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LETTER TO THE EDITOR

Cluster–cluster aggregation with dipolar interactions

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Abstract. The hierarchical cluster-cluster aggregation model is extended in the presence of dipolar interactions between the magnetic dipoles attached to each individual particle. It is found that the fractal dimension of the resulting clusters decreases when the intensity of the momenta increases, as observed in recent experiments.

There has recently been much theoretical progress in understanding aggregation phenomena [1]. Two diffusion-limited aggregation models, particle-cluster [2] and cluster-cluster aggregation [3], have been introduced and extensively studied by means of numerical simulations, leading to fractal aggregates whose fractal dimensions have been recovered in several experiments. In particular, the cluster-cluster aggregation model was able to describe quantitatively the fractal structure of some aerosol [4] and colloid aggregates [5]. In its original form the cluster-cluster model is a very rough simulation of physical reality. In particular, the particle-particle interactions are sketched by an infinite positive potential for interparticle distances smaller than the particle diameter, an infinite negative potential at the particle diameter and a strictly vanishing potential for all larger distances. This is relatively well justified in the case of van der Waals interactions which are strongly decreasing with interparticle distance (taking into account the fact that the details of the potential curve only affect the short-distance structure, as recently confirmed by Langevin molecular dynamics [6]). However, this is not the case when dipolar interactions are present. Some experiments have led to fractal dimensions smaller than those predicted by the original model, and polarisability effects have been invoked to explain this discrepancy. A crude model, the tip-to-tip model, has been introduced [7], able to explain quantitatively the fractal dimension of aluminium hydroxide aggregates, as measured by low-angle x-ray scattering [8]. The same kind of experiments have also been performed on iron hydroxides [9], leading to a smaller fractal dimension. This low fractal dimension could be due to the effect of long-range dipolar magnetic interactions. The same effect has been recently observed in experiments done with magnetic (cobalt and iron) aerosols where it has been clearly observed that the fractal dimension decreases when the magnetic moment on the individual particles increases [10]. In this letter we extend the cluster-

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cluster model to simulate this physical situation. Rigid magnetic dipoles are now attached to the particles and both the rotational diffusion motion of the clusters and the orientations of the dipoles are influenced by long-range dipolar interactions.

For simplicity we have used the hierarchical scheme [11] for cluster-cluster aggregation which, in the original version, is known to give the same quantitative results demanding less computational time. In this scheme successive generations of clusters with equal numbers of particles 2, 4, 8, ..., 2^n are built, starting from a collection of identical spherical particles of unit diameter. A cluster of the new generation always results from the sticking of two clusters of the old generation. Here, we have used a qualitatively different and more realistic procedure than in the original scheme. In particular, we have considered off-lattice motions and, for the first time, we have included three-dimensional rotational Brownian diffusion (to our knowledge rotational diffusion has been up to now only studied in two dimensions in the cluster-cluster model [12]). Also, to each individual particle was attached a unitary vector, $\boldsymbol{u}$, defining the direction of its momentum, which was randomly oriented in the beginning.

When starting a collision process, two clusters of the old generation are randomly rotated and placed apart in space with their centres of mass R_0 apart. It could be thought that the choice of R_0 should be crucial, since, in presence of long-range interactions, R_0 must, in principle, be chosen sufficiently large to avoid the influence of the initial conditions. In practice, we have observed that this choice is not so important and we have finally chosen $R_0 = 2(R_1^M + R_2^M)$, where R_i^M is the maximum radius of cluster i. In one example, in the presence of dipolar interactions, we have varied R_0 up to three times this value with no significant change (within the error bars) in the resulting fractal dimension, but with a dramatic increase in computing time!

The two clusters being placed at their initial positions, two types of Brownian movements are then performed alternately, translations and rotations. The translation occurs in a randomly chosen direction and it is of one unitary distance, except when an overlap occurs, when it is chosen in such a way that one particle of cluster 1 becomes exactly tangent to one particle of cluster 2. The rotation is performed in one of the three planes (randomly chosen) defined by two of the three axes, either in a given direction or another. Following a prescription already adopted in two dimensions [12], the absolute value for the rotation angle is the one which allows for the most distant particle (with respect to the centre of mass of its cluster) a translation of one unitary distance. Here also it is chosen smaller if an overlap were to occur. For numerical ease one of the clusters is the one which translates and the other one is the one which rotates. Also, as usually in such a hierarchical procedure, when the two centres of mass reach a distance apart greater than a given value, R_1, the collision process is reinitialised. Here also we have studied the influence of the choice of R_1, and to avoid large errors and to stay within reasonable computation times we have finally chosen $R_1 = 2R_0$.

After the calculation of each movement, the quantity

$$P = \exp(-K\Delta u)/(1+\exp(-K\Delta u))$$

is computed. Here Δu is the change in the dipolar energy resulting from the movement. The dimensionless dipolar energy is calculated as a sum over all the pairs of particles of the two clusters:

$$u = -\sum_{i \neq j} \boldsymbol{u} \cdot \boldsymbol{H}_{ij}$$

with

$$\boldsymbol{H}_{ij} = [3(\boldsymbol{u} \cdot \boldsymbol{r}_{ij})\boldsymbol{r}_{ij} - r_{ij}^2 \boldsymbol{u}_i]/r_{ij}^5$$

and

$$\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$$

where $\boldsymbol{r}_i$ (counted in particle diameter units) denotes the position of the centre of particle i. The dimensionless parameter K is then given by

$$K = \mu^2/(d^3 kT)$$

where μ is the intensity of the individual momenta, d is the particle diameter and T is the temperature.

After P is calculated, the movement is effectively performed with probability P. This means that for very large momenta (or zero temperature) the movement is only performed if it lowers the energy. On the other hand, for vanishing momenta the movements are performed with a probability ($P = \frac{1}{2}$) independent of the change of energy. This is a realistic procedure quite similar to standard Monte Carlo algorithms [13].

After each pair of movements (performed or not) a relaxation of the momenta may be done. For this we mean visiting, in a random order, all the particles of the two clusters and, for each of them, orienting its momentum in the direction of the total field, at its position. This procedure physically assumes a quite short relaxation time for dipole orientations.

Finally, as in the standard hierarchical procedure, the cluster of the new generation is defined as the ensemble of the two clusters at their positions just after sticking.

In presence of dipolar interactions, the time of computing quickly becomes very high and so we limited ourselves to relatively modest aggregates of 128 particles. The fractal dimensions reported below were estimated from the plot of the radius of gyration as a function of the number of particles after averaging over 15 independent samples.

We have first checked that, without dipolar interactions, without rotational diffusion and without momentum relaxation, a value very close to the one already known for translational Brownian diffusion in three dimensions [14] is recovered. In fact we recover $D = 1.75 \pm 0.08$, a value within the error bars but somewhat smaller than the expected one (1.78 ± 0.05). The difference can very well be attributed to finite-size effects. We have then studied the influence of Brownian rotational diffusion. As in the previous two-dimensional study [12], the fractal dimension is slightly reduced. For the absolute angle of rotation chosen as described above, we find $D = 1.72 \pm 0.08$. Thus the relative lowering of D is of the same order as in two dimensions [12]. A typical cluster is shown in figure 1. Here the arrows showing the momenta are randomly oriented and did not play any role in the diffusion-sticking process.

In a second series of calculations we have taken into account the dipolar interactions without momentum relaxation. In the limit of very large momenta (i.e. for $K^{-1} = 0$), we find $D = 1.35 \pm 0.08$, a value significantly smaller than the preceding one. A corresponding typical cluster is shown in figure 2. Here also, all the momentum orientations are present but one can observe that locally some correlated orientations appear.

Finally, we have included relaxations of the momenta in our calculations. In the limit of zero temperture, we find $D = 1.34 \pm 0.08$, a value very close to the one without relaxation. A typical sample is shown in figure 3. Even if the fractal dimension is almost the same as in the sample of figure 2, a great difference is observed in the orientations of the dipoles. They are now quite well aligned. We have also tested that,

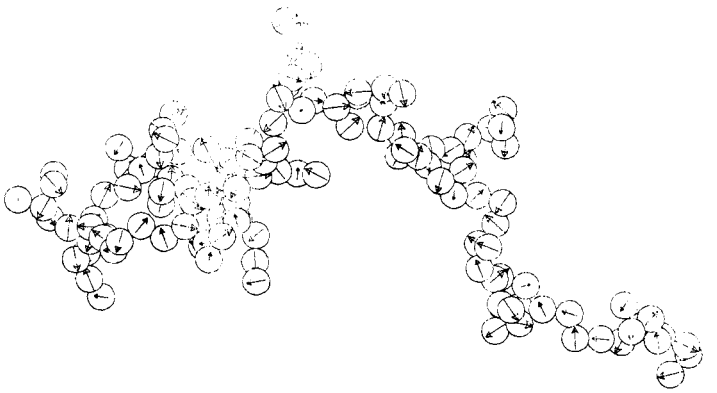

Figure 1. A typical cluster of 128 particles obtained without taking into account dipolar interactions nor the orientational dipole relaxation.

Figure 2. A typical cluster of 128 particles obtained in the presence of strong dipolar interactions ('zero-temperature limit') but without including dipole relaxations.

as expected, the effect of reducing the intensity of the momenta is to increase the resulting fractal dimension. For $K^{-1} = 0.001$ a value of $D = 1.50$ is recovered.

The main conclusion of our study is that including a relaxation of the momenta has a strong effect on the local orientations of the momenta but does not influence the fractal dimension of the resulting cluster as much. The main effect comes from long-range interactions which oblige the clusters to stick on their neighbouring tips, as in the previous tip-to-tip model [7]. It is worth noting that, although slightly smaller, the fractal dimension recovered here, in the limit of very large momenta ('zero-temperature' limit) is very close to the one of the tip-to-tip model in three dimensions

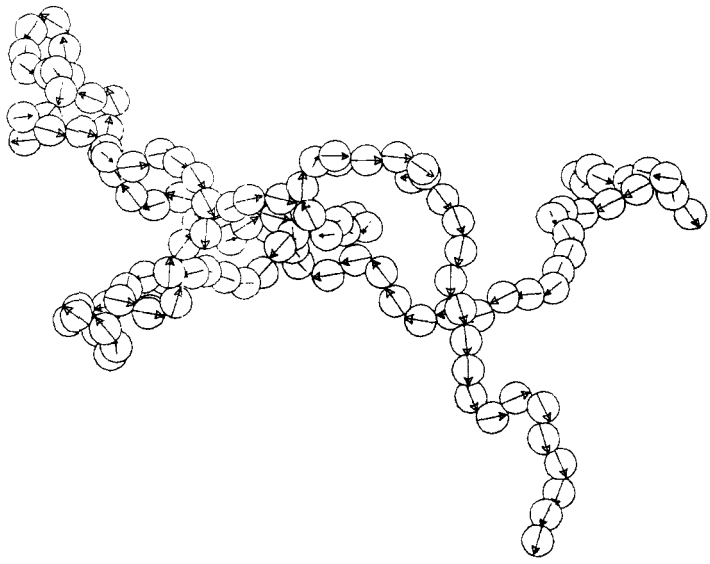

Figure 3. A typical cluster of 128 particles obtained in the presence of strong dipolar interactions and dipole relaxations.

($D = 1.42 \pm 0.05$) [7]. However no more serious comparisons can be done because in the crude tip-to-tip model, no diffusion (either translational or rotational) was allowed. Moreover, the reduction of the fractal dimension with increasing momentum is in good agreement with recent experiments on magnetic aerosols [10]. The fractal dimensions for iron (high momentum) and cobalt (low momentum) aggregates are found to be 1.54 and 1.72, respectively, varying in the right direction and both located within our limited values, 1.34 (infinite momentum) and 1.72 (zero momentum). However, no more quantitative comparison can be done due to our large error bars.

Even if the main effect of reduction of the fractal dimension is here recovered, we must pursue the present study, in particular by extending the original cluster–cluster model in a box [3] in the presence of dipolar interactions. This is essential to study the kinetics, but also to study the effect of an external field which is known to reduce the fractal dimension considerably [10].

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