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Phase transition in diffusion limited aggregation with patchy particles in two dimensions

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ABSTRACT

The influence of patchy interactions on diffusion-limited aggregation (DLA) has been investigated by computer simulations. In this model, the adsorption of the particle is irreversible, but the adsorption occurs only when the 'sticky patch' makes contact with the sticky patch of a previously adsorbed particle. As we vary the patch size, growth rate of the cluster decreases, and below a well-defined critical patch size, p_c the steady state growth rate goes to zero. The system reaches an absorbing phase producing a non-equilibrium continuous phase transition. The order parameter close to the critical value of the patch size shows a power law behavior $\rho(\infty) \sim (p - p_c)^{\beta}$, where $\beta = 0.2840$. We have found that the value of the critical exponent convincingly shows that this transition in patchy DLA belongs to the directed percolation universality class.

1. Introduction

Self-assembly of colloidal particles has become a subject of theoretical, experimental and simulation interest especially in developing novel devices. Among the models that are developed for understanding the aggregation process, diffusion limited aggregation proposed by Witten and Sander [1] is a widely studied model. In this model, firstly, a seed particle is placed and particles are released one by one very far from the seed particle. The released particle performs random walk and once it reaches the seed or already deposited particle, it sticks irreversibly. This process continues to cluster growth. In spite of simplicity, this growth exhibits complex scaling properties described by fractal geometry. This model successfully has been used to represent different structure formation in electro deposition [2,3], colloidal aggregation, crystal growth [4], viscous fingering [5], biological cells [6], dielectric breakdown [7–10]. Fractal structures are currently useful in technological applications especially in nano electronic devices [11,12]. In one study it has been shown that the capacitance density of the fractal capacitor is about twice that of the standard parallel plate capacitor [13]. Several generalization studies on DLA have received considerable attention for experimental applications. Among these are the effect of long range attraction [14], effect of electric field on DLA structures [15], slippery diffusion-limited aggregation to mimic aggregation of non-shear bonds in colloidal systems [16], random walkers with drift [17], DLA aggregation of persistent random walkers [18].

But all these studies consider the particle interactions to be isotropic. The focus has now shifted to the study of the characteristic features induced by the anisotropy. Few works have been reported on the particle shape anisotropy. Liu et al. [19] studied the particle anisotropy and concluded that they can still form the fractal aggregates. Studies by Mohraz et al. [20] on the anisotropy of the particle concluded that the fractal dimension increases with increasing the rod aspect ratio. Deng et al. [21] studied off-lattice DLA simulations with different particle shapes of triangle, quadrangle, pentagon and octagon and concluded that only different particle shapes can change the local structure of the cluster, and they have no effect on the apparent global structure of the formed fractal cluster. Braga et al. [22] analyze the formation of DLA cluster with different cluster size and show that the aggregates are formed by an angle selection mechanism on dendritic growth that influences the shielding effect of the DLA edge.

But over the last couple of decades, advances in the particle synthesis techniques have made it possible to prepare colloidal particles with structured surfaces. These are known as 'patchy particles'. Such particles interact with each other in a highly anisotropic way, quite unlike the colloids with homogeneous surfaces, which interact isotropically. Therefore many patchy particles self-assemble in ways strikingly different from the homogeneous

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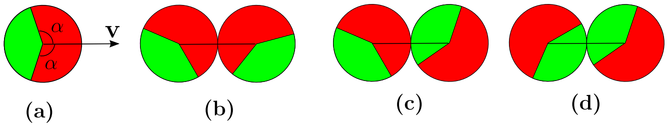

Fig. 1. (Color online) The patchy particle interactions. (a) The red sector is the sticky patch, whose orientation is specified by the vector **v**, and the angular size by the angle α, or the patch size $p = \alpha/\pi$. (b) A typical contact between the two particles when they bind together irreversibly and an adsorption occurs. (c) and (d) Typical non-binding contacts which do not result in any adsorption.

particle colloids. Such self-assemblies have been studied quite extensively, both experimentally and theoretically. Most of these studies are on the aggregation of patchy particles under equilibrium conditions [23–29]. But colloidal particles often aggregate in far-from-equilibrium conditions. This happens when the forces between the particles are strong and short range. These aggregates are often observed in the experiments and have fractal nature. Recently some studies have been done on the patchy particle aggregation from the substrates [30–32].

Thus with all the current interest in the aggregation of the patchy particles, a natural question to ask is: what is the nature of DLA when the particles interact through strong and highly directional forces? Now the growth process critically depends on the angular range of their interaction with other particles. In this letter, we have studied the DLA with patchy particles by Monte-Carlo on lattice simulations. The results will be useful to understand the aggregation of the patchy disks and colloidal particles.

2. Model description

In the present study we have considered a model to describe the scenario described above. We have considered a model, the so called 'Kern–Frenkel model' proposed for studying aggregation of the colloidal particles with anisotropic interaction. The model for the patchy particle interactions is shown in Fig. 1. This is adapted from the model proposed by Kern and Frenkel for particles with strongly directional interactions [33–35]. The 2-dimensional particle is a circular disc divided into two sectoral parts, one of them with semi-angular amplitude α is the active or the sticky patch (Fig. 1(a)). We call the 'patch size' the fractional area of the patch $p = \alpha/\pi$, which can vary from 0 to 1. The vector **v** specifies the orientation of the patch, which bisects the sticky patch. A particle binds to another particle irreversibly if the line connecting the centers of the two particles passes through sticky patches of *both* the particles, as in Fig. 1(b). If the line connecting the centers passes through only one sticky patch (Fig. 1(c)) or neither (Fig. 1(d)), no binding results. It should be noted that the patch size p actually stands for the angular interaction range of the particle, rather than the spatial extent of the patch. The $p = 1$ case corresponds to the isotropically interacting particle.

The Patchy DLA model considered in this work is a modification of the well known standard DLA process [1]. The modification in our model is that the particle gets adsorbed only when patch-interaction condition is satisfied. If the condition is not satisfied the particle continues with its random walk. The particle is killed if approximately 1000 subsequent non-satisfied conditions occur. Then a new particle is released from the random direction on the launching circle. If the particle performing random walk goes beyond the killing circle radius, the particle is killed. Here radius of the killing circle is chosen to be 20 times of the launching circle. Simulations were carried out on a square lattice. The number of the contacts made by the particles provides a measure of time. The growth rate is the time rate of particle adsorption $\rho(t) = \frac{dN_a(t)}{dt}$ (where $N_a(t)$ is the number of adsorbed atoms at time t), and the steady state value of this growth rate $\rho(\infty) = \lim_{t\to\infty} \rho(t)$ is taken

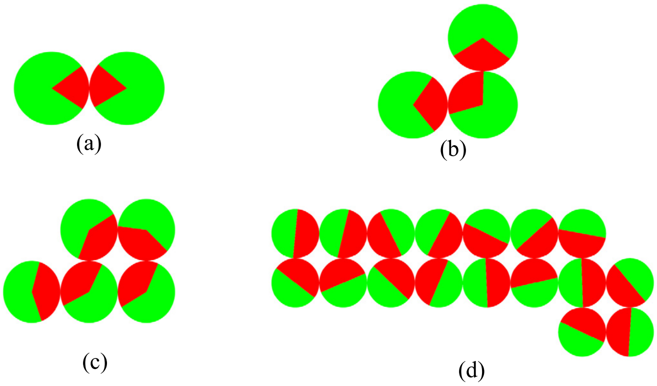

Fig. 2. (Color online) The structures generated for patchy DLA. Here (a) $p = 0.2$, (b) $p = 0.3$, (c) $p = 0.4$, (d) $p = 0.5$.

as the order parameter. All the quantities are averaged over 100 to 1000 independent realizations.

3. Results and discussions

In the present study, for $p = 0$, no deposition takes place and for $p = 1$, we recover the pure DLA in 2D. Fig. 2 gives the typical structure of the clusters for different values of patch size with $p < 0.5$. It is clear from the Fig. 2 that when the value of the patch size, $p < 0.5$ is small, the clustering of the patchy particles is restricted only to 5–6 clusters. The incoming particle finds a dead site and the growth of the cluster stops. When the patch size is further increased to 0.5 which corresponds to the Janus like particle forms a bed like structure. Experimental work carried out by Chen et al. [28] on aggregation of the Janus particles has demonstrated a formation of chain like structures in moderate salt solution.

For $0.5 < p < 0.6$, a sudden structural change is observed in the aggregation process. We found that the clusters are of finite sizes and the interface is capped by the non-adsorbing patch. Therefore we see that the system goes to an absorbing phase when p is small. There is quite a bit of similarity in the clusters formed in our study when $p < 0.7$ and the clusters formed by the Janus particles on the oil–water interface observed by Park et al. [29]. They have shown that the undulating hydrophobic and hydrophilic interface on the DDT-Au-PS sphere give rise to the capillary interactions between the particles. This leads to an attractive force which allows the particles to aggregate on oil–water interface. When the patch size is increased beyond $p = 0.605$, the system reaches a 'growing phase' where the particle aggregation never stops. With increase in the value of patch size the structure evolves towards the normal DLA structure.

From the above Figs. 2 and 3, it is clear that for patch size $p < p_c$ (critical patch size), the system reaches an 'absorbing phase', and above p_c we obtain a 'growing phase'. The clustering behavior observed in our present study now critically depends on patch size. Recently Iwashita and Kimura conducted an experimental study on Janus particles prepared using gold coated silica particle confined to two dimensions [36]. They observed that for high binding energy, valence structure of cluster is responsible for the formation of long chain of tetramers from low valence trimers. This can be realized in our present study for patch size $p > p_c$. The valence of deposited clusters increases with increasing patch size which ultimately leads to 'growing phase'. The dependence of patch size of one-patch colloidal particles in two dimensions on the growth of the clusters is also further carefully studied in [37]. They were able to vary the patch size and binding energy between the patches. The observations done in the high binding energy is quite similar to the results reported here. In their study, trimers are dominated in clusters for patch size $p \approx 59°$. Similar clusters