

# Monte Carlo Simulation for Aggregative Mixing of Nanoparticles in Two-Component Systems

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ABSTRACT: Gas-to-particle synthesis under high temperature is one of the most important methods for producing multicomponent nanoparticles. The volume enlargement of particles due to aggregation accompanies the component mixing within particles in a nonreactive system. To tailor nanocomposites, it is essential to gain an insight into the dynamic evolution of compositional distributions. In this paper, the differentially weighted Monte Carlo (DWMC) method for population balance modeling is used to simulate the process of aggregative mixing. On the methodological end, a new shift action is proposed to regulate a limited number of simulation particles to be distributed as homogeneously as possible over high-dimensional and inhomogeneous joint space of multiple components, where some simulation particles in less-populated regions are split into more simulation particles in order to increase sample space for stochastic statistics and then fatigue against statistical noise, at the same time a certain number of simulation particles in densely populated regions are randomly removed from the simulation to reduce computational demands. The DWMC with the new shift action is used to simulate the aggregative mixing process of bicomponent nanoparticles with compositional-independent or -dependent Brownian coagulation kernel in the free-molecular regime. It is found that the compositional distributions satisfy self-preserving formulation as the particle size distribution in monocomponent systems; and the extent of the time evolution of the degree of mixing (the mass-normalized power density of excess component A) corresponds with that of self-preserving distributions. The compositional distributions and the degree of mixing predicted by the DWMC agree well with theoretical models, while the constant-number method (using equally weighted simulation particles) fails in the more advanced stages of aggregative mixing.

## 1. INTRODUCTION

The behavior of multicomponent particles is of interest in a variety of processes involving dispersed systems, such as atmospheric aerosols, synthesis of nanocomposites, polymerization, granulation, combustion, crystallization, precipitation, catalytic chemical processes, food processes, etc. In these processes, the binary collision of particles forming larger particle units often represents the main mechanism, whereas nucleation, breakage, condensation, surface growth, and sedimentation can also contribute to the dynamic evolution of the particle population. These binary collisions can be denoted as coagulation, agglomeration, aggregation, or coalescence, with different definitions being used in different fields of science. In this paper, we apply the term "aggregation", as the actual form of the particle is not considered. In a nonreactive system, the volume enlargement of particles due to aggregation accompanies the component mixing within particles. The process is referred to as "aggregative mixing" by some authors.<sup>1,2</sup>

One of the most interesting issues, in addition to the dynamic evolution of particle size distribution (PSD), is the distribution of the individual components over the aggregates. The governing equation for aggregative mixing is given by extending Smoluchowski's equation for single-component aggregation to a multivariate population balance equation (PBE). A simpler bivariate PBE for bicomponent aggregative mixing in spatially homogeneous

systems is given by

$$\begin{aligned} \frac{\partial n(m_{\rm A}, m_{\rm B}, t)}{\partial t} &= \frac{1}{2} \int_{0}^{m_{\rm A}} \int_{0}^{m_{\rm B}} \beta(m_{\rm A} - m_{\rm A}^{'}, m_{\rm B} \\ &- m_{\rm B}^{'}; m_{\rm A}^{'}, m_{\rm B}^{'}) n(m_{\rm A} - m_{\rm A}^{'}, m_{\rm B} - m_{\rm B}^{'}, t) n(m_{\rm A}^{'}, m_{\rm B}^{'}, t) \, \mathrm{d}m_{\rm A}^{'} \, \mathrm{d}m_{\rm B}^{'} \\ &- n(m_{\rm A}, m_{\rm B}, t) \int_{0}^{\infty} \int_{0}^{\infty} \beta(m_{\rm A}, m_{\rm B}, m_{\rm A}^{'}, m_{\rm B}^{'}, t) n(m_{\rm A}^{'}, m_{\rm B}^{'}, t) \, \mathrm{d}m_{\rm A}^{'} \, \mathrm{d}m_{\rm B}^{'} \end{aligned}$$
(1)

The underlying nature of eq 1 is that a two-component aggregation event between a particle of state  $(m_A, m_B)$  and a particle of state  $(m_A, m_B)$  results in a new particle of state  $(m_A + m_A, m_B + m_B)$ and the death of the two parent particles. A bicomponent particle is characterized by the masses  $m_A$  and  $m_B$  of the two components within the particle. In eq 1,  $n(m_A, m_B, t)$  is the number density function at time t such that  $n(m_A, m_B, t) dm_A dm_B$  represents the number concentration of particles in the mass range of one component,  $m_A$  to  $m_A$ +  $dm_A$ , and the mass range of another component,  $m_{\rm B}$  to  $m_{\rm B}$  + d $m_{\rm B}$ ;  $\beta(m_{\rm A}, m_{\rm B}; m_{\rm A}, m_{\rm B})$  is the aggregation rate coefficient between a particle of state  $(m_A, m_B)$  and another particle of state  $(m_A, m_B)$ .

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There is a limited number of studies dealing with a theoretical analysis of the general dynamic behavior of bicomponent mixing. Lushnikov has investigated aggregative mixing of two components with composition-independent kernels analytically.<sup>3</sup> Gelbard and Seinfeld have extended the analysis of multicomponent aggregation to continuous systems with an arbitrary number of components.<sup>4</sup> Krapivsky and Ben-Naim have developed a twoparameter scaling law for analytical solution of bicomponent aggregation with a constant aggregation kernel, which is characterized by Gaussian statistics.<sup>5</sup> Vigil and Ziff further extended the scaling theory of bicomponent aggregation to nonconstant kernels that may be composition-dependent or -independent, and showed that the compositional distribution within each size class is a Gaussian function, irrespective of the kernel and the initial condition.<sup>6</sup> More recently, Matsoukas and his colleagues have formulated the PBE for bicomponent aggregation with composition-independent or -dependent kernels and derived equations for the evolution of the bivariate distribution (in size and composition), the size distribution, the compositional distribution, and the degree of mixing.<sup>1,2,7</sup> Worth noting is that they found from the mean-field PBEs that the mass-normalized power density of excess solute, which is utilized to quantify the degree of mixing in the population, always reaches steady-state value in all cases, while aggregation proceeds and large size particles are formed. Note that in this terminology the two-component system is composed of a solute A and a solvent B, but the term solute can also be used to denote the minor component. Although these above-mentioned theoretical models can give analytical solutions for special cases with considerable simplifications of specific kernels (e.g., constant,<sup>3,4,8</sup> sum,<sup>8,9</sup> product,<sup>8</sup> and composition-independent<sup>1,2</sup> kernels) or specific initial bivariate distributions (e.g., monodisperse,<sup>3,4,8,9</sup> bidisperse,<sup>3,4,8,9</sup> and exponential<sup>3,6</sup> distributions) or even both, our aim is to find a method which enables precise numerical solutions of the bivariate population balance without simplifications.

The numerical solution of the bivariate PBE eq 1 is challenging due to the double integral and the nonlinear behavior of aggregative mixing. Basically, it is possible to distinguish between deterministic methods based on differential equations and stochastic methods. The deterministic methods directly calculate the double integral either through an appropriate discretization scheme such as in sectional methods or by quadrature which is applied in the method of moments. Among the sectional methods for aggregative mixing the following methods have been applied: the fixed pivot technique,<sup>10–12</sup> the cell average technique,<sup>13</sup> the finite volume method,<sup>14</sup> the finite element method,<sup>15</sup> and the high-resolution method.<sup>16</sup> The momentbased methods include the quadrature method of moments<sup>17</sup> and the direct quadrature method of moments.<sup>18</sup> These deterministic methods are computationally less demanding and can be combined with computational fluid dynamics (CFD) to simulate spatially dependent aggregative mixing. However, if more than two internal particle properties have to be included in population balance equations in the simulation, these deterministic methods lead to too complicated mathematical equations. As an example we cite here multicomponent nanoparticle synthesis in the gas phase at high temperature where in addition to chemical composition and size also the surface area of the aggregates has to be described during process simulation. On the contrary, the stochastic methods, or the population balance-Monte Carlo (PB-MC) methods, which directly simulate the dynamic evolution of a finite sample of particles having specific sizes and compositions

using a Monte Carlo (MC) technique, are capable of dealing with high-dimensionality problems (so-called multivariate population balances) in a simple and straightforward manner. The stochastic methods can also be divided into two classes: the "particle-based algorithm" and the "species-based algorithm" (in the nomenclature of Laurenzi et al, they are "particle accounting algorithm" and "species accounting algorithm";8 while Kraft et al. used "mass flow algorithm" and "direct simulation algorithm" to distinguish them<sup>19</sup>). With regards to the particle-based algorithm, the particle population is represented by a finite number of simulation particles, each of which is identified by several internal variables such as size and composition. By simulating the dynamic evolution of these simulation particles the statistical behavior of the population is determined. The constant-volume method,  $^{20-22}$  stepwise constant-volume method,  $^{23-25}$  time-driven direct simulation Monte Carlo method,  $^{26,27}$  constant-number (CN) method,  $^{1,2,7,28-30}$  differentially weighted (DW) method,<sup>31-35</sup> and majorant-kernel method<sup>36</sup> belong to the particle-based algorithm. These MC methods differ in the treatment of time-step (time-driven or event-driven), the restoration of the number of simulation particles (constant number or stepwise restoration), particle weighting scheme (equally weighted or differentially weighted), and the stochastic model (normal Markov model or jump Markov model). Because the history of each simulation particle can be retained, the extension of these MC methods from monovariate systems to multivariate systems is in principle only by assigning multiple internal variables (in this paper, additional to particle volume the mass of chemical components) to individual simulation particles. Obviously, the direct extension does not increase the complexity of the MC code, while the numerical operation increases linearly as the increment of internal variables.<sup>8</sup> In species-based algorithm, the particles with size in a specified interval are viewed as pseudochemical species, and the stochastic simulation algorithm for chemical kinetics is adopted to define the state of an aggregating system in terms of "aggregate species".<sup>22</sup> The species-based algorithm also has a variety of different implementations by different researchers such as Laurenzi et al,<sup>8</sup> Irizarry,<sup>37,38</sup> Kraft et al,<sup>39,40</sup> and Debry et al.<sup>41</sup> Although these stochastic methods exhibit an excellent improvement in efficiency and memory demand compared to a traditional particlebased algorithm (direct simulation Monte Carlo), they are usually at the cost of complicated algorithms and are less sensitive to the innate fluctuations for aggregation processes which are also stochastic in nature.

Owing to the dramatic increase in computational power over the past decade, the particle-based algorithm is increasingly used in fields where the population is characterized by several internal variables, for example volume and composition. Because the numerical accuracy of the stochastic algorithm increases with the number of simulation particles but its computational efficiency decreases with increasing particle number, the sample size has to be controlled within appropriate bounds to attain an optimal combination of high accuracy and high efficiency. For this requirement, a constant number of simulation particles throughout the simulation is highly recommended. In this respect, the constant-number method by Matsoukas et al<sup>28-30</sup> and the differentially weighted method by the authors<sup>31-34,42,43</sup> are two appropriate candidates. On the other hand, it must be noted that the MC method still leads to a great deal of statistical noise in the distribution functions if there is an insufficient number of simulation particles in a specific region of the internal variables.

This becomes especially clear for bicomponent aggregation because even when millions of simulation particles are used, there may still be only few or even no simulation particles at the edges of the compositional distributions. This makes it impossible to determine the compositional distributions in this region using a MC method. To determine accurately the distributions of internal variables over their full spectrum, not only the total number of simulation particles but also the number of simulation particles of all specified sections of the internal variables should be controlled within appropriate bounds. In other words, it is necessary to specify a finite number of simulation particles to be distributed homogeneously over the multidimensional joint space of internal variables, rather than to let them evolve freely. In the constant-number method, the number of simulation particles at the edges of the size distribution is very limited (see Figure 9 in ref 34). The constant-number method does not allow the restriction of the number of simulation particles in each section of distributions of internal variables within prescribed bounds due to its inherent equally weighting scheme. On the contrary, in the differentially weighted method, 34,35 we proposed a special action to limit the number of simulation particles in densely populated regions and to increase their number in lesspopulated regions by splitting some simulation particles in lesspopulated regions into more simulation particles and randomly removing some simulation particles in densely populated regions from the simulation. This "shift" action can only be used by a differentially weighted method as the action necessitates consideration and recalculation of individual weights. However, the original shift action described in refs 34 and 35 may slightly disturb dispersed systems, especially particle mass concentration, because of the random removal of a certain number of simulation particles. Furthermore, although the simulation particle number in the differentially weighted method is constant between two shift actions, the shift action changes the number of simulation particles (in most of cases, an increase) because the number of added simulation particles may be unequal to that of removed simulation particles. One of aims of this paper is to improve the shift action, shown for a multivariate population balance.

Another aim of this paper is to simulate realistic cases of aggregative mixing leading to nanocomposite particles. Nanocomposite particles having special properties such as superconductivity, superparamagnetism, or increased catalytic activity, can be produced from a mixture of precursors.<sup>44</sup> In that case, Brownian aggregation in the free molecular regime is one of the most important formation mechanisms, and the compositional distribution over the aggregates largely determines the functionality of the composite nanoparticles. Thus, insight into the evolution of compositional distribution is important for optimizing the synthesis process and for tailoring functional particles. To the best of our knowledge, there exists no study for aggregative mixing of nanocomposite particles with Brownian coagulation kernel in the free-molecular regime. The Brownian aggregation kernel in the free-molecular regime is either composition-independent or compositional-dependent kernel, depending on whether the material density of the components is equal or not, respectively. We will utilize two different MC methods, the constant-number method<sup>30</sup> and the differentially weighted method,<sup>35</sup> to simulate a typical case of aggregative mixing of nanoparticles. These simulation results will be compared with available theoretical predictions. On the one hand, the performance of two MC methods can be evaluated; on the other hand, the usability of available theoretical models is assessed.

This paper is organized as follows: in section 2.1, the differentially weighted method for multivariate population balance is briefly introduced, including its theoretical model and numerical realization. Section 2.2 describes an improved shift action which limits the number of simulated particles below a specified value and leads to less stochastic fluctuations. Section 3.1 shows some definitions relative to two-component aggregation; section 3.2 shows the results for composition-independent aggregative mixing of nanoparticles using the two MC methods, and composition-dependent aggregative mixing of nanoparticles is discussed in section 3.3.

## 2. THEORY AND METHODS

**2.1. The Theoretical Model and Numerical Realization.** We have already proposed a differentially weighted MC (DWMC) method for particle coagulation in monovariate systems.<sup>32,34</sup> The DWMC method can be directly extended to two-component coagulation processes as follows:<sup>35</sup>

At the start of the simulation, simulation particles are (1)differentially weighted on the basis of the initial compositional distributions. First, two individual compositional spectra are respectively divided into intervals by laws which can be freely adapted to the problems to be solved, resulting in a sectionalized two-dimensional space of compositional distribution. The section (p,q) represents particles having component masses centered at  $(m_{A,p}, m_{B,q})$ , to be more precise: particles having A-component masses between  $m_{A,p}^-$  and  $m_{A,p}^+$  and B-component masses between  $m_{B,p}^-$  and  $m_{B,p}^+$ , and the number concentration of particles in this section is  $n(m_{A,p}, m_{B,q}, 0) \times$  $(m_{\rm A,p}^+ - m_{\rm A,p}^-)(m_{\rm B,p}^+ - m_{\rm B,p}^-)$ . The real particles from this section are represented by a certain number of weighted simulation particles. The mean weight of simulation particles for the section (p,q) is thus calculated as

$$\overline{w}_{pq}(m_{A,p}, m_{B,q}) = n(m_{A,p}, m_{B,q}, 0)(m_{A,p}^{+} - m_{A,p}^{-})$$
$$\times (m_{B,q}^{+} - m_{B,q}^{-})V/N_{s}(m_{A,p}, m_{B,q})$$
(2)

where  $N_s(m_{A,p},m_{B,q})$  is the number of simulation particles located at the section (p,q); V is the volume of the simulated system. In the DWMC method,  $N_s$  is prescribed to be more than a fixed minimum number  $N_{s,min}$ but less than a maximum number  $N_{s,max}$ . Sections where the number density of real particles is high are thus designated to have simulation particles with larger weight values than sections where number density is low.

(2) The time step is determined from local mean-field coagulation rate:

$$\Delta t = pN_{\rm st} / \sum_{i=1}^{N_{\rm st}} (VC'_i) \tag{3}$$

where the parameter *p* is recommended to have values among  $2/N_{st}$  and 0.05;  $N_{st}$  is the total number of simulation particles in the system;  $C'_i$  (with dimension of m<sup>-3</sup> · s<sup>-1</sup>) is the total aggregation rate of simulation particle *i*.  $C'_i$  is calculated from the probabilistic aggregation rule for an aggregation event between two differentially weighted simulation particles.<sup>32,34</sup> In this rule, for a aggregation event between simulation particle *i* and *j*, it is imagined that each real particle from *i* undergoes a real coagulation event with a probability of min( $w_i w_i$ )/ $w_i$ , and each real particle from *j* does so with a probability of  $\min(w_i, w_j)/w_j$ , where  $w_i$  and  $w_j$  are the private weights of *i* and *j*, respectively.  $C'_i$  is thus calculated as<sup>32,34</sup>

$$C_{i}^{'} = \frac{1}{V^{2}} \sum_{j=1, i \neq j}^{N_{st}} \left[ \frac{2\beta_{ij}w_{j}\max(w_{i}, w_{j})}{w_{i} + w_{j}} \right] = \frac{1}{V^{2}} \sum_{j=1, j \neq i}^{N_{st}} \beta_{i}^{'}$$
(4)

where  $\beta_{ij}$  is the aggregation kernel between particle *i* and particle *j*, m<sup>3</sup> · s<sup>-1</sup>;  $\beta_{ij}$  is a normalized kernel that relates not only to the states (e.g., masses) but also to the weights of the two simulation particles.

It has to be noted that the DWMC method can evolve either in event-driven mode or in time-driven mode according to the value of parameter *p*. If  $p = 2/N_{stv}$  the resultant time-step,  $2/(V\Sigma C_i)$ , is just the waiting time between two successive aggregation events, and the DWMC method evolves in the event-driven mode, where only one aggregation event occurs within this time-step. If  $p > 2/N_{str}$  there are  $pN_{st}/2$  coagulation events in average within the time-step and the DWMC method evolves in the time-driven mode. The event-driven mode is more accurate because aggregation events are fully uncoupled, while the time-driven mode is faster because more events are simulated within one time step. In the following simulation, time-driven mode is used, and p = 0.01.

- (3) Within the time step Δt the interacting particle pair(s) is (are) selected with probability β'<sub>ij</sub>/Σ<sub>i</sub>Σ<sub>j,j≠i</sub>β'<sub>ij</sub>. Either the cumulative probabilities method or the acceptance-rejection method can be adopted to determine the coagulated pair(s) in either event-driven mode or time-driven mode, as described in ref 35.
- (4) An aggregation event results in simulation particles with new states and weights according to the probabilistic aggregation rule. As for the *i*-*j* aggregation event, two new simulation particles replace the "old" particles *i* and *j*, as formulated by

$$\text{if } w_{i} \neq w_{j} \begin{cases} w_{i}^{*} = \max(w_{i}, w_{j}) - \min(w_{i}, w_{j}); m_{i}^{*} = m_{k}|_{w_{k} = \max(w_{i}, w_{j})}; v_{i}^{*} = v_{k}|_{w_{k} = \max(w_{i}, w_{j})}; m_{A,i}^{*} = m_{A,k}|_{w_{k} = \max(w_{i}, w_{j})}; \\ m_{B,i}^{*} = m_{B,k}|_{w_{k} = \max(w_{i}, w_{j})}; \\ w_{j}^{*} = \min(w_{i}, w_{j}); m_{j}^{*} = m_{i} + m_{j}; v_{j}^{*} = v_{i} + v_{j}; m_{A,i}^{*} = m_{A,i} + m_{A,j}; m_{B,i}^{*} = m_{B,i} + m_{B,j} \end{cases}$$

$$\text{if } w_{i} = w_{j}, \begin{cases} w_{i}^{*} = w_{i}/2; m_{i}^{*} = m_{i} + m_{j}; v_{j}^{*} = v_{i} + v_{j}; m_{A,i}^{*} = m_{A,i} + m_{A,j}; m_{B,i}^{*} = m_{B,i} + m_{B,j}; \\ w_{j}^{*} = w_{j}/2; m_{j}^{*} = m_{i} + m_{j}; v_{j}^{*} = v_{i} + v_{j}; m_{A,i}^{*} = m_{A,i} + m_{A,j}; m_{B,i}^{*} = m_{B,i} + m_{B,j} \end{cases}$$

$$(5)$$

where the asterisk indicates a new value of weight or state after the aggregation event;  $m_i$  and  $v_i$  are the total mass and volume of simulation particle *i*;  $m_{A,i}$  and  $m_{B,i}$  are the mass of component A and component B in simulation particle *i*. It is obvious eq 5 satisfies the laws of conservation of mass, and also keeps the number of simulation particles constant. The particle diameter (*d*) which is necessary for calculating the aggregation kernel is obtained from particle volume, assuming the aggregates rapidly attain a spherical shape due to fast coalescence or sintering.

- (5) The total aggregation rate of each particle is updated after  $\Delta t$  using the smart-bookkeeping technique.<sup>34</sup>
- (6) When certain conditions are reached, for example, when the number concentration of real particles is halved, a shift action is performed which restricts the number of simulation particles in predefined size intervals of each component space within prescribed bounds. Section 2.2 describes this shift action in detail.
- (7) Step 2-6 are repeated until the desired end time.

**2.2.** Improving the Shift Action. 2.2.1. The Original Shift Action. First the original shift action for two-component aggregation is briefly introduced.<sup>35</sup> It is numerically realized as following: First, the distribution of each component is sectionalized by some prescribed laws (e.g., logarithmical spaced sections for an initially continuous distribution) and the number of simulation particles in the chosen intervals of each component-A space or component-B space, it is checked whether the simulation particle number in the interval is within prescribed bounds, i.e., between the prescribed minimum  $N_{s,min}$  and maximum  $N_{s,max}$ . If yes, no action is implemented; otherwise, either an adding action or a removing action is utilized. The section (p,q) of the

two-component space is taken as an example to illuminate its numerical realization. The numbers of simulation particles in the interval p of component-A space and the interval q of component-B space are  $N_{sA,p}$  and  $N_{sB,q}$ , respectively. If min $(N_{sA,p}, N_{sB,q})$  $< N_{s,min}$ , the adding action is performed. A simulation particle *i* in the section (p,q) is equally split into new simulations particles with an integer number  $[N_{s,min}/min(N_{sA,p},N_{sB,q})]$ . These new particles have the same internal variables as their parent particle *i* and have a weight of  $w_i/[N_{s,min}/min(N_{sA,p},N_{sB,q})]$ . One daughter particle replaces the position of its parent particle *i*, and other daughter particles are added to the array of simulation particles. Further, when no simulation particles are present in an interval, for example, in the early stage of aggregation of initially monodisperse particles, no addition action is performed in this section. It is worth emphasizing that the adding action does not change the compositional distributions, and it also conserves the history of the particles but at the cost of more simulation particles; on the other hand, if  $\max(N_{sA,p}, N_{sB,q}) > N_{s,\max}$  the removing action is initiated. A simulation particle j in the section (p,q) can be randomly removed with a probability of  $P_{\text{rem}}$ ,  $P_{\text{rem}} = [\max(N_{\text{sA},p})$  $N_{\mathrm{sB},q}) - N_{\mathrm{s,max}} ]/\mathrm{max}(N_{\mathrm{sA},p},N_{\mathrm{sB},q}) = 1 - N_{\mathrm{s,max}}/\mathrm{max}(N_{\mathrm{sA},p},N_{\mathrm{sB},q}) = 1 - N_{\mathrm{s,max}}/\mathrm{max}(N_{\mathrm{sB},q},N_{\mathrm{sB},q}) = 1 - N_{\mathrm{s,max}}/\mathrm{max}(N_{\mathrm{sB},q},N_{\mathrm{s$  $N_{sB,q}$ ). A random process is used to decide whether simulation particle *j* is removed or not. If a random number *r* from a uniform distribution in the interval [0,1] is less than  $P_{\text{rem}}$ , *j* is removed and its open position is taken by the last particle in the simulation particle array. If not, the number weight of *j* is corrected by a multiple factor  $1/(1 - P_{rem})$ , that is,  $max(N_{sA,p},N_{sB,q})/N_{s,max}$ . That is,  $(w_j)_{new} = (w_j)_{old} / (1 - P_{rem}).$ 

The original shift action effectively leads to shifting simulation particles from densely populated regions where already enough simulation particles are present to less-populated regions.



Figure 1. The mass concentration as a result of the original and the improved shift action in the case of bicomponent aggregation.

The shift action is capable of regulating the population of simulation particles so that it is distributed homogeneously over composition space. The numerical results shown in ref 35 (Section 3.2) has proven the shift action is very useful for obtaining more accurate results in the less-populated regions of compositional distributions. However, it also showed that the shift action leads to errors in the global moments of the distributions because removing simulation particles by a stochastic game adds random noise to the real particle population. In the removing action, every simulation particles in a densely populated section has the same removal probability Prem, but their weights may be very different. For a simulation particle with large weight, either being removed or being changed in weight can introduce a remarkable disturbance to the real particle population. Only when simulation particles in a densely populated section have the same weight the removing action using the uniform removal probability is capable of conserving the real particle population exactly. For more general cases, the removing action leads to errors in the global moments and the compositional distributions. Figure 1 shows the mass concentration in the case of two-component aggregation as described in Section 3.2. The original shift action is unable to conserve the mass concentration.

Furthermore, although the number of simulation particles in the differentially weighted method is constant between two shift actions, the original shift action makes the simulation particle number change (in most of cases, an increase) because the number of added simulation particles may be unequal to that of removed simulation particles. In view of the computational cost, the total number of simulation particles should be controlled to be less than a prescribed constant value.

2.2.2. The Improved Shift Action. The shift action can be improved in two aspects: (1) The removal probability of a simulation particle in a densely populated section depends on its private weight and the number of simulation particles in the section. The more simulation particles there are in the section, the larger the removal probability these simulation particles have; the smaller the weight of the simulation particle is, the larger the removal probability it has. (2) A better control over the total number of simulation particles, so that a given maximum number of simulation particles is not surpassed. Both considerations are included into the improvement of the shift action, described hereafter.

In the improved shift action, the sectionalization in composition and the adding action are same as in the original shift action. After this, the number of added simulation particles,  $N_{st,add}$ , and the number of simulation particles in a section (p,q),  $N_{s,pq}$ , are all known. A two-step removing action sequentially removes simulation particles from densely populated regions. The first step is to choose a section in the densely populated regions from which a simulation particle has to be removed. These sections are the ones where  $N_{s,pq} > N_{s,max}$ . A section (p,q) is chosen with the following probability

$$G_{pq} = \frac{N_{s,pq}\delta(\max(N_{sA,p}, N_{sB,q}) > N_{s,\max})}{\sum_{p} \sum_{q} [N_{s,pq}\delta(\max(N_{sA,p}, N_{sB,q}) > N_{s,\max})]}$$
(6)

where  $\delta$  is Dirac delta function. Thus, if the following condition is met, one simulation particle will be removed from the section (p,q):

$$\sum_{\phi=1}^{p} \sum_{\varphi=1}^{q-1} G_{\phi\varphi} \le r \le \sum_{\phi=1}^{p} \sum_{\varphi=1}^{q} G_{\phi\varphi}$$

$$\tag{7}$$

In fact, selecting a section with probability  $G_{pq}$  is a standard process of the cumulative probabilities method, and the probability  $G_{pq}$  satisfies nearly an exponential distribution. Similar scheme is used to select a simulation particle from the section (p,q) for removal in the second step. For a simulation particle *i* in section (p,q), the removal probability  $P_{\text{remv}i,pq}$  is designed as

$$P_{\text{rem},i,pq} = \frac{1/w_i}{\sum_{j=1}^{N_{s,pq}} (1/w_j)}$$
(8)

The simulation particle i is removed if

$$\sum_{j=1}^{i-1} P_{\text{rem},j,pq} \le r \le \sum_{j=1}^{i} P_{\text{rem},j,pq}$$
(9)

Another simulation particle *j* in the section (p,q) is selected at random to merge with the simulation particle *i*. That is, the weight of *j* is replaced by the sum of its old weight and the weight of *i*,  $(w_j)_{new} = (w_j)_{old} + (w_j)_{old}$ . The open position of *i* can now be occupied by one of the simulation particles produced by the adding action. Because *i* and *j* fall into the same section and have similar internal variables, the removal of *i* and then the merge of *i* and *j* only have very little influence on the real particle population. It is shown in Figure 1 that the new shift action is now able to simulate the mass concentration with high accuracy.

The two-step removing action is repeated  $N_{\text{st},\text{add}}$  times to remove  $N_{\text{st},\text{add}}$  simulation particles from densely populated regions. It is important, however, that the selection probability of section (p,q),  $G_{pq}$ , and the removal probability of a simulation particle *i* in the section (p,q),  $P_{\text{rem},i,pq}$ , are updated before the next removing action.

There are six remarks on the new shift action.

(1) At the initial stage of MC simulation compositional distributions are usually very narrow. It is not necessary to use too many simulation particles to represent the narrow distributions from the viewpoint of saving CPU time. So, the MC simulation can be started with an appropriate number of particles (for example, 10000 simulation particles in this paper where an initial bidispersed distribution is used). Although in individual sections the prescribed values of  $N_{\rm s,max}$  can be initially exceeded, the removing action is enabled only when the total number of simulation particles exceeds the prescribed value  $N_{\rm st,max}$  (for example, 30000 in this paper). In such a way, the number of simulation particles adapts to the compositional distributions automatically, step by step, and on the other hand it is limited although the compositional distributions may continuously expand along with the MC simulation.

- (2) In the original shift action, the maximum number of simulation particles in a discrete interval,  $N_{s,max}$ , is usually prescribed to be larger than  $N_{s,min}$  (for example,  $N_{s,min}$  is usually 100, and  $N_{s,max}$  is 600 in the monovariate population balance<sup>34</sup> or 1000 in the bivariate population balance<sup>35</sup>) in order to avoid too many simulation particles being removed from the simulation which adds random noise to the particle population. On the contrary, it is suggested that  $N_{s,max} = 2N_{s,min}$  in the improved shift action. The reason is that the more candidates there are for the stochastic removing action, the less stochastic noise there is to the real particle population. In the following simulation,  $N_{s,max} = 2N_{s,min} = 200$ .
- (3) Depending on the particular problem, a different number of internal variables is required. The improved shift action described above, which distributes the simulation particles over the 2-dimensional component space, is developed for the bivariate population balance. The shift action for a monovariate or multivariate population balance is in principle straightforward. However, the shift action for multivariate population balances with more than two variables may meet difficulties such as insufficient computer memory or CPU speed. A four-component system, for example, needs at least four internal variables to determine its state, The simulation particle number is within  $N_{
  m s,min} imes N_{
  m di,A} imes N_{
  m di,B} imes N_{
  m di,C} imes N_{
  m di,D}$  and  $N_{
  m s,max} imes$  $N_{\rm di,A} \times N_{\rm di,B} \times N_{\rm di,C} \times N_{\rm di,D}$ , where  $N_{\rm di,k}$  (k = A, B, C, D) is the number of sections of the k-component space. If  $N_{\rm s,min}$  = 100,  $N_{\rm s,max}$  = 200, and  $N_{{\rm di},k}$  = 100, the total number of simulation particles is required to be 10<sup>10</sup> at minimum and 2  $\times$  10<sup>10</sup> at maximum. This clearly surpasses the current computing power. To overcome the difficulty, we suggest the following solution: first, one or two of the most important internal variables is selected; then the simulation particles are distributed only over the 1-dimensional or 2-dimensional space of the interesting internal variable(s) using the new shift action. With regards to aggregative mixing of a two-component system, it is found in the following simulation that distributing simulation particles over one compositional distribution by the new shift action is able to satisfy general requirements in engineering. In the following simulation, it is considered the mass of component A is the most interesting internal variable. Our results show that the compromise between more simulation particles for problems with more than two internal variables and higher accuracy for compositional distributions is very effective. Furthermore, it is worth emphasizing that, although a compromise is used to overcome the difficulty of the shift action for problems with more than two

internal variables, the DWMC method still has the advantage of dealing with high-dimensionality problems in a simple and straightforward manner.

- (4) Apart from the fact that the new shift action exhibits better mass conservation, the new shift action shows similar performance as the old shift action in terms of number concentration, the moments of the bivariate compositional distributions  $(M_{ij})$ , and compositional distributions within selected size intervals and at specified time-points. These results are not shown here because of space limitations. Furthermore, the computational efficiency is also nearly same (in a general desktop PC quipped with CPU of Inter(R) Core(TM)2 Quad Q9300 @2.5 GHz and memory of 4GB, about 7131 s with the new shift action, while 7956 s with the old shift action).
- (5) The shift action is a numerical tool, which adheres to the DWMC method. The shift action will cost about 10 s each time for the case described later. There, the shift action runs only 18 times because it is performed only when the number concentration is halved. The CPU time consumed in the shift action is about 2.5% of the total CPU time of the MC simulation. Considering that the shift action improves greatly the accuracy of compositional distributions, it is a good compromise between computational efficiency and precision.
- (6) In the improved shift action, it is possible to select a simulation particle for removal with other probabilities such as  $w_i / \sum_{j=1}^{N_{s,pq}} w_j$  or  $(1/w_i^2) / \sum_{j=1}^{N_{s,pq}} (1/w_j^2)$ . Applying such different removal probabilities has practically no influence on computational accuracy and efficiency. This is also found when the particle which merges with the removed particle is selected with uniform probability, or with probability  $(1/w_i) / \sum_{j=1}^{N_{s,pq}} (1/w_j)$ . We do not show these results here because of space limitations. Considering that the new shift action presented above is capable of conserving mass and is simple in theory and in programming, it is suggested for application in aggregative mixing of particles in multicomponent systems.

## 3. RESULTS AND DISCUSSION

Nanoparticle synthesis from the gas phase has attracted growing interest because it can produce high-purity nanoparticles with specifically tailored chemical and physical properties. Typically in the processes, highly concentrated nanosized nuclei grown by nucleation undergo rapid Brownian aggregation. This occurs usually in the free-molecular regime, where particle diameter  $(d_p)$  is far less than the mean free path of gas molecular  $(\lambda)$ , or conveniently described as the region where the Knudsen number  $(Kn = 2\lambda/d_p) > 10$ . The Brownian aggregation kernel can in that case be obtained from kinetic gas theory:

$$\beta_{ij} = \left(\frac{\pi k_{\rm B}T}{2}\right)^{1/2} \left(\frac{1}{m_i} + \frac{1}{m_j}\right)^{1/2} (d_i + d_j)^2 \tag{10}$$

where  $k_{\rm B}$  is the Boltzmann constant and *T* is the absolute temperature of system. If the material density of component A ( $\rho_{\rm A}$ ) is different from that of component B ( $\rho_{\rm B}$ ), the kernel is

naturally composition-dependent. If  $\rho_A = \rho_B = \rho$ , the kernel is composition-independent, and eq 10 can be rewritten to the following general formula:<sup>45</sup>

$$\beta_{ij} = \left(\frac{3}{4\pi}\right)^{1/6} \left(\frac{6k_{\rm B}T}{\rho}\right)^{1/2} (\nu_i^{1/3} + \nu_j^{1/3})^2 \sqrt{\frac{1}{\nu_i} + \frac{1}{\nu_j}} \qquad (11)$$

The characteristic aggregation time scale,  $\tau$ , is defined as  $1/(\overline{\beta}_0 N_0)$  for an initially bidisperse distribution, where  $N_0$  is the initial number concentration of particles;  $\overline{\beta}_0$  is the mean kernel over all possible particle pairs at time t = 0.

At high temperature, the resultant nanoparticles may fully coalesce into dense spheres almost instantaneously. With regards to two-component nanoparticle synthesis, primary particles containing only component A and primary particles from component B are first generated, then aggregate to form larger particles which do not react chemically. This leads to aggregative mixing. One is usually interested in compositional distributions as a function of time or particle size, and the degree of mixing along with time or particle size, and, furthermore, how to reach a certain level of mixing by control of initial feeding conditions such as the concentration and species of gas precursors. As an example, in the synthesis of FePt nanoparticles to be used in thin films for magnetic recording it is important that the L1<sub>0</sub> phase which has the desired magnetic properties is formed. However, this phase can only be formed when between 40 and 60 mol % Pt is present in the particle.<sup>46</sup> It is therefore important to be able to calculate the compositional distribution in the particles.

The objectives of the following section are (1) to compare the performance of two PB-MC methods, the differentially weighted MC and the constant-number method, in describing two-component Brownian aggregation with a composition-independent kernel, (2) to validate the numerical results by comparing with available theoretical predictions of the degree of mixing and the compositional distribution, and (3) to demonstrate the practical applicability of the numerical method to describe aggregative mixing with a composition-dependent Brownian aggregation kernel.

**3.1. Definitions.** Compositional Distribution. We consider a population of particles made out of two components A and B, with  $\phi$  as the overall mass fraction of component A. In an initially bidisperse and bicomponent population expressed in terms of mass concentration  $M_{A}$ , initial number concentration  $N_{A0}$ , and initial particle mass  $m_{A0}$  for component A and related ones for component B, we can write:

$$\phi = M_{\rm A} / (M_{\rm A} + M_{\rm B}) = M_{\rm A} / M$$
  
=  $N_{\rm A0} m_{\rm A0} / (N_{\rm A0} m_{\rm A0} + N_{\rm B0} m_{\rm B0})$  (12)

The state of an individual particle is given by the mass of the components A and B within the particle,  $m_A$  and  $m_B$ , respectively. It can also be expressed in terms of the composition or mass fraction *c* of component A, which is defined as  $c = m_A/m$ . The compositional distribution of component A is denoted by the probability density function  $g(m_A|m) dm_A$  which is the fraction of particles of mass *m* that contains component A in the mass amount  $(m_A, m_A + dm_A)$ . The distribution  $g(m_A|m)$  of component A of mass  $m_A$  within a large aggregate of mass *m* is found to be a Gaussian function from the random-mixing theory and

central-limit theorem:<sup>1,2,7</sup>

$$g(m_{\rm A}|m,t) = \frac{1}{\sqrt{2\pi m\chi}} \exp\left[-\frac{(m_{\rm A} - \phi m)^2}{2m\chi}\right]; \text{ or}$$
$$G(c|m,t) = \frac{1}{\sqrt{2\pi\chi/m}} \exp\left[-\frac{(c-\phi)^2}{2\chi/m}\right]$$
(13)

In this equation,  $g(m_A|m) dm_A = G(c|m) dc$ .

*Degree of Mixing.* The compositional distributions are associated to the overall degree of mixing, which can be conveniently expressed by the mass-normalized power density of excess component A, defined as<sup>1</sup>

$$\chi = \frac{X^{2}}{M}$$

$$= \frac{\int_{0}^{\infty} dm_{A} \int_{0}^{\infty} dm_{B} x^{2} n(m_{A}, m_{B}, t)}{\int_{0}^{\infty} dm_{A} \int_{0}^{\infty} dm_{B} (m_{A} + m_{B}) n(m_{A}, m_{B}, t)}$$

$$= \frac{\int_{0}^{\infty} dm \int_{0}^{m} dm_{A} x^{2} f(m, t) g(m_{A}|m, t)}{\int_{0}^{\infty} dm \int_{0}^{m} dm_{A} m f(m, t) g(m_{A}|m, t)}$$
(14)

where f(m,t) is the component-independent particle size distribution function such that f(m,t) dm represents the number concentration of particles in the mass range of *m* to m + dm; *x* is the amount of component A in excess of the amount  $\phi m$ :

$$x = m_{\rm A} - \phi m = m_{\rm A} - \phi (m_{\rm A} + m_{\rm B}) \tag{15}$$

The smaller  $\chi$  is, the better the mixing of the two components. Since  $\chi$  almost does not vary during the aggregation, a more practical parameter measuring the degree of mixing is the segregation index (S.I.), defined as<sup>7</sup>

$$S.I. = \chi/\bar{m} \tag{16}$$

where  $\overline{m}$  is the mean mass of aggregates. Theory predicts the S.I. scales as  $1/\overline{m}$ .<sup>2</sup>

*Moments.* The moments of the monovariate distribution f(m,t),  $M_i(t)$ , and the moments of the bivariate distribution  $n(m_{\rm A},m_{\rm B},t)$ ,  $M_{ij}(t)$ , are respectively defined as

$$M_{i}(t) = \int_{0}^{\infty} m^{i} f(m, t) dm;$$
  

$$M_{i,j}(t) = \int_{0}^{\infty} \int_{0}^{\infty} m^{i}_{A} m^{j}_{B} n(m_{A}, m_{B}, t) dm_{A} dm_{B}$$
(17)

Some statistical parameters over all particles (for example, relative number concentration  $N(t)/N_0$ , mean mass  $\overline{m}(t)/\overline{m}(0)$ , and geometric standard deviation  $\sigma_{\rm g}$  based on particle volume) can be derived from the monovariate moments. And the mass-normalized power density of excess component A is also a function of several bivariate moments,<sup>18</sup>

$$\chi = (1 - \phi)^2 \frac{M_{20}}{M} - 2(1 - \phi)\phi \frac{M_{11}}{M} + \phi^2 \frac{M_{02}}{M}$$
(18)

Dimensionless Distributions. In the self-preserving formulation, the dimensionless particle mass is defined as  $\eta = Nm/M = m/\overline{m}$ ,



Figure 2. Self-preserving number distribution function as function of (a) dimensionless particle mass and (b) dimensionless mass of component A.

and the dimensionless number distribution function as  $\Psi = Mf(m,t)/N^{2}$ ,<sup>47</sup> where  $\overline{m}$  is the average mass, M is the total mass concentration and N is the total number concentration. Similarly, the dimensionless mass of component A is  $\eta_A = N_A m_A/M_A$ , the dimensionless component-A distribution is  $\Psi_A = M_A f_A(m_A,t)/N_A^2$ , where  $M_A$  is the total mass concentration of component A in particles,  $N_A$  is the total number concentration of particles containing component A,  $f_A(m_A,t)$  is the number density distribution of particles containing component A of mass  $m_A$ , such that  $f_A(m_A,t)dm_A$  is the number concentration of particles containing component A of mass  $m_A$ , such that  $f_A(m_A,t)dm_A$  is the number concentration of particles containing component A in the mass range of  $m_A$  to  $m_A + dm_A$ .

**3.2.** Composition-Independent Aggregative Mixing. 3.2.1. *Case Description*. A reference case with two initially monodisperse components having the same density  $(21.45 \times 10^3 \text{ kg m}^{-3})$  but different initial diameters and number concentrations are defined. At t = 0,  $N_{A0} = 9N_{B0}$ ,  $d_{A0} = 0.5d_{B0} = 1$  nm. The resulting mass fraction of component A is  $\phi = 0.5294$ , and  $\chi_0$  is calculated with help of<sup>18</sup>

$$\chi_{0} = \frac{\sum_{i=1}^{N_{A0}} (m_{A0} - \phi m_{A0})^{2} + \sum_{i=1}^{N_{B0}} (0 - \phi m_{B0})^{2}}{M_{A0} + M_{B0}}$$
$$= (1 - \phi)\phi(m_{A0}(1 - \phi) + m_{B0}\phi)$$
(19)

to be  $\chi_0 = 1.3167 \times 10^{-23}$  so that  $\chi_0/m_{A0} = 1.1724$ .

The differentially weighted method starts from 10000 simulation particles and limits the simulation particle number to 30000, while the constant-number method always tracks 30000 simulation particles. The MC simulations are repeated five times using different seeds for the random number generator.

3.2.2. Self-Preserving Distributions. The self-preserving distribution for the Brownian coagulation case will be obtained after a time-lag.<sup>48,49</sup> We compare the results at  $100000\tau$  with results from a sectional model,<sup>48,49</sup> which were obtained for a single component. The dimensionless distribution functions as function of particle mass and of mass of component A are shown in Figure 2a and 2b, respectively.

As shown in Figure 2, the differentially weighted MC, which is capable of tracking the distributions over the full range, shows higher accuracy in the distribution in less-populated regions (e.g.,  $\eta$  or  $\eta_A$  in the ranges of 0.01 to 0.001 and beyond 10) as compared to the CN method and the sectional method.<sup>48,49</sup> This should be attributed to the fact that the method is capable of assigning enough simulation particles to each discrete interval through the improved shift action described in Section 2.2.



Figure 3. Number concentration  $N(t)/N_0$ , mean mass  $\overline{m}(t)/\overline{m}(0)$ , and geometric standard deviation  $\sigma_e$  against time.

Furthermore, it is found that the distribution of component-A mass can be described with the same self-preserving function as the total particle mass. This can be understood from the fact that after many coagulation events, the components are relatively well distributed over the particles, as will be shown in the following sections.

3.2.3. Moments of the Distribution. The time evolution of several monovariate moments or their derivations is shown in Figure 3: the dimensionless number concentration  $N(t)/N_0$ , the dimensionless mean mass  $\overline{m}(t)/\overline{m}(0)$ , and the geometric standard deviation  $\sigma_g$  based on particle volume. There is nearly no difference in the behavior of  $M_i$  from the numerical results of the DW method and these of the CN method, except that the steady-state value of  $\sigma_g$  is 1.46 in the DW method rather than 1.45 in the CN method.

3.2.4. Degree of Mixing. In an earlier report it was found that the mass-normalized power density of excess component  $A(\chi)$ will reach a steady-state value,  $\chi_{\text{steady-state}}$ , with sufficient processing time for any initial condition (monodisperse, bidisperse, or exponential distributions) and any aggregation kernels (composition-dependent or -independent), and  $\chi_{\text{steady-state}}$  is approximated to the initial  $\chi$ ,  $\chi_0$ .<sup>7</sup> Indeed, a steady-state value of  $\chi$  develops, as shown in Figure 4. It shows the dependency of the dimensionless mean mass  $\overline{m}(t)/\overline{m}(0)$ . In both MC simulation methods,  $\chi$  first decreases and then reaches a steady state. Surprisingly, in the CN method  $\chi$  starts to increase sharply at  $1000\overline{m}_0$  (or from the time moment  $100\tau$ ), and ends with



**Figure 4.** Mass-normalized power density of excess component A ( $\chi$ ) and the segregation index (S.I. =  $\chi/\overline{m}$ ) against mean mass (a); and against time (b).



Figure 5. Compositional distributions in selected size intervals at  $t = 1000\tau$ : (a) logarithmic scaling for Y-axis; (b) linear scaling for Y-axis.

 $4.37 \times 10^{-22}$  (about 43 times larger than the steady value from the DW method) at  $t = 10^{5}\tau$ . With more simulation particles (e.g., 50000) in the CN method, the value of  $\chi$  is kept constant over a wider range, and is closer to the excepted constant value at larger extents of evolution. In fact,  $\chi$  depends on the two-dimensional

compositional distribution (see eq 14), and it is calculated in MC by taking into account all simulation particles:  $\chi = \sum_{i=1}^{N_{st}} [w_i \times (m_{A,i} - \phi m_i)^2 / \sum_{i=1}^{N_{st}} (w_i m_i)$ . The more simulation particles are tracked and the more uniformly these simulation particles are distributed over the two-dimensional joint space of internal



Figure 6. Compositional distributions within full range at several time-moments.

variables, the more accurate the result of  $\chi$  will be. With respect to the CN's inability for steady  $\chi$ , we argue that the CN method, which is an equally weighting method in nature, is unable to capture accurately the aggregative mixing of components within larger and smaller particles (they are usually with low number concentrations). More simulation particles are used, more accurate results on composition mixing are obtained in the CN method. On the contrary, even when a smaller number (10000) of simulation particles are used in the DW method (where no shift action is adopted and the DW method tracks 10000 simulation particles throughout the MC simulation), high-precision results are obtained. This is attributed to different weights, which effectively increase the number of simulation particles in the edges of compositional distributions. However in the DW method with less simulation particles and without the shift action,  $\chi$  also diverges from a steady state as time evolves. It is because simulation particles with limited number are not uniform over compositional distributions. From this perspective, the shift action is essential. In Figure 4 another important quantity, the segregation index (S.I. =  $\chi/\overline{m}$ ), is shown. The numerical result from the DW method agrees well with the theoretical predication in which the S.I. scales as  $1/\overline{m}$ , while the CN method fails at larger times.

From Figure 4b, it is noted that there are three stages of the evolution of  $\chi$ . (1) Stage 1: within 0 and  $\tau \chi$  starts to change slightly once aggregation occurs. Because within this time range the aggregation degree is relative smaller,  $\chi$  is basically close to its initial value. (2) Stage 2: within  $\tau$  and 12.7 $\tau$  (it is the time-lag reaching to self-preserving state of Brownian coagulation in the free-molecular regime)  $\chi$  deviates from the initial value more and more, and approaches to a constant value. In fact, within the time range larger particles are formed and the distribution of particle population becomes self-preserving. (3) Stage 3: when  $t > 12.7\tau \chi$  becomes time invariant and keeps unchanged. We thus conclude that the time-lag for  $\chi$  reaching to a steady state is equal to the time-lag for self-preserving distribution.

3.2.5. Compositional Distributions. We further examine the distribution of components. The compositional distributions with selected size intervals  $(m_{sp}^- \sim m_{sp}^+)$  from the two MC

methods are compared with theoretical predictions, which are calculated as follows:

$$G(c|m) = \frac{1}{(m_{\rm sp}^+ - m_{\rm sp}^-)} \int_{m_{\rm sp}^-}^{m_{\rm sp}^+} \frac{\exp\left(-\frac{(c-\phi)^2}{2\chi/m}\right)}{\sqrt{2\pi\chi/m}} \, \mathrm{d}m, \text{ where } m \in [m_{\rm sp}^-, m_{\rm sp}^+]$$
(20)

Figure 5 shows the compositional distributions in selected size intervals at  $t = 1000\tau$ . At this time-moment, the mean mass of particles is 1600  $\overline{m}_{0}$ ;  $N(t)/N_{0} = 6.26 \times 10^{-4}$ ;  $\chi$  reaches to a steady-state value,  $1.0 \times 10^{-23}$ , in the DW method, while in the CN method  $\chi$  gradually increase from the steady-state value and approximates to  $\chi_0$  until  $t = 1000\tau$ . The two MC methods demonstrate similar performance for compositional distributions with same number of simulation particles. At the peak of compositional distributions, the CN method is more accurate since there are more simulation particles in these very densely populated regions (near  $c=\phi$ ) in the CN method, while the DW method produces results more fitting the theoretical predications for these particles in less-populated regions (the two edges of the computational distributions). And, for these particle in lesspopulated regions (especially at the right edge of compositional distributions), their compositional distributions from the CN method fit more the predictions from eq 20 with  $\chi = \chi_0$  while the results of the DW method approximate to the theoretical predications using  $\chi = \chi_{\text{steady-state}}$ . These findings validate the availability of the theoretical models, and, on the other hand, provide the evidence in support of our argument that the differentially weighting methodology and the shift action are essential for describing accurately the mixing of components within particles.

The distributions of component A within the full range, which is calculated as  $N(c)/N/(c^+-c^-)$ , against the mass fraction of component A(*c*) is shown in Figure 6, where N(*c*) is the number concentration of particles having A-component mass fraction of *c*, *N* is the total number concentration,  $c^+$  and  $c^-$  are respectively the upper and lower limit of a interval of *c*. It is clear that the CN method is unable to track these particles with low number concentrations. On the contrary, the DW method is capable



**Figure 7.** Power density of excess component A ( $\chi$ ) and segregation index ( $\chi/\overline{m}$ ) for composition-dependent aggregative mixing.



Figure 8. Compositional distributions within selected intervals for composition-dependent aggregative mixing.

of capturing more accurately the process of component mixing within not only these particles (e.g., these particles whose *c* approximates to  $\phi$ ) which are comparatively uniformly mixed and occupy the large number share in particle population but also these particles (e.g., these particles whose *c* approximates 0 or 1) which are not or weakly mixed in composition and are less-populated. These results further support the power of the DW method as compared to the CN method. From Figure 6 it is found that the compositional distribution becomes narrower and narrower along with the process of aggregative mixing, which shows the degree of component mixing is better and better, and the mass fraction of component A in any particle is closer and closer to the overall mass fraction of component A,  $\phi$ .

**3.3. Composition-Dependent Aggregative Mixing.** In real cases, the Brownian aggregation kernel in the free-molecular regime is composition-dependent because the component's density is different. Now the kernel is a function of the sizes of two interacted particles and their densities, which are associated with component amounts within the particles. The reference case described in Section 3.2.1 is still simulated by the DW method, except that  $\rho_A \neq \rho_B$ . Here,  $\rho_A = 7.87 \times 10^3$  kg m<sup>-3</sup>,  $\rho_B = 21.45 \times 10^3$  kg m<sup>-3</sup>, thus  $m_{A0} = 4.1207 \times 10^{-24}$  kg,  $m_{B0} = 8.9849 \times 10^{-24}$ 

 $10^{-23}$  kg,  $\phi = 0.2922$ ,  $\chi_0 = 6.0321 \times 10^{-24}$ ,  $\chi_0/m_{A0} = 1.4638$ ,  $\tau = 1.6342 \times 10^{-7}$  s.

We first plot the evolution of  $\chi$  and S.I. in Figure 7. As expected, the  $\chi$  is time invariant at the larger extents of evolution, and S.I. eventually scales as  $1/\overline{m}$ . And, the three-stage time evolution of  $\chi$  (i.e.,  $0 < t < \tau$ ,  $\tau < t < 12.7\tau$ ,  $t > 12.7\tau$ ) still holds. By the way, we point out the self-preserving distribution in terms of either the mass of whole particle or the mass of one component is still obtained while large size particles are formed. The compositional distributions with selected intervals are also shown in Figure 8. The compositional distributions still follows Gaussian function and can be fitted using eq 20, although now it is composition-dependent kernel. It is deduced that these conclusions on the time evolution of  $\chi$ , S.I., and compositional distributions should be valid for any composition-independent or —dependent kernel. Matsoukas et al. have similar conclusion.<sup>7</sup>

### 4. CONCLUSIONS

In this paper, the differentially weighted Monte Carlo (DW-MC) method is used to simulate bicomponent aggregative mixing in spatially homogeneous systems. The method allows the use of differentially weighted simulation particles, in such a way that more simulation particles with less private weights are assigned to represent these sparse regions (for example, two edges of compositional distributions), and the number of simulation particles in dense regions can be effectively reduced by increasing their weights. Another feature of the DWMC method is to use so-called shift action which is capable of regulating a limited number of simulation particles so that they are distributed homogeneously over composition space. In the original shift action, removing simulation particles by a stochastic game adds random noise to the real particle population because the removal probability of simulation particles in dense regions is the same, independent of their private weights and number density. In the new shift action, the removal probability of a simulation particle in a densely populated section depends on its private weight and the number of simulation particles in the section. The more simulation particles there are in the section, the larger the removal probability these simulation particles have; the smaller the weight of the simulation particle is, the larger the removal probability it has. The cumulative probability method is used to first choose a densely populated section, then choose a simulation particle to be removed from the section. Furthermore, the number of simulation particles added into less-populated regions is equal to that of simulation particles removed from densely populated regions in such a way that the total number of simulation particles is kept constant throughout the simulation. These new features (especially, the differentially weighting scheme and the improved shift action) results in low statistical noise for simulating aggregative mixing of multiple components.

From a comparison of the differentially weighted MC and the constant-number method (a typical equally weighted MC) with theoretical predictions, it is found for composition-independent aggregative mixing that the constant-number method demonstrates obvious errors in the degree of mixing and compositional distributions, especially at larger times. In the constant-number method, the degree of mixing (mass-normalized power density of excess component A,  $\chi$ ) will gradually deviate from the steady-state value of  $\chi$  predicted by theory at larger times; and the segregation index ( $\chi/\overline{m}$ ) will tend to be stable along with time evolution while it is theoretically predicted to be inversely

proportional to the mean mass of particles  $(\overline{m})$ . Correspondingly, the Gaussian-type compositional distributions predicted by the constant-number method have the wrong variance  $(\chi/\overline{m})$ . On the contrary, the simulation results from the DWMC method agree well with the theoretical predictions, due to their high precision in these less-populated regions where the equally weighted MC methods place insufficient simulation particles to obtain an inaccurate solutions. It is worth noting that, although the constant number method exhibits low resolution for particles in less-populated regions of compositional distributions, it is more accurate at the peak of compositional distributions since there are more simulation particles in these very densely populated regions. Finally, the DWMC method is utilized to simulate a realistic case of composition-dependent aggregative mixing where Brownian aggregation kernel is associated with the sizes of two interacted particles and their component amounts. The results show that the degree of mixing becomes steady when the size distributions and compositional distributions reach the the self-preserving state, and the compositional distributions satisfy Gaussian function as in composition-independent aggregative mixing (where the Brownian aggregation kernel is a function of the sizes of two interacted particles).

Worth noting is, although in this paper the DWMC method is utilized to simulate typical cases of aggregative mixing with the Brownian aggregation kernel in the free-molecular regime, it should be effective for aggregative mixing with any kind of kernels. It can be deduced that the DWMC method and the improved shift action work well for other cases. The functionality of the DWMC method and the improved shift action is independent of aggregation kernels and initial conditions.

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