
</tr>
<tr>
<td>( 1/k_BT_{sol} )</td>
<td>reduced solute–solute well depth</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>( 1/k_BT_{sol} )</td>
<td>reduced solute–solvent well depth</td>
<td>2\sqrt{2}</td>
<td>n/a</td>
</tr>
<tr>
<td>( 1/k_BT_{sol} )</td>
<td>reduced solvent–solute well depth</td>
<td>1</td>
<td>n/a</td>
</tr>
<tr>
<td>( f_c,solvent )</td>
<td>solvent vol fraction</td>
<td>0.44</td>
<td>n/a</td>
</tr>
<tr>
<td>( f_c,solute )</td>
<td>solute vol fraction</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>particle diameter</td>
<td>(3.4 \times 10^{-10} ) m</td>
<td>(3.4 \times 10^{-10} ) m</td>
</tr>
<tr>
<td>( D_{sol}/\alpha_{sol} )</td>
<td>dimensionless diffusion coeff</td>
<td>n/a</td>
<td>0.262</td>
</tr>
<tr>
<td>( \alpha_{sol}/\alpha_{sol} )</td>
<td>dimensionless simulation time</td>
<td>329.8</td>
<td>329.8</td>
</tr>
</tbody>
</table>

* Particle interactions were modeled using Lennard-Jones potentials. MD simulations were carried out using the LAMMPS software package.
cluster size distributions that decay monotonically in size, whereas the BD simulations produce cluster size distributions that exhibit a maxima in $N_k$, as illustrated in Figures 9 and 10 for clusters with $d_f \approx 2.6$, which is a relatively large value indicating that the clusters are quite compact. Indeed, this fractal dimension is comparable to the value produced in processes with diffusion-limited growth by other methods. Although the Giro et al. study showed that in nonaggregating dilute systems the potential of mean force for BD could be inferred by curve-fitting the equilibrium pair correlation function $W(r) = -k_BT \ln g_{ss}(r)$, this approach is not feasible in aggregating systems. One reason is because the pair correlation function is itself evolving as the system aggregates. It is possible that matching the pair correlation function from a BD simulation to the corresponding MD simulation of an aggregating system is a necessary condition for an accurate simulation. Subramaniam and Pai outline an approach for deriving the evolution equation of the pair correlation function in MD simulations that reveals the importance of the relative velocity and relative acceleration between particle pairs, conditional on their separation distance. It is possible that matching the conditional relative acceleration statistics from MD to BD through the potential for mean force specification can guarantee the matching of the pair-correlation function.

However, it is important to note that the cluster size distribution that determines important aggregation statistics contains more information regarding connectivity of the monomers in clusters that is not available in the pair-correlation function. The requirement for matching moments of the cluster size distribution, and their relation to the pair correlation function, can provide a rational specification for model coefficients in the BD equations.

Clearly the progress of aggregation as characterized by $\xi$ is another important quantity that BD simulations should capture accurately. Although this may seem to be closely related to the accuracy of BD in predicting the diffusivity of monomers, the issues involved are somewhat more complex. As noted earlier, even the notion of computing a diffusivity from mean-squared displacements of the monomers is questionable in aggregating systems, and therefore it is unclear whether the trends in predicted diffusivity from dilute nonaggregating BD simulations can be used to infer the physics of aggregating systems. Second, it seems more likely that the mean relative velocity between particle pairs conditional on their separation (or the implied second-order diffusivity) determines aggregation, rather than the single particle diffusivity.

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Literature Cited


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