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Manuel Rottereau, Jean-Christophe Gimel, Taco Nicolai, Dominique Durand. Influence of the Brownian step size in off-lattice Monte-Carlo simulations of irreversible particle aggregation.. European Physical Journal E: Soft matter and biological physics, 2005, 18, pp.15-19. 10.1140/epje/i2005-10027-5 . hal-00015713

HAL Id: hal-00015713

<https://hal.science/hal-00015713>

Submitted on 12 Dec 2005

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Influence of the Brownian step size in off-lattice Monte-Carlo simulations of irreversible particle aggregation

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(Dated: December 12, 2005)

The influence of the Brownian step size in off-lattice Monte-Carlo simulations of the aggregation and gelation of spheres is studied. It is found that the kinetics are strongly influenced if the step size is larger than the mean smallest distance between the sphere surfaces. The structure of the clusters and the gels is influenced, but only over length scales smaller than the step size. Using large step sizes leads to a narrower size distribution of the clusters. Implications of the present results are discussed for simulations reported in the literature in which the Brownian step size was chosen equal to the sphere diameter.

PACS numbers: 0.270.Tt, 05.10.Ln, 82.70.Dd, 82.70.Gg

I. INTRODUCTION

In recent years a number of computer simulations have been reported on off-lattice irreversible aggregation and gelation of spherical particles [1–5]. The objective of these simulations is to determine the structural evolution of the system as a function of the particles volume fraction. In short, the simulation involves the following steps: 1) randomly select a particle or a cluster of connected particles; 2) move the particle a step length in a random direction; 3) if the movement leads to overlap with another particle or cluster then truncate the movement at the point of contact; 4) bind particles that come in contact with a chosen probability. If the binding probability is unity diffusion limited cluster aggregation (DLCA) is simulated, while in the opposite limit of very low probability reaction limited cluster aggregation (RLCA) is simulated. In order to simulate Brownian diffusion, clusters are moved in a random direction with a probability that is inversely proportional to their characteristic radius. The starting point of the simulation is usually a random distribution of spheres at a given volume fraction ϕ .

If the simulations are on a cubic lattice, particles or clusters are moved one lattice unit in one of six directions. Clearly, the local structure of clusters formed on a lattice cannot be realistic. In off-lattice simulations any direction and step size can be chosen, but the simulation takes longer if the step size is smaller. Therefore the Brownian step size was still chosen to be the same as the diameter of the spheres in earlier off-lattice simulations. Gonzalez [1] investigated the influence of the step size on simulations of RLCA. He found little influence on the fractal dimension of the clusters, but a strong influence on the aggregation rate. In recent simulations of DLCA we found that the step size can have a profound influence unless it is chosen small enough. In [4, 5] we presented

the results of these simulations using Brownian step sizes that were small enough so that the effect of using a finite step size was insignificant. The objective of the present paper is to show the influence of varying the step size on simulations of DLCA and to establish the extent of validity of earlier simulations.

II. SIMULATION METHOD

The simulation method used involves the following: 1) N spheres with unit diameter are randomly placed in a box with size L so that the volume fraction is $\phi = \pi/6 \cdot N/L^3$. 2) A cluster is chosen randomly and moved in one of the 2500 equally distributed directions over a distance s . 3) If the movement leads to overlap with another cluster then it is truncated at the point of contact and connected. A chosen cluster is moved with probability R_0/R_g , where R_g is the radius of gyration of the cluster and R_0 that of the individual sphere. The simulation is continued until all spheres are connected. For volume fractions higher than 0.385 spheres cannot be randomly positioned in the box simply using a sequential addition [6] due to the lack of free space. Instead they are regularly distributed on a cubic lattice and are moved without forming bonds using very small Brownian step sizes. We have shown in [7] that very short step sizes were needed in this concentration range ($0.385 < \phi < \pi/6$) to obtain perfectly thermalized distributions. Finite box size effects have been estimated by varying L and are negligible for the results shown here. We have used box sizes from $L = 50$ to $L = 200$ depending on the volume fraction.

The number of simulation steps (n) is incremented by one unit after N_c clusters have been chosen, where N_c is the number of clusters at the start of the simulation step. The unit of time (t) is defined as the time needed for an individual sphere to diffuse over a distance equal to its diameter, i.e. unity. It is directly related to n and s through:

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FIG. 1: Weight average aggregation number m_w as a function of time for different Brownian step sizes s indicated on the figure. (a) $\phi = 0.4$, $L = 50$. (b) $\phi = 0.02$, $L = 100$. The data are obtained from a single run.

FIG. 2: (a) Gel time t_g as a function of the Brownian step size s at different volume fractions indicated on the figure. Dotted lines are guides to the eyes. (b) Same as in (a) but $t_g(s)$ has been normalized by $t_g(0)$ and s by $(\Delta - 1)$. The dotted line is a guide to the eyes. The solid line has a slope of 2. The data are obtained by averaging over up to 100 runs.

III. RESULTS AND DISCUSSION

A. Time dependence

Fig.1 shows the influence of s on the increase of the weight average aggregation number (m_w) with time for two volume fractions ($\phi = 0.4$ and $\phi = 0.02$). As explained in detail in [4] m_w increases and diverges at the gel time (t_g) when a cluster percolates the system.

$$t = n \cdot s^2 \quad (1)$$

FIG. 3: Schematic representation of the Brownian step size s and the average distance to the first neighbor Δ . $\Delta - 1$ represents the average smallest distance between 2 sphere surfaces.

For small s the growth of m_w is independent of s , but at larger aggregation is slower. Notice, however, that growth takes fewer simulation steps with increasing s . Increasing s implies increasing the time per simulation step (see Eq.1) and for larger s many bonds are formed in a single simulation step.

The influence of s on the gel time is shown in fig.2(a) for a range of volume fractions. The gel time is not influenced by s at small values of s , but increases strongly for larger s . The transition occurs at smaller s for higher volume fractions. The effect of s can be better understood if one compares s with the average distance between nearest neighbors of randomly distributed spheres (Δ), see fig.3. Torquato [8] has derived an analytical expression for Δ as a function of the volume fraction that agrees well with simulation results. Remarkably, the results at each volume fraction superimpose if $t_g(s)$ is normalized by the value for $s \rightarrow 0$ ($t_g(0)$) and s is normalized by $(\Delta - 1)$, i.e. the average distance between the surfaces of nearest neighbors, see fig.2(b).

If s is much smaller than $(\Delta - 1)$ the gel time is independent of s because the particles perform a diffusional motion between collisions. However, if s is much larger than $(\Delta - 1)$ each movement has a high probability to lead to collision and thus to be truncated at a shorter distance than s . In this case the motion of the particles between 2 collisions is close to ballistic. The implication is that the evolution of the system per simulation step no longer depends on s , but only on the number of simulation steps so that $t_g(s) \propto n \propto t_g(0) \cdot s^2$. $t_g(s)$ is within 10% of $t_g(0)$ for $s < 0.5(\Delta - 1)$, while $t_g(s) \propto s^2$ for $s > 3(\Delta - 1)$. Since Δ is a strong function of ϕ , the influence of taking a fixed Brownian step size (e.g. $s = 1$) depends on the volume fraction. $\Delta - 1 = 1$ for $\phi \approx 0.01$ and the influence of using $s = 1$ on t_g is significant for $\phi > 0.01$. Hasmy et al. [9] simulated DLCA using $s = 1$

FIG. 4: Aggregation number (m) as a function of the radius of gyration (R_g) for different step sizes (s) indicated on the figures. The solid lines have a slope of respectively 1.8 and 2.5. (a) $\phi = 0.02$, $L = 100$. (b) $\phi = 0.4$, $L = 50$. The data are obtained from a single run.

and presented t_g as a function of ϕ . In view of the present results it is clear that those results are biased by taking a unit Brownian step size at larger ϕ .

B. Structure

During the aggregation process the clusters are initially on average far removed, at least for small ϕ , but as they grow they occupy more and more space and at some point overlap between aggregates will become important. Close to the gel point overlap is very strong and

FIG. 5: Evolution of the fraction of monomers (N_1/N) as a function of t/t_g for different step sizes indicated on the figure at $\phi = 0.4$ and $L = 50$. The data are obtained from a single run.

further growth can be well described by a static percolation process [4, 5]. In each case the aggregates have a self similar structure and there is a power law relationship between the aggregation number (m) and the radius of gyration (R_g) of the clusters: $m \propto R_g^{d_f}$, where d_f is the so-called fractal dimension. However, the fractal dimension of clusters formed by the initial flocculation process is smaller ($d_f = 1.8$) than that of clusters formed by the percolation process ($d_f = 2.5$). The transition between the two limiting regimes occurs at a characteristic aggregation number (m_c) that decreases with increasing volume fraction.

We have checked if this behaviour is influenced by s used in the simulations. Fig.4 shows the dependence of m on R_g using different s for two volume fractions. Within the experimental error the results obtained at different step sizes are the same even for $s = 1$. Apparently, the size of the clusters with a given aggregation number is the same regardless whether the motion between collisions is ballistic or diffusional. It is not surprising that the structure is insensitive to the details of motion in the percolation regime because there the structure is essentially determined by the relative position of the strongly overlapping clusters not their motion. However, the results in the flocculation regime can appear to contradict earlier simulations in which it was found that the fractal dimension of dilute clusters formed by ballistic motion is different ($d_f = 1.9$). The reason is that the limiting behaviour of the flocculation regime can only be observed at low volume fractions where $\Delta - 1$ is close to or above

FIG. 6: Pair correlation function ($g(r)$) of the final state for 2 different s indicated in the figure. (a) $\phi = 0.005$, $L = 200$. (b) $\phi = 0.1$, $L = 50$. The data are obtained from a single run and Monte Carlo sampling was used over about 10^{10} pairs of particles.

unity. In addition in the flocculation regime the distance between nearest neighbours that are part of different clusters increases as the clusters grow. That means that the limit of ballistic motion cannot be reached even at $s = 1$, which is the largest value that could be used in our simulations. As mentioned in the introduction Gonzalez [1] did not observe a significant variation of d_f with s ($s < 1$) in simulations of RLCA in the flocculation regime.

C. Size distribution

The polydispersity of the clusters for a given value of t/t_g decreases if s is increased above $\Delta - 1$. The reason is that the fraction of monomers and oligomers decreases faster as a function of t/t_g if s is increased. Fig.5 shows the evolution of the fraction of monomers (N_1/N) as a function of t/t_g for various step sizes. A relatively faster decrease of small clusters is expected because the probability to collide during one simulation step increases with increasing s . If $s \gg \Delta - 1$ monomers have very little chance to survive up to the gel point.

D. Pair correlation function

The influence of the Brownian step size on the pair correlation function ($g(r)$) is shown in fig.6 for gels at two volume fractions in the final state. As explained in [5] connecting the particles leads to a delta peak at $r = 1$ that is proportional to the average number of bonds per sphere and to a discontinuity at $r = 2$. The effect at larger integer values decreases rapidly below the noise level. The most important effect of s occurs at r close to unity, i.e. on the depletion of particles close to the surface of a given sphere. In essence the influence of the step size on this depletion layer is felt for $r < (1 + s)$, as might be expected because the motion of the particles is not diffusional at length scales smaller than s . The effect on the local structure of the clusters does not depend on the volume fraction, but it depends on the absolute value of s even if $s \ll (\Delta - 1)$. The implication is that for a correct description of the local structure of aggregates formed even in dilute solution it is necessary to take very small Brownian step sizes.

Lattuada et al. [10] presented recently a detailed de-

scription of dilute clusters formed by a DLCA or RLCA process obtained by dynamic Monte-Carlo simulations using $s = 1$. They obtained a power law increase of $g(r)$ between $r = 1$ and $r = 2$ and related this dependence to the distribution of angles between 3 randomly connected spheres. Clearly these results were biased by the step size. We found that the distribution of angles between 3 randomly aggregated spheres is also influenced by s .

At larger values of r the influence on $g(r)$ is small and choosing $s = 1$ does not modify the position of the weak minimum of $g(r)$. This means that the values of the minimum position as a function of the volume fraction reported by Hasmy and Jullien [9] are not biased by using $s = 1$.

The corresponding structure factors ($S(q)$) have been shown for $s \ll \Delta - 1$ in ref. [5]. The effect of using larger s is relatively small and only visible at $q \approx 2\pi$. For large q , $S(q)$ is determined by the average number of contact per monomer which is always 2 independently of s [4]. For small q , $S(q)$ is determined by $g(r)$ for $r > 2$ and therefore also not influenced by s .

IV. SUMMARY

The Brownian step size used in dynamic Monte-Carlo simulations of cluster aggregation influences the aggregation rate and the structure of clusters. The effect on the aggregation rate and thus the gel time, depends on the ratio between s and the average nearest distance between randomly distributed spheres. If $s < 0.5(\Delta - 1)$ the influence is small because the motion between collisions remains diffusional, but if $s > 3(\Delta - 1)$ the influence is strong because the motion becomes essentially ballistic. The influence on d_f and on the structure of the clusters and the gels is small at large length scales, but the local structure is modified for distances smaller than s .

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