Gel formation by reversible cluster-cluster aggregation

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Based on the reversible diffusion-limited cluster-cluster aggregation (DLCA) algorithm, a model for gel formation is proposed, where the interaction energy between particles is considered as a parameter. Unlike the irreversible DLCA models, which study only rigid motion of the clusters, the reversible DLCA model simulates explicitly the kinetics of the particles of the clusters, such as restructuring within the same cluster or breaking away from it. Precisely because of the decrease in the compactness of the clusters with interaction energy ϵ between the particles, our simulation reveals that the sol-gel transition point c_g of the particle concentration decreases with increasing ϵ. The most important result of our study is that the value of c_g is greater than zero and independent of the system size (i.e., the side length L of the two-dimensional square lattice) when the interaction energy ϵ is below 1.5. The zero-c_g difficulty encountered by the irreversible DLCA models is therefore removed. In addition, the fractal dimension D of the clusters is found to decrease with ϵ and converge to the value obtained by irreversible DLCA models when ϵ goes to infinity. [S1063-651X(96)06107-7]

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I. INTRODUCTION

Because of its importance in diverse processes in nature and synthetic industries, as well as the rich physics involved, the sol-gel transition has recently been extensively studied. However, since the transition itself is a nonequilibrium process with several controlling parameters that complicate the issue, the understanding of the basic mechanism that leads to the formation of the gel network is far from complete. Several models have been proposed, namely, the kinetic equation approach [1], the bond percolation model [2], and the kinetic aggregation models [3–6]. Among them, the diffusion-limited cluster aggregation (DLCA) algorithm [4,5] is perhaps the most important and represents a great advance in the understanding of the gel formation. In DLCA algorithms, particles, as well as clusters of particles, are allowed to diffuse randomly and stick irreversibly when they touch each other. However, the model has a fundamental difficulty in predicting the concentration threshold c_g for the sol-gel transition and gives a zero value for c_g in the thermodynamic limit of an infinitely large system size L [7,8]. In other words, the gelation can take place at any particle concentration c no matter how low the value is, which is not true for many aggregation processes in the real world except for a few examples [9]. In an effort to overcome this difficulty, Jullien and Hasmy [8] recently proposed a modified DLCA (MDLCA) model by allowing cluster deformation in the aggregation process, where they introduced an adjustable tuning flexibility parameter F to allow internal movements in addition to the rigid motion of the clusters. However, the

introduction of the tuning flexibility parameter merely gives a phenomenological description of the movements of the particles inside the clusters and the kinetics of these internal movements is not thoroughly explored. As pointed out by Meakin [10], a reasonably complete model for the cluster aggregation process should include such effects as long- and short-range interactions [11], particle size distribution and irregular shapes, hydrodynamic interactions [12], clustering of clusters [13], and many others.

Indeed, many experiments [14–19] have already indicated that the interaction energy between particles plays a very important role in the aggregation process. When the particles are bonded only by short-range van der Waals attractive forces (i.e., the electrostatic interaction is fully screened), which are usually very strong, the aggregation process is diffusion limited and described by the standard DLCA model [4,5]. On the other hand, in the case where, in addition to the short-range van der Waals attractive forces, the particles also possess a repulsive part in their interactions (i.e., the electrostatic interaction is partially screened), the aggregation process is reaction limited and the reaction-limited cluster-cluster aggregation (RLCA) model [20] applies. It is worth noting that in either the standard DLCA or RLCA, the aggregation process is irreversible in the sense that once the particles are bonded together they cannot break up due to the deep attractive well. However, there exist situations where the effective attractive forces are relatively weak [19] or the experimental temperature is sufficiently high so that the particles have high probability to escape the attractive well and break up. The corresponding aggregation process is reversible and described by the reversible DLCA model [21,22] in which the particles are allowed to restructure within the clusters or even break apart from them.

In this work, we study exactly the influence of the inter-

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action energy between the particles on sol-gel transition process. Specifically, a model for gel formation is proposed where, besides a few details, the kinetics is the same as in the reversible DLCA model. We find a nonzero concentration threshold c_g above which gelation can take place and, most important, when the interaction energy between particles is not very strong, c_g is independent of the system size, as it should be. Therefore, in the thermodynamic limit of infinitely large system, the difficulty regarding the zero c_g is overcome by our model.

II. MODEL

A Monte Carlo simulation is carried out on an $L \times L$ square lattice with unit lattice constant and periodic boundary conditions in the x and y directions. For a given concentration c, the particles occupy a total of cn lattice sites, where $n = L^2$ is the total number of sites. Both nearest-neighbor (NN) and next-nearest-neighbor (NNN) interactions are considered and, for simplicity, NN and NNN interactions are assumed to be the same, i.e., $\epsilon_{jk} = -\epsilon$ ($\epsilon > 0$) when particles j and k have either NN or NNN contact. The inclusion of NNN interactions serves to reduce the arbitrary directional asymmetry imposed by the square lattice on the particles that possess spherical symmetry in most of the examples of gel formation in the real world. Some tests are also carried out where only NN interactions are considered (see the discussion below). The steric restriction is applied, i.e., double occupancy of any lattice site is forbidden. Initially, N ($=cn$) particles are randomly distributed on the lattice subject to steric restriction and are allowed to diffuse randomly. Two particles stick and merge into one cluster when they have NN or NNN contact. The clusters behave the same way as the particles, that is, when any one particle in one cluster has NN or NNN contact with the particles of a second cluster, the two clusters stick to merge into a new cluster. Furthermore, unlike in the irreversible DLCA model, the particles are allowed to rearrange their positions within the same cluster or break apart from it. The probability of such a move depends on the change in energy ΔE and is proportional to $\exp(-\Delta E/kT)$, where k is the Boltzmann constant and T the temperature of the system. The mobility η of each cluster (or particle) is assumed to be inversely proportional to its mass m, i.e., $\eta \propto m^{-\alpha}$ with $\alpha = 1$. Other values of the exponent α have also been used in the literature; however, neither the dynamics nor the final geometry of the aggregates changes too much [4,5]. A standard Metropolis algorithm [23] is employed to sample the states with the correct thermodynamic distribution proportional to $\exp(-E/kT)$, where E (which is the summation of the interaction energies between the particles) is the total energy of each configuration. Any attempted move consistent with the steric restriction is accepted when the condition $\min[\exp(-\Delta E/kT),1] \geq \zeta$ is also satisfied, where min stands for taking the minimum of the two quantities, $\Delta E = E_f - E_i$ is the change in energy due to the move, and ζ is a random number uniformly distributed between zero and unity. Starting from some initial configuration, the system is allowed to evolve according to the above condition until a final stable state is reached. The evolution time is measured in Monte Carlo steps, which is the number of attempted moves of the particles.
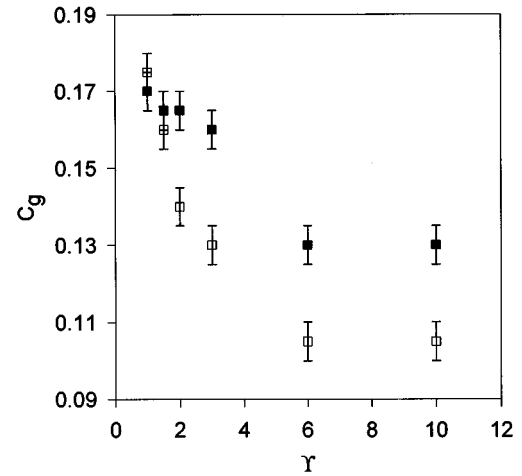

FIG. 1. Dependence of sol-gel transition point c_g on $\gamma = \epsilon/kT$. The filled and open symbols are, respectively, the data for systems of lattice length $L = 60$ and 100. The error bar is shown as the short line attached to the symbol and the same convention is also used in Figs. 2 and 3.

III. RESULTS AND DISCUSSION

The main objective of this work is to study the influence of the interaction energy between particles on the sol-gel transition point c_g, which is determined by the following procedure. For a certain value of particle concentration c, 20 independent computer runs (with different sets of random numbers) are carried out and if the largest cluster spans the square lattice in either the x or y direction the system is considered to be in the gel state, since with the periodic boundary condition this cluster actually spans the whole space. The number of computer runs (out of a total of 20 runs) that end up with a gel state increases with the value of the particle concentration c. The gelation point c_g is defined as the value of c for which 10 out of 20 computer runs end up with a gel state. Figure 1 shows the dependence of c_g on $\gamma = \epsilon/kT$, in which the filled and open symbols are, respectively, the data obtained from system of side length $L = 60$ and 100, and the error bar is represented by the short vertical lines attached to the symbols. In both cases, c_g first decreases with γ and then approaches a constant. When γ is small, the particles have relatively high probability to restructure their positions within the same cluster or completely break apart from it, because the attractive well is not deep and therefore the energy barrier for such a move is low. As a result, the clusters assume rather compact structures, giving rise to a high value of the critical sol-gel transition point c_g. As γ increases, the probability for restructuring and breaking up decreases and so does the compactness of clusters, leading to a lower value of c_g. As γ increases further, the above probability approaches zero and there is virtually no breaking up; therefore the compactness of the clusters and hence the value of c_g remain unchanged. Figure 1 also shows that for small γ ($\gamma \lesssim 1.5$ here), the value of c_g is actually the same (within numerical accuracy) for systems of size length $L = 60$ and 100, while for large values of γ, the difference in c_g between the two systems is evident. In what follows this point will be discussed in detail.

In Fig. 2 we present the variation of the critical concentration c_g with the size length L of the system where the
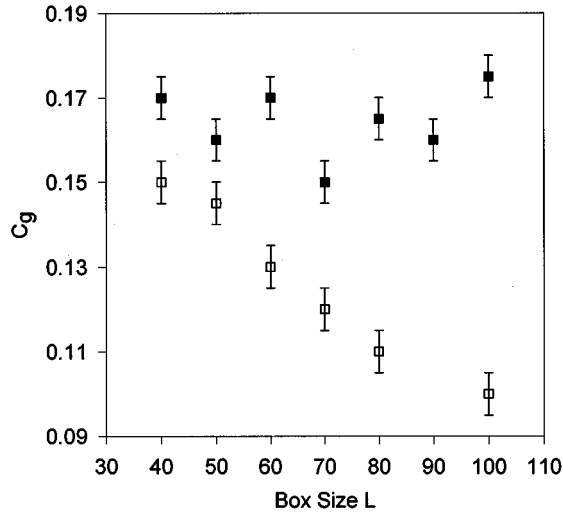
FIG. 2. Variation of c_g with side length L of the system. The filled and open symbols represent the data for interaction energy $\gamma=1.0$ and 10.0, respectively.

filled symbols are the data for interaction energy $\gamma=1.0$, the open symbols represent the data for $\gamma=10$, and the short vertical line at each data point is again the error bar. For $\gamma=10$, it is seen that c_g decreases with increasing L. By extrapolating, we conjecture that the sol-gel transition point c_g will approach zero in the thermodynamic limit of $L\rightarrow\infty$, which is in accord with the result of Kolb and Herrmann [7] and is the main difficulty of the irreversible DLCA models. However, for $\gamma=1.0$ (filled symbols), c_g behaves completely differently and on average the value of c_g stays around 0.165 as L changes. Even though it is not possible to carry out calculations in the thermodynamic limit of $L\rightarrow\infty$, our observation strongly indicates that under the specific condition (i.e., $\gamma=1.0$) the critical value of c_g is independent of the system size L. This result suggests that in the present model, the zero-c_g difficulty encountered by the irreversible DLCA models can be overcome provided that the interaction energy between particles is weak. Physically, when $\gamma=\epsilon/kT\sim1.0$ the thermal energy of the particles (about the order of kT) is comparable with the interaction energy ϵ between the particles; hence the particles are capable of escaping the attractive well by thermal motion, which makes the aggregation process reversible. It is this reversibility that removes the zero-c_g difficulty. In order to test if the above result depends on the details of the interaction energy, several computer runs are carried out where only NN interactions are considered. The conclusion is the same, that is, the sol-gel transition point c_g is independent of the system size L. The value of c_g, however, is different and equals 0.19 for NN-only interactions, which is larger than that in the case of NN plus NNN interactions. This is because the maximum number of bonds of a particle in the case of NN plus NNN interactions is 8, while it is only 4 in the case of NN-only interactions. Consequently, for a given interaction energy ϵ and temperature T, it is easier for the particle to escape the attractive well in NN-only interactions than in NN plus NNN interactions, giving rise to more compact aggregate structures and hence a larger value of c_g. We recall that in their MDLCA model [8] Jullien and Hasmy described the internal motions of the particles inside the clusters by an adjustable parameter F with-
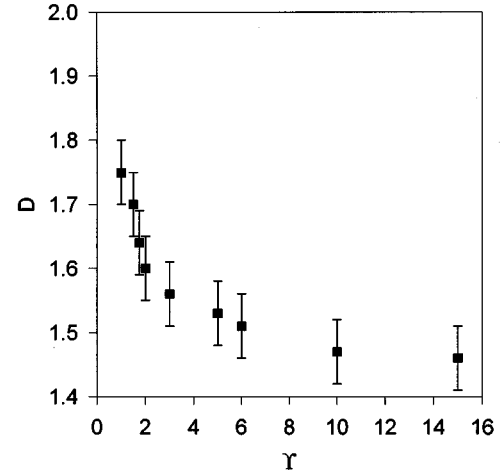

FIG. 3. Dependence of the fractal dimension D on interaction energy γ. The data were obtained from the system of side length $L=80$ with particle concentration $c=0.10$.

out specifying the details of their kinetics. Our model, on the contrary, takes care of the kinetics of the internal motions to some extent, i.e., the restructuring of the particle positions within the clusters and the breaking apart of the particles from them are natural consequences of energy consideration. We point out that other internal motions, such as bond and cluster rotational diffusions, are neglected in the present model, which might be important for some systems. In the irreversible DLCA models the gelation point c_g can be estimated from a simple scaling argument. It is known that in the irreversible model, only one cluster exists in the system at the final stage of the aggregation process. When this cluster (of mass m) spans the whole system (of size L), c_g can be calculated as $c_g\sim m/L^d\sim L^D/L^d=L^{-(d-D)}$, where d and D refer, respectively, to the dimensionality of Euclidean space ($d=2$ here) and the cluster. Since the fractal dimension D is always smaller than d, we have $c_g=0$ when L goes to infinity. This scaling argument, however, cannot simply apply here because, due to the reversibility of the model, several clusters coexist in the system at the final stage of the aggregation process. For the particle concentration $c<c_g$ the individual clusters cannot span the whole system, so no gel can form; however, when c increases and exceeds c_g, at least one cluster spans the whole system to form a gel.

The fractal dimension D is calculated from the relationship $R_g\sim N^{1/D}$ in the scaling region, where N is the number of particles in the cluster and R_g is the radius of gyration of the cluster defined as [21]

$$R_g=\frac{1}{2N^2}\sum_{\substack{j,k=1\\(j\neq k)}}^{N}|\mathbf{r}_j-\mathbf{r}_k|,\qquad(1)$$

where $\mathbf{r}_j$ and $\mathbf{r}_k$ are the positions of particles j and k and the summation is over all the particles inside the cluster. We first plot $\ln N$ versus $\ln R_g$ to determine the fractal dimension D and then examine how the fractal dimension varies with interaction energy γ. The result is presented in Fig. 3, where the data were obtained from the system of side length $L=80$ with particle concentration $c=0.10$. We observe from Fig. 3 that D first decreases very rapidly with increasing γ and then

reaches a constant value of about 1.45. As mentioned earlier, the compactness of the clusters decreases with the increase of the interaction energy and hence D decreases with γ. The value of 1.45 at large γ is comparable with those obtained by the irreversible DLCA models that reported $D=1.45–1.50$ [4] and 1.38 ± 0.06 [5] in the low particle concentration regime. Therefore, when γ is very large the present model is similar to its irreversible counterparts, since the attractive well is so deep and therefore the energy barrier is so high that no breaking up is possible. It is worth pointing out that even for very large values of γ (i.e., in the limit of $\gamma\to\infty$) our model is still different from the irreversible ones in that local restructuring is always allowed if such a move decreases the energy of the system or keeps it unchanged, while in the irreversible models no restructuring is allowed at all. The fact that our value of D for large γ is the same as that in the irreversible models (within numerical accuracy) leads us to conclude that the actual value of D is not sensitive to the details of the models.

IV. CONCLUSION

We have studied a gel formation mechanism based on a reversible DLCA algorithm, in which the interaction energy between particles plays an important role. By allowing the particles to restructure within the clusters or even break up from them, our model simulates not only the rigid motion of the clusters but also the kinetics of individual particles of the clusters. We find that there exists a nonzero concentration threshold c_g for the sol-gel transition that is independent of the system size when the interaction energy between particles is not very strong.

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