Flocculation and percolation in reversible cluster-cluster aggregation

S. Babu, M. Rottereau, T. Nicolai\textsuperscript{a}, J.C. Gimel\textsuperscript{b}, and D. Durand

Polymères Colloïdes Interfaces, UMR 6120 CNRS – Université du Maine, 72085 Le Mans Cedex 9, France

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Abstract. Off-lattice dynamic Monte-Carlo simulations were done of reversible cluster-cluster aggregation for spheres that form rigid bonds at contact. The equilibrium properties were found to be determined by the life time of encounters between two particles ($t_e$). $t_e$ is a function not only of the probability to form or break a bond, but also of the elementary step size of the Brownian motion of the particles. In the flocculation regime the fractal dimension of the clusters is $d_f = 2.0$ and the size distribution has a power law decay with exponent $\tau = 1.5$. At larger values of $t_e$ transient gels are formed. Close to the percolation threshold the clusters have a fractal dimension $d_f = 2.7$ and the power law exponent of the size distribution is $\tau = 2.1$. The transition between flocculation and percolation occurs at a characteristic weight average aggregation number that decreases with increasing volume fraction.

PACS. 05.10.Ln Monte Carlo methods (see also 02.70.Tt, Uu in mathematical methods in physics; for Monte Carlo methods in plasma simulation, see 52.65.Pp) – 82.70.Dd Colloids – 82.70.Gg Gels and sols

1 Introduction

Random aggregation of small particles is a commonly observed phenomenon and may lead to the formation of gels [1–4]. The initial stage of the aggregation process in dilute systems has been extensively studied using computer simulations [5–9]. Kinetic equations with the appropriate kernels have been used to model the growth [8–10]. Much less attention has been given to the situation where the clusters can no longer be considered dilute [11–14]. As the clusters grow their cumulated volume fraction increases and at some point they will start to interpenetrate. Eventually irreversible aggregation leads to gelation at any concentration. If the aggregation process is irreversible a steady state will be reached at a more or less advanced stage depending on the ratio of the aggregation and fractionation rate [15–24]. Also in this case the clusters may percolate the system, but now the gel is only transient [18,19,25–27].

In recent work we have simulated irreversible diffusion limited cluster-cluster aggregation (DLCA) from the initial state of monomers to the final state where all particles form a single percolating cluster [28,29]. We have shown that as long as the average distance between the clusters is large (flocculation regime) they have a self-similar structure characterized by a fractal dimension $d_f = 1.8$. With increasing cluster size the average distance between the clusters decreases and at a characteristic aggregation number ($m = m_c$) and radius of gyration ($R_g = R_c$) they fill up the whole space and start to interpenetrate. The aggregation of clusters larger than $R_c$, which leads to gelation, can be described by the percolation model [13,14,28,30]. As a consequence the structure of the clusters on length scales larger than $R_c$ is characterized by $d_f = 2.5$. Also the size distribution changes from relatively monodisperse for clusters formed in the flocculation regime, i.e. $m < m_c$, to the power law size distribution for clusters formed in the percolation regime: $N(m) \propto m^{-2.2}$ for $m > m_c$.

This paper reports a study of the effect of bond breaking on the aggregation of spheres. A bond is formed at collision with probability $\alpha$, and the bond breaks at each diffusion step with probability $\beta$. The two limiting cases of diffusion (DLCA) and reaction limited (RLCA) cluster aggregation are obtained by setting $\alpha = 1$ and $\alpha \ll 1$, respectively. If $\alpha/\beta$ is small the equilibrium state contains essentially monomers, while if it is large most particles will be part of a single percolating cluster. The fact that the particles stick only at contact implies that solely binary collisions occur and thus no loops can be formed. Since the bonds are rigid loops cannot be formed at a later stage either. As a consequence, the average number of neighbours per particle cannot exceed two. This means that reversibility does not lead to densification and phase separation. The latter does occur if the interaction range is finite or if the bonds are not rigid [22,25,31,32]. The present model of cluster-cluster aggregation is thus probably the simplest one that includes reversibility. We note

\textsuperscript{a} e-mail: taco.nicolai@univ-lemans.fr
\textsuperscript{b} e-mail: Jean-Christophe.Gimel@univ-lemans.fr
that for lattice simulations more than one contact can be formed per collision so that densification and phase separation do occur [19,33].

The paper is organized as follows. We will first explain the off-lattice simulation method used for this study and discuss the distinction between encounters and collisions. This distinction was discussed earlier by Odriozola et al. [10,34] in the context of irreversible RLCA and reversible DLCA. During one encounter the particles may have many correlated collisions before they move apart. In order to model the early stage of irreversible RLCA or reversible aggregation it is necessary to account for the number of collisions per encounter. It will be shown that the important parameter in the simulations is not the life time of a single bond, but the life time of an encounter \( t_e \). \( t_e \) is a function both of \( \alpha/\beta \) and the number of collisions per encounter. The latter increases when the step size of the Brownian motion \( (s) \) is decreased. However, the simulations are independent of \( s \) if \( \alpha/\beta \) is chosen in such a way that \( t_e \) is constant.

Next we will discuss the results obtained in the flocculation regime in terms of mean field theory using kinetic equations containing both an aggregation and a fragmentation kernel. These results will be compared with earlier simulations of reversible DLCA reported by Odriozola et al. [34]. Finally, we will show that if the fragmentation rate is decreased transient gels are formed and that the sol-gel transition can be described by the percolation model.

## 2 Simulation method

A cluster is chosen randomly and is moved with step size \( s \) in a random direction. The movement of a cluster occurs with a probability inversely proportional to its diameter. This means that the clusters diffuse with a diffusion coefficient that is inversely proportional to their diameter. We thus simulate Brownian motion. We have shown in reference [28] that this method gives the correct time dependence of the average molar mass for the case of irreversible DLCA. If the displacement of a cluster leads to overlap between two spheres or the wall it is truncated at contact. The displacement procedure is repeated a number of times equal to the total number of clusters in the box. Then bonds are formed with probability \( \alpha \) between spheres in contact and bonds are broken with probability \( \beta \). In the present simulation the attempt rate to break and form bonds is the same as the attempt rate for each cluster to move one step. Notice that large clusters need on average many attempts before they move. We have tested the effect of varying the attempt rate to break and form bonds. No significant effect is observed if the rate is increased, but, of course, it increases the CPU time. If the attempt rate to break and form bonds is slower than the movement an effect is observed that is similar to the one observed if both \( \alpha \) and \( \beta \) are reduced by the same factor, see below and Figure 3.

This cluster formation procedure defines the clusters that are moved in the subsequent displacement procedure. After these two procedures the simulation time \( (t_{\text{sim}}) \) is incremented by 1 and the whole process is repeated until equilibrium is reached. Contrary to Odriozola et al. [34]. We do not move the clusters automatically apart when the bond is broken. If the clusters have not moved apart in the following movement procedure the bonds will be formed again with probability \( \alpha \) in the next cluster formation procedure.

The starting configuration consists of \( N \) randomly positioned spheres with unit diameter in a box with size \( L \) at volume fraction \( \phi \). The physical time \( (t) \) unit is defined as the time needed for an individual sphere to diffuse a distance equal to its diameter: \( t = s^2 \cdot t_{\text{sim}} \). For example the time unit would be 0.4 s for spheres with a diameter of 1 \( \mu \text{m} \) in water at 20 \( ^\circ \text{C} \). The displacement of the clusters is diffusional and independent of \( s \) for distances larger than 3\( s \). As mentioned above, bonds are attempted to be broken and formed at each simulation step. As a consequence the attempt rate in terms of the physical time decreases with increasing step size and is equal to \( s^{-2} \).

The effect of finite box size was studied and is negligible as long as the largest cluster in the box is smaller than \( L \). The results shown in this paper are not influenced by finite size effects.

## 3 Encounter versus collision

Two initially decorrelated spheres that collide will have on average \( N_{\text{col}} \) collisions before they move apart and their positions become decorrelated again. The number of collisions per encounter is, of course, independent of \( \alpha \) and \( \beta \), but does depend on \( s \). We have done simulations following the diffusion of two spheres that collide at \( t = 0 \). They show that \( N_{\text{col}} \) increases linearly with \( s^{-1} \): \( N_{\text{col}} = 2.36/s + 1 \), see Figure 1. Here, we also count as a collision the event when two unbound spheres at contact move into each others direction and therefore remain at contact after the displacement procedure. This event will account on average for half of the collisions. Each collision leads to a delay of the diffusion process proportional to \( \alpha/\beta \) corresponding to the average time during which the particles are bound per collision. We will call the average time that the particles are bound during an encounter the life time of an encounter, which is a linear function of \( \alpha/\beta \) and \( s \), see Appendix A:

\[
t_c = (2.36 + s) \cdot \alpha/\beta \cdot s.
\]

The distinction between collisions and encounters is important, because the properties of the system are not determined by the life time of a single bond, but by the total time that two spheres are bound during an encounter. We have verified that the same simulation results are obtained for different values of \( s \) and \( \alpha/\beta \) if \( t_c \) remains the same. However, \( s \) needs in any case to be much smaller than the average distance between the surfaces of the spheres in order to assure Brownian motion between encounters as was discussed elsewhere for the case of irreversible aggregation [35].