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Abstract: This work aims to find a particle agglomeration simulation method, such that the collided particles stick irreversibly and remain fixed at the first contact point. However, the method shall avoid global interactions as they occur in rigid bodies. To that end, several models are considered, in which the particle-particle connections are created dynamically when the particles come into contact. The models use non-bonded strongly attractive interactions, bonded interactions and binding agents placed at the point of contact to connect the collided particles. In order to understand which model is capable of simulating particle agglomeration without restructuring, different Molecular Dynamics simulations have been performed. The results are analyzed in terms of the stability, shape, and fractal dimension of the agglomerates. Models using spherically symmetric non-bonded or bonded interactions are found to form compact agglomerates and are therefore unsuitable to study agglomeration. Models based on binding agents preserve connectivity within the agglomerates and prevent restructuring of the agglomerates. The fractal dimension of the predefined agglomerate is practically conserved. Finally, well-known diffusion-limited agglomeration (DLA) simulations have been performed to validate the new model implementation.

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Significance and Novelty

We propose a novel strategy for the simulation of nanoparticle agglomeration using a local bonding model. Unlike standard bonds, our proposed mechanism restricts rotation around formed bonds, allowing for perfect sticking of particles after collision. This is important to avoid the sliding of particles within the formed agglomerate, which may lead to rather compact clusters. The introduction of virtual particles at the point of contact, that are fixed in a reference frame attached to each particle, ensures that upon forming the bond, the particles cannot slide around the binding site. This preserves the fractal dimension of the agglomerate after collision and throughout the remainder of the simulation. In comparison to existing, alternative methods for the simulation of nanoparticle agglomeration such as Monte Carlo (MC) methods or Rigid-body Dynamics, our model allows for

1. a consistent coupling of the particle motion with any (laminar or turbulent) flow motion of the surrounding gaseous phase and
2. an efficient parallelization using Molecular Dynamics due to the ideal scaling of systems with local interactions only.

The proposed model therefore provides an ideal tool for the analysis of particle agglomeration in turbulent environments.

How to model nano-particle agglomeration using molecular dynamics software

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Abstract

This work aims to find a particle agglomeration simulation method, such that the collided particles stick irreversibly and remain fixed at the first contact point. However, the method shall avoid global interactions as they occur in rigid bodies. To that end, several models are considered, in which the particle-particle connections are created dynamically when the particles come into contact. The models use non-bonded strongly attractive interactions, bonded interactions and binding agents placed at the point of contact to connect the collided particles. In order to understand which model is capable of simulating particle agglomeration without restructuring, different Molecular Dynamics simulations have been performed. The results are analyzed in terms of the stability, shape, and fractal dimension of the agglomerates. Models using spherically symmetric non-bonded or bonded interactions are found to form compact agglomerates and are therefore unsuitable to study agglomeration. Models based on binding agents preserve connectivity within the agglomerates and prevent restructuring of the agglomerates. The fractal dimension of the predefined agglomerate is practically conserved. Finally, well-known diffusion-limited agglomeration (DLA) simulations have been performed to validate the new model implementation.

Keywords: nanoparticle, agglomeration, MD, DLA

1. Introduction

Particle agglomeration is an abundant process in nature and in many industrial processes such as spray drying and particle flame synthesis, but also in water purification, mineral beneficiation and biological separation processes [1, 2]. It is a mass conserving growth mechanism that starts after the primary particles (sized between 1 nm and 100 nm) are formed by nucleation and surface growth. Usually, the particles are dispersed in a fluid (liquid or gas) and the agglomeration can be driven both by flow and/or by Brownian motion that induce relative motion between the particles [3, 4, 5]. Due to their relative motion, the particles collide and adhere when the net interparticle attractive force overcomes the thermal agitation and the hydrodynamic drag [6, 7]. The composition size and shape of the formed clusters depends on the specific formation and

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growth mechanisms, and we need either experimental methods or computer simulations to obtain quantitative information on the respective mechanisms that govern the agglomeration process.

Experimental studies provide information on the size and shape of selected agglomerates, but not on the history of the agglomeration process or the intermolecular forces within the agglomerates that are of importance for the dynamics of the formation of the final product [8, 9, 10, 11]. Therefore, computer simulations have been used, since they allow for the tracking of individual particles at all times and provide a better understanding of the agglomerate's growth and morphology. Peng *et al.* [12] used a discrete element method (DEM) to simulate the nanoparticle agglomeration due to random Brownian diffusion. The aggregate growth was examined in terms of longest distance, coordination number and fractal dimension of each aggregate. Even though the simulation results were found to be in good agreement with experimental data, the coordination numbers were too high. Binder *et al.* [13] compared the Lattice Boltzmann method with the accelerated Stokesian dynamics method to investigate the hydrodynamic drag force on agglomerates. Both models were coupled with a Monte Carlo approach to model the agglomeration of spherical particles that were allowed to overlap. A restructuring yielded compact agglomerates that were exposed to a high drag force in both models. Recently, Drossinos *et al.* [14] investigated numerically the agglomeration of nanoparticles that underwent Brownian motion and stuck irreversibly when coming into contact. Due to the spherically symmetric and isotropic interactions between the particles, the model could not prevent the relative motion of connected particles within the agglomerates. The aggregates were found to be compact, tubular and elongated.

These numerical studies highlight a common issue, namely the sliding of particles within an agglomerate. This sliding, which leads to rather compact agglomerates as time proceeds, may or may not be physical. Particles that are tied together by weak physical van der Waals forces (soft agglomerates) may restructure when heated or exposed to high tension [15]. However, the particle bonds within hard agglomerates are sufficiently strong and restructuring after collision does not appear. This may also be true for soft agglomerates such as agglomerates of real silica or titania that tend to break rather than to restructure. Compact clusters are not found. Hence rigid bonds between collided particles need to be introduced in computational models to achieve a more physical realization of the temporal evolution of many particle agglomeration processes. Kusaka *et al.* [16], Kempf *et al.* [17], and Iglberger *et al.* [18] coupled their nanoparticle motion models with a rigid body motion model, such that hereafter the collision, the total force and torque were applied to the center of mass of the collided particles and they moved together. Although the *Rigid-Body Dynamics* model solves the undesired restructuring, it has drawbacks when coupled with thermal simulation models. As the clusters grow, the torques generated at the boundaries of large objects increase, and smaller time steps become indispensable to resolve the rotational fluctuation of the large rigid clusters. As a consequence, the computational requirements increase and the approach may not be very efficient. Moreover, *Rigid-Body Dynamics* is not easily parallelizable as large objects require global communication, in contrast to the ideal scaling of systems with only local interactions.

In our study, we seek a model with purely local interactions to model the particle agglomeration in which the collided particles remain fixed at the initial point of contact. Different algorithms are developed (Table 1) that are based on van der Waals interparticle forces, bonding forces or on additional external point particles to inhibit the particle sliding away from the first contact point during the simulations. The Brownian motion of the interacting particles are modeled by solving the Langevin equation of motion using e.g. Molecular Dynamics, and the particle interactions are taken to be a Lennard-Jones intermolecular potential assuming all primary particles are spherical and have the same (known) diameter. This is, however, not a limitation of the

model, but a simplifying assumption that we make to assess differences between other models.

This paper is organized as follows: Section 2 reports the theoretical account of the intermolecular and bonded potentials and Langevin equation of motion for Brownian particles and describes the simulation models. Section 3 briefly describes the simulations and the results are reported including an investigation and comparison of the fractal and morphological properties of the agglomerates for each model. The optional model is selected by evaluating the results of these different algorithms. Section 3 also reports the time step dependency analysis and the diffusion limited agglomeration model for which some other numerical studies exist, such that the accuracy of the optional model can be reliably evaluated. Finally, Section 4 summarizes the conclusions.

2. Numerical Methods

Simulations are performed using the Molecular Dynamics (MD) software package ESPResSo [19]. It provides all the required interactions plus a number of additional features such as electrostatic or hydrodynamic interactions, that might be of interest for future studies of agglomeration.

2.1. Relevant interactions between particles

The traditional (12-6) Lennard-Jones potential between particles is used to model interactions between non-polar molecules. It combines a long-range attractive force (the $1/r^6$-term) with a short-range repulsive force (the $1/r^{12}$-term) between the particles,

$$V_{LJ}(r) = \begin{cases} 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + c_{shift}\right) & \text{, if } r_{min} < r < r_{cut} \\ 0 & \text{, otherwise} \end{cases} \tag{1}$$

where r is the particle distance, σ is the radius of the primary particle and ϵ is the depth of the attractive potential, defining the maximum attractive energy between two particles. The attraction between the particles starts beyond $r = 2^{1/6}\sigma$. The shift, c_{shift} is chosen as $c_{shift} = \left(\frac{\sigma}{r_{cut}}\right)^{12} - \left(\frac{\sigma}{r_{cut}}\right)^{6}$, which corrects for the discontinuity of the potential at $r = r_{cut}$.

In addition adjacent particles can be combined via a 2-body spring potential, 3-body angular potentials and 4-body dihedral potentials.

The 2-body spring bond (harmonic bond) potential is given by

$$U_{harmonic-bond} = k(r_{ij} - r_0)^2, \tag{2}$$

where $r_{ij} = \|\vec{r}_j - \vec{r}_i\|$ gives the distance between the particles, r_0 is the equilibrium distance, and k is the spring constant. This potential describes the vibrational motion between an (i, j)-pair of bonded particles.

The 3-body angular bond is used to fix the angle between the position vectors from the center particle to the two other particles. The energy configuration of the angular bond potential is

$$U_{angle} = k_\theta(\theta - \theta_0)^2, \tag{3}$$

where θ is the angle in radians between vectors $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ and $\vec{r}_{kj} = \vec{r}_j - \vec{r}_k$, θ_0 is the equilibrium angle, and k_θ is the angle constant.

The dihedral potential describes the angular spring between the planes formed by the first three and last three atoms of a consecutively bonded (i, j, k, l)-quadruple of particles [20]. Then, the dihedral potential is given by

$$U_{dihedral} = k(1 - \cos(n\phi - p)), \tag{4}$$

where n is the multiplicity of the potential and can take any integer value (typically from 1 to 6), p is a phase parameter and k is the bending constant of the potential. ϕ is the dihedral angle between the particles defined by the particle quadrupel p_1, p_2, p_3 and p_4, i.e. the angle between the planes defined by the particle triples (p_1, p_2 and p_3) and (p_2, p_3 and p_4).

2.2. Equations of motion

The Langevin equation of motion is used to model the particle motion including Brownian motion. We use a Velocity-Verlet-integrator plus a Langevin thermostat to integrate the Langevin equation [21]. At each time step all particles are subjected to a random force and a frictional force such that these two forces satisfy the fluctuation-dissipation theorem and balance each other. In this formalism, the Langevin equation for the i-th particle [22] is given by

$$m\dot{u}_i(t) = -\gamma u_i F_C + W_i(t), \tag{5}$$

where F_C are conservative forces, γ is the friction constant between the primary particles and surrounding fluid, u_i is the velocity of the i-th particle and $W_i(t)$ is Einstein's white noise term, which is a Gaussian random source [23, 24]. The noise models the random kicks of the fluid molecules to the particles with zero-mean and satisfies,

$$< W_i(t) >= 0, \qquad \langle W(t)W(t')\rangle = 2kT\delta(t - t'). \tag{6a}$$

The exact modeling of the friction coefficient may also depend on the Knudsen number Kn, which is the ratio of the fluid molecules mean free path length l_{fluid} to the particle radius, $Kn = 2l_{fluid}/d_p$ [25]. For large particles ($Kn << 1$), the flow is in the continuum regime and the well known Stokes law applies,

$$\gamma = 3\pi\mu_f d_p. \tag{7}$$

For smaller particles ($Kn > 1$), however, a slip velocity between the particle and the surrounding fluid will exist. The friction coefficient will be lower than the Stokes law would predict and the so-called Cunningham correction, C_C, needs to be introduced as is indicated by equations (8a) and (8b) [26],

$$\zeta = \frac{3\pi\mu_f d_p m}{C_C} \tag{8a}$$

$$\text{with } C_C = 1 + Kn\left(A_1 + A_2 \cdot \exp\left[\frac{-2A_3}{Kn}\right]\right). \tag{8b}$$

2.3. Particle agglomeration models

The physical and chemical reasons behind the particle sticking are attractive forces that bring the particles together and/or chemical bonds. When the particles meet, they either feel a short-range attraction (that arises because of the induced-dipole forces) that results in an elastic deformation leading to a flattening of the particles in the contact region and thus strengthens the contact, or they create bridges from one particle to another. Spherically symmetric interactions

Table 1: Summary of the five different agglomeration formation models

Model Number	Model Name	Model Description	Acronym
i	Lennard Jones model	collision model with highly attractive Lennard Jones potential	LJ
ii	Single bond model	single bond potential between collided particles model	SB
iii	All bonds model	single bond, angle and dihedral potentials model	AB
iv	Single bonded virtual sites model	collision model with two virtual particles at the contact point and connected by a spring bond	SBV
v	Angle bonded virtual sites model	collision model with two virtual particles connected through angle potential	AnBV

are not capable of modeling these physical processes since due to the deformations, the particles are not spherical anymore. Despite this fact, one can *model* the sticking of particles by introducing intermolecular, bonded potentials, or binding agents that break the spherical symmetry of the particles.

In the present study, five different models that simulate the simultaneous formation and growth of agglomerates, are considered. They are summarized in Table 1 and described in the 5 subsections below.

2.3.1. Model using highly attractive Lennard Jones potentials (LJ)

In this model, the particles interact by highly attractive Lennard-Jones potential forces. When particles come close, the strong attraction makes them very unlikely to separate. However, the interactions are still rotationally invariant. For the LJ model simulations, the σ and ϵ values are set such that, for small distances between the two particles, highly attractive forces act on both particles. These forces can be expressed by Equation (1).

2.3.2. Single bond model (SB)

For the "single bond" model, a distance-dependent bond potential (i.e. harmonic bond potential) is used to connect the colliding particles. When particles come close, the 2-body bond potential acts on both particles to keep the particles together.

2.3.3. All bonds model (AB)

The "all bonds" model uses the 3-body angular bond and dihedral bond potentials to represent the adhesion of the particles in addition to the 2-body potential. In this model, the 2-body potential is defined to keep particles together, and the 3-body and 4-body potentials are defined to avoid the sliding of connected particles.

2.3.4. Single bonded virtual particles model (SBV)

Our goal is that the particles should always be connected at the particular point where they initially touched. This can be achieved by using so-called virtual particles, i.e. particles that are not integrated by the equations of motion, but are placed strictly relative to a given other particle. This requires that particles carry a co-moving reference frame that is integrated by rotational Langevin dynamics. In our model, they are dynamically created during the simulation and move with the Brownian particles they are attached to.

For the "single bonded virtual particles" model, two virtual particles are created at the point of contact, fixed in the reference frame of the two colliding particles. The virtual particles are bound together by a bond potential with an equilibrium distance equal to zero. In addition, a normal bond is formed between the two collided particles as a control criterion to avoid collision duplication and to introduce a higher stiffness of the bond (Fig. 1).

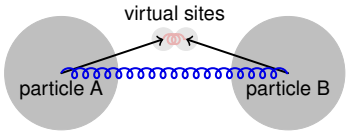


Figure 1: SBV model, collided particles are attached to each other through the virtual particles placed at the collision point.

2.3.5. Angle bonded virtual particles model (AnBV)

Similar to the SBV model, two virtual particles are created at the point of contact and the collided particle pair is attached to these virtual particles. However, the virtual particles are connected both to the collided particles and to each other by an angle-dependent potential with angle $\theta = 180°$ as shown in Figure 2.

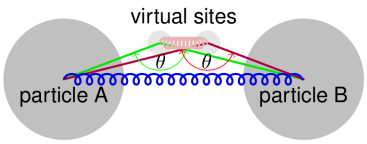


Figure 2: AnBV model, two virtual particles are placed at the collision point and angle potential (with $\theta = 180°$) is defined through two collided particles and virtual particles.

The bond between the centers of the colliding particles prevents significant motion around the point of contact, and the angular potential through collided and virtual particles prevents the particles from sliding around each other.

2.4. Simulation parameters

In this study, the simulations are carried out with a system consisting of spherical Lennard-Jones particles placed in a cubic box with periodic boundary conditions for all sides. The surrounding fluid is assumed to be air.

We use "reduced units", in which three reference quantities define the unit system. These are the units of energy (ϵ^*), length (σ^*) and mass (m^*). All other quantities are expressed in units that

Table 2: Simulation parameters

	Cross-Shape Test	Randomly Placed Particles Test	DLA Test
Case Names	Case-1	Case-2	Case-3
Number of Particles	17	500	215
Normalized Lennard-Jones Parameters	$\widetilde{\epsilon}$=1 $\widetilde{\sigma}$=1 $\widetilde{r}_{cut}$=2.5σ	$\widetilde{\epsilon}$=1 $\widetilde{\sigma}$=1 $\widetilde{r}_{cut}$=2.5σ	$\widetilde{\epsilon}$=1 $\widetilde{\sigma}$=1 $\widetilde{r}_{cut}$=2.5σ
Normalized Box Length	36$\widetilde{\sigma}$	40$\widetilde{\sigma}$	20$\widetilde{\sigma}$

can be derived from (ϵ^*), (σ^*) and (m^*). In the following, the reference values of energy, length and mass are set to the thermal energy of the system ($\epsilon^* = 1\ kT$), the diameter of the particle, and the mass of the particle, respectively. The normalized key quantities of the MD simulation are then calculated by dividing the real values by the reference units (i.e. $\widetilde{\epsilon} = \epsilon/\epsilon^*$, $\widetilde{\sigma} = \sigma/\sigma^*$).

The time step ($\widetilde{\tau} = \tau/\tau^*$) of the MD simulations plays an important role in solving the equation of particle motion. For the reduction of the computational time it should be as large as possible without violating energy conservation. To obtain reliable simulations, the simulation time step should be much smaller than the relaxation time of the particles, which is the characteristic time for a particle to adjust its velocity. The relaxation time of a Brownian particle is given by,

$$\tau_B = \frac{m}{\gamma} = \frac{\rho d_p^2 C_C}{18\mu}. \tag{9}$$

The normalized time step of all test case simulations is initially set to $\widetilde{\tau}$=0.01 which is smaller than the relaxation time of Brownian particles. However, the strong bonds in some systems, especially for the SB and AB models, increase the instabilities and results in diverging energy. The largest, acceptable normalized time steps are found to be $\widetilde{\tau}$=0.01 for the LJ, SBV and AnBV, $\widetilde{\tau}$=0.001 for the SB and $\widetilde{\tau}$=0.0001 for the AB model simulations. In order to ensure the numerical stability throughout the respective computations, $\widetilde{\tau}$=0.0001 is chosen for Case-1 and Case-2 simulations and $\widetilde{\tau}$=0.01 is chosen for Case-3 simulation.

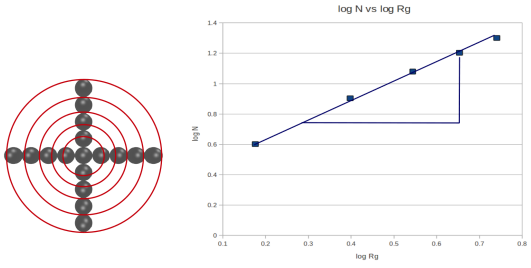
The other simulation parameters for the different simulation cases are listed in Table 2. For all simulations, the canonical ensemble is assumed, where the number of particles N, the volume V and the temperature T are fixed.

3. Results and Discussion

In this section we present the results of the different test cases summarized in Table 2. The cases are designed to demonstrate the capabilities of the different agglomeration models to represent a realistic formation and growth process of agglomerates in MD simulations.

3.1. Fractal dimension

The fractal dimension is used as a measure of the structure of the agglomerates. D_f is measured from the slope of the double logarithmic plot of the radius of gyration, R_g, versus the number of particles, N, in a corresponding concentric circle as shown in Figure 3. For compact objects, the fractal dimension coincides with the usual dimension, thus, a sphere has the dimension D_f=3, a disk has the fractal dimension D_f=2. The loose structures of the agglomerates can also have broken dimensions.



(a) (b)

Figure 3: Fractal analysis of an agglomerate, (a) initially generated cross-shape agglomerate, the concentric circles corresponding to different Rg, (b) log-log plot of radius of gyration and particle number.

3.2. Simulations of the pre-defined agglomerate - Case-1

In this case, the initial positions of particles are given by the shape of a cross. The distance between neighboring particles is closer than the predefined collision criteria in our simulations. Hence the agglomerates are formed before the iterations start, and the initial shape should be preserved. The initial fractal dimension of the cross-shaped agglomerate is, thus, measured as D_f = 1.31 due to its limited size.

Figure 4 shows the configuration of the cross-shaped agglomerate at the end of the simulations using the different models. With the exception of the SBV and the AnBV models, the agglomerates do not preserve their initial configuration and change their connectivity. When using the SBV model, the particles rotate around the connection points within the agglomerates, however, the connectivity is preserved.

The change in the fractal dimension of the cross-shaped agglomerate during the Case-1 simulation is depicted in Figure 5, showing how D_f of each agglomerate varies with time. This change is small for the SBV and AnBV models when compared to the SB and AB model simulations. Moreover, there is no systematic change in the fractal dimension for the SBV and AnBV models. This is in contrast to the other more conventional model implementations.

For the LJ model, a fractal dimension cannot be defined due to the breakage of the agglomerates. Further simulations have been carried out using increasing attractive potential depth (ϵ)-values to avoid breakage of the agglomerates.

The simulation results indicate that small values of the potential depths cannot avoid breakage while larger ϵ values yield rather compact agglomerates that do not preserve the initial shape (Figure 6).

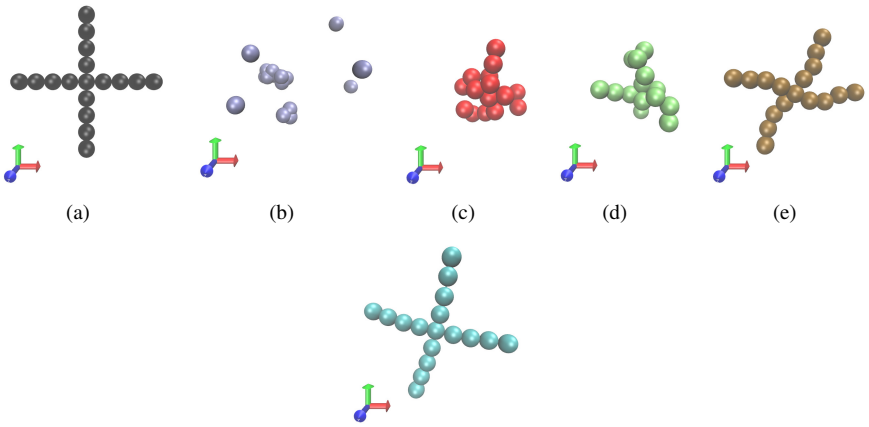


Figure 4: (a) The initial configuration of the cross-shaped agglomerate, and its final configurations obtained from (b) LJ model, (c) SB model, (d) AB model, (e) SBV model, (f) AnBV model simulations.

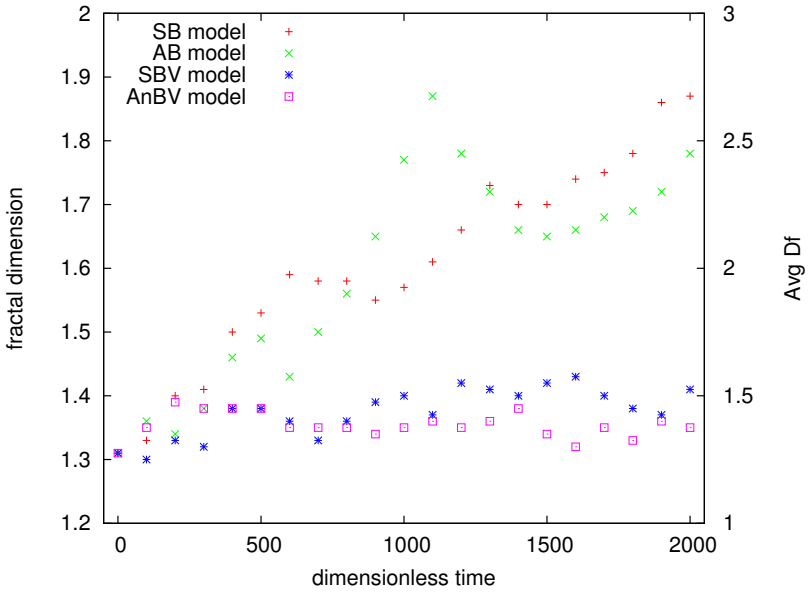


Figure 5: Change in fractal dimension of initially generated cross-shaped agglomeration for different simulation models.

In the SB and AB models, particles rotate around the bonds. If the particles do not have strong repulsive interactions, this might lead to the formation of further bonds within the cluster, resulting in a rather bulky agglomerate. Figure 7 displays both the number of bonds and

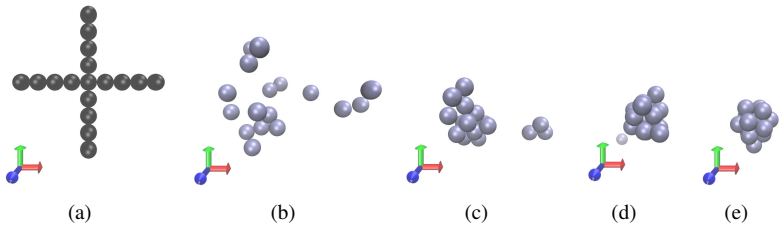


Figure 6: different Lennard Jones attractive potential depth values for LJ-model: (a) The initial configuration of cross-shaped agglomerate, (b) $\epsilon = 1$, (c) $\epsilon = 5$, (d) $\epsilon = 50$, (e) $\epsilon = 500$.

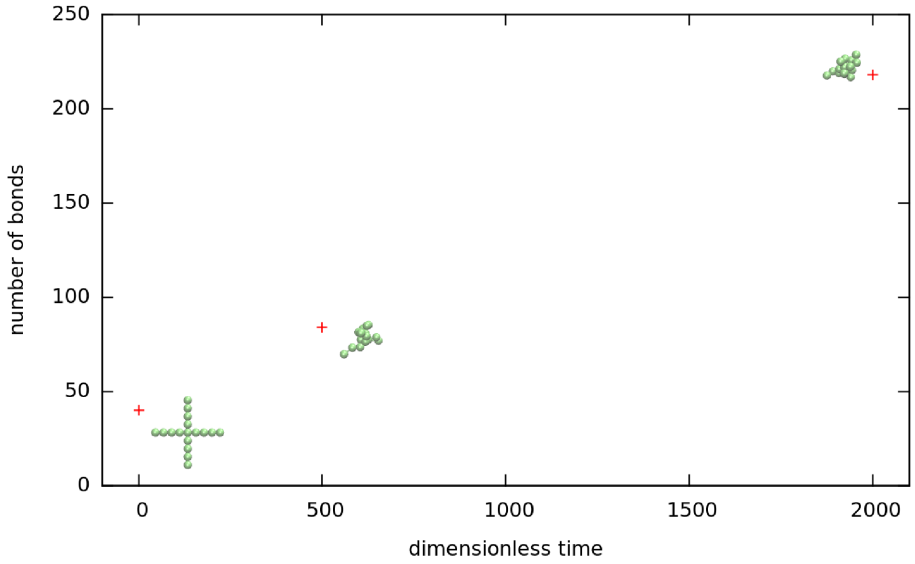


Figure 7: Change in number of bonds during the AB model simulation of cross-shaped agglomerate.

the agglomerate shape within the cross-shaped agglomerate during the AB model simulation of Case-1. Clearly, a lot of additional bonds is formed, leading to the bulky shape.

According to the computations of Case-1, the SBV and AnBV model algorithms are more promising for preserving the agglomerate shape. Further parameter studies have been performed to identify the differences for the SBV and AnBV models.

3.3. Simulations of the randomly placed particles - Case-2

Case-2 simulations are carried out to provide quantitative and qualitative information on the agglomerate structure that are formed from primary particles due to their relative velocity induced by Brownian motion. The agglomerates are formed by the collisions of single Brownian particles and/or collisons of clusters during the simulation. Since the clusters are formed by bonded particles, they move naturally following the same equations as the nano-particles.

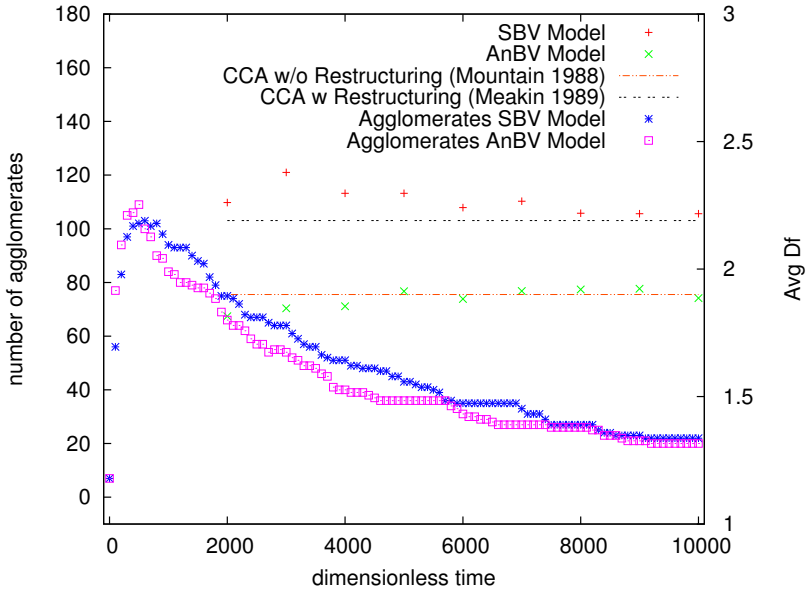


Figure 8: Number of agglomerates and average fractal dimension of the system for SBV and AnBV model simulations.

The agglomeration growth and fractal dimension of formed agglomerates are assessed and shown in Figure 8. At the beginning of the simulations randomly placed 500 particles collide and create clusters, and then with time cluster-cluster collisions form larger clusters.

At any time of the computation the average D_f of the agglomerates that are formed using the SBV model is higher than the respective value of the AnBV simulation. The mean fractal dimension varies between D_f=2.1 and D_f=2.3 for the SBV model simulation. This agrees well with the numerical studies by Meakin and Jullien [27] and Jullien and Meakin [28] for cluster-cluster aggregates (CCA) grown by diffusion-limited aggregation (DLA) including impact restructuring. In their studies, the aggregates might fold, bend and twist. The fractal dimension was found as D_f=2.09 if the agglomerates were allowed to bend, D_f=2.17 if both bending and folding were allowed and D_f=2.19 if the complete restructuring stages were included for CCA grown by DLA.

The restructuring process for the SBV model simulation of Case-2 can be more clearly seen in Figure 9.

Here, we show the change in the morphology of a selected agglomerate using the SBV model simulation of Case-2. At early times, the agglomerate has D_f=1.74, but at later times the particles reorientate themselves, and the number of particle contacts is maximized. This results in a more compact structure with a higher fractal dimension (D_f=2.4 at the end of the simulation).

In contrast, the mean fractal dimension varies between D_f=1.78 and D_f=1.9 for the AnBV model simulation. This result indicates that no significant restructing occurs and agrees well with the measured fractal dimensions of the cluster-cluster aggregates obtained by numerical and experimental studies done by various investigators and summarized by Megaridis *et al.* [29].

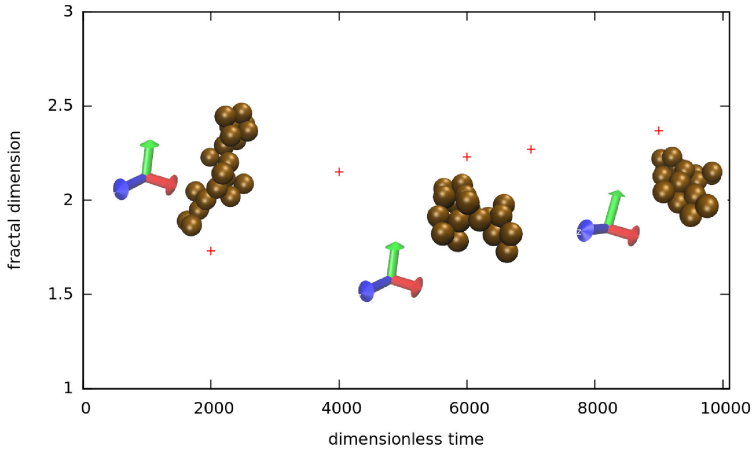


Figure 9: Change in structure of a selected agglomerate (N=22) during SBV model simulation of Case-2.

3.4. Time step dependency analysis for the AnBV model

Additional AnBV model simulations were performed to analyze the sensitivity of the determined agglomerate structure and rigidity to the simulation time step.

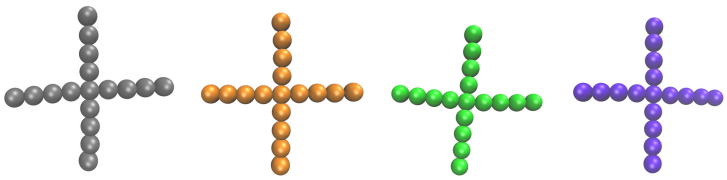


Figure 10: The final configuration of the cross-shaped agglomerate in the AnBV model simulations with, (a) τ=0.00001, (b) τ=0.0001, (c) τ=0.001, (d) τ=0.01.

Figure 10 shows the cross-shaped agglomerate structure at the end of different AnBV model simulations. For all time steps, the agglomerate preserves its shape during the simulations. In this respect, the AnBV model gives time step independent results and even allows for relatively large time steps when compared to the more traditional SB and AB models.

3.5. Diffusion limited agglomeration - Case-3

Another test case (Case-3) is the simulation of the well-known Diffusion Limited Agglomeration (DLA) to validate the developed AnBV model. We study DLA of the irreversible growth of a single cluster grown from a seed particle fixed in three-dimensional space. The growth rule is remarkably simple, in which the first particle is fixed in the center of the system, and the following particle is then released from a random position far away and is allowed to move due to Brownian motion. If it collides with the first particle, it is connected according to the rules

in our AnBV model algorithm and becomes part of the agglomerate. Then, further particles are launched one-by-one and each of them is connected to the cluster after hitting any of the particles belonging to the cluster.

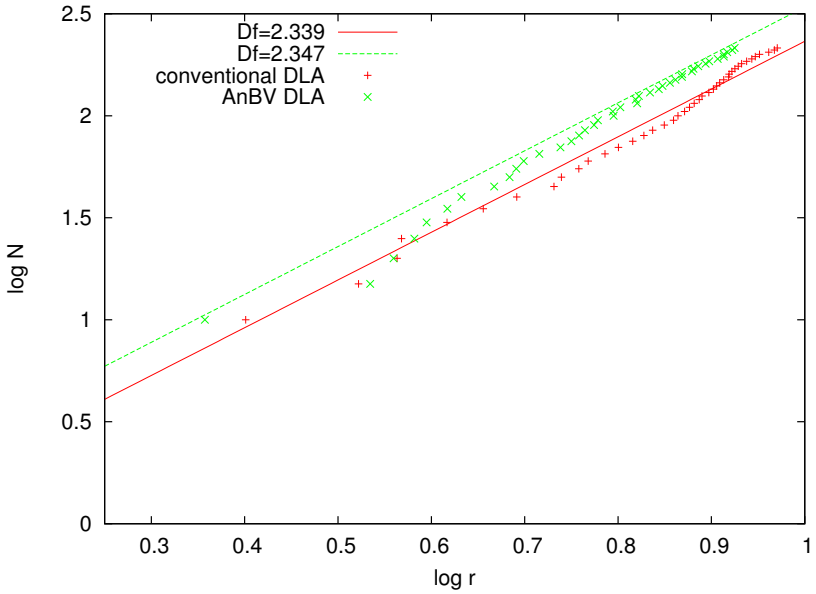


Figure 11: The logarithms of the number of particles, N, and the radius of gyration, R_g of the growing DLA, comparing the conventional model and the AnBV model.

Two realisations are compared in Figure 11. The growth mechanisms are same for the both cases and explained above. However, in the "conventional DLA" model, when the released particles hit any particle of the cluster, they stop as in the classical DLA model, i.e. the formed clusters are immobile. In the "AnBV DLA" model, the aggregate itself is moving, increasing the collision chances. The fractal dimensions of the DLAs are found to be D_f=2.35±0.1 and D_f=2.34 for the AnBV and the conventional DLA models. Thus the motion of the cluster has little influence on the DLA, as expected.

4. Conclusions

In this study, we demonstrated the capability of five different models to simulate the nanoparticle agglomeration process. All 5 models require local bonding only. Analyzing the shape and structure of both pre-defined and randomly formed agglomerates in terms of fractal dimension, it became evident that only the so-called AnBV model is capable of modeling nanoparticle agglomeration without undergoing any restructuring process. In our investigations, we find that using only non-bonded interactions (LJ model) is not sufficient to hold particles together and to prevent sliding around the contact point of individual particles. Also, the SB and AB models including bonded potentials do not fix the particles at their contact points and allow restructuring. Hence, only bulky and compact agglomerates are formed. In addition, the large number of formed bonds increases the system energy during the runtime of the simulation and thus limits the

time step. Our SBV model prevents restructuring but particles can fluctuate considerably around the connection point, which still leads to some restructuring on large scales. Performing different AnBV model simulations using different time steps, the results indicate that this model can avoid restructuring even at relatively large time steps. Furthermore, the AnBV model simulations of both well known diffusion limited particle-cluster agglomerates and cluster-cluster agglomerates obtained by collisions of randomly placed Brownian particles have been investigated. The fractal dimensions of analyzed agglomerates are in good aggreement with other simulations and experiments, thus, our AnBV model is capable of describing agglomeration with completely local interactions.

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