LETTER TO THE EDITOR

Cluster–cluster aggregation with random bond breaking

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Abstract. It is argued that a model of cluster–cluster aggregation with random bond breaking leads to an equilibrium regime in which all configurations with the same number of bonds have equal probability to occur. Thus our model of cluster–cluster aggregation with random bond breaking and branched polymers (lattice animals) belongs to the same universality class. The results are compared with numerical observations.

Irreversible aggregation, either particle–cluster or cluster–cluster aggregation, of diffusive clusters (particles) leads to growth of fractal structures [1]. For irreversible growth, the probability for a certain configuration to occur depends on the number of distinct histories this configuration can be grown and on the weight each of these histories has [2]. This turns irreversible aggregation into a complicated statistical problem. On the other hand in equilibrium structures, like lattice animals or branched polymers [3], all configurations with the same number of bonds have equal probability to occur.

The irreversible diffusion-limited particle–cluster aggregation model (DLA) has been modified by allowing for aggregation and disaggregation [4] and recently it has been proved that this model reaches an equilibrium identical with branched polymers [5]. Similarly, diffusion-limited cluster–cluster aggregation (DLCA) has been modified in a simulation by allowing for random bond breaking yielding the fractal dimension of equilibrium structures [6]. In contrast, DLCA with *non-random* bond breaking has been shown numerically [7] and experimentally [8] to yield structures with a fractal dimension continuously depending on a binding energy between particles. In this paper we show that reaction-limited cluster–cluster aggregation (RLCA) with random bond breaking, assuming that clusters are stable when exploring mutual configurations, reaches an equilibrium identical with branched polymers. For DLCA with random bond breaking we argue that with the assumption that a cluster typically breaks bonds and aggregates with its own fragments—assumed to be stable— many times before the cluster or its fragments aggregate with other clusters, a cluster relaxes towards equilibrium-branched polymers. In this equilibrium regime the cluster structure is independent of the cluster mobility which, however, influences the cluster-mass distribution.

In DLCA with random bond breaking as simulated by Kolb [6], particles are placed on a lattice at random. No two particles are allowed to occupy the same site and no bonds are yet formed. Particles undergo a random walk. If a particle attempts to move to an already occupied site, it will not be allowed to move; instead a bond

will be placed between the neighbouring particles which have just collided. Clusters continue the random walk and its particles obey the same rule for bond formation with particles from other clusters as described above. In the case of more than one pair of particles colliding simultaneously one of them is chosen at random to form a bond, leading to loopless clusters. The diffusing velocity v of a cluster of mass m is characterized by an exponent α in $v(m) = m^\alpha$. To this point the model is identical with DLCA. Now we allow for bond breaking. Bonds are broken randomly and independently with a probability $1/\tau$ per unit time. Initially aggregation will dominate until the clusters are large enough, such that the bonds formed and the bonds broken balance. The characteristic time to reach this equilibrium regime is determined by α and τ. Kolb's simulation yielded that in the equilibrium regime the clusters have a fractal dimension $D = 1.57 \pm 0.06$ (2.03 ± 0.05) in two (three) dimensions, independent of α. The cluster-mass distribution depends on α. A sticking probability, $p = 0.05$, does not affect D [6].

The distinction between lattice animals and branched polymers, which are believed to lie in the same equilibrium universality class, lies in how bonds are counted. In lattice animals all adjacent pairs of sites are deemed equivalently bonded, whereas in branched polymers explicit bonds are required and loops of bonds are excluded. The branched polymer version is the key to connections with kinetic bond-breaking and aggregation models. In particular it ensures that clusters with contacting loops retain memory of how the loop was made (as an explicit bond) and therefore how this process can be uniquely reversed. This enables steady-state distributions to be understood as equilibria with the strong but simple-to-prove condition of detailed balance.

For reversible cluster–cluster aggregation a mean-field rate equation models the time evolution of the cluster-mass distribution [9]

$$\frac{dc(s)}{dt} = \frac{1}{2} \sum_{i+j=s} [K(i,j)c(i)c(j) - F(i,j)c(s)]$$

$$- \sum_{j=1}^{\infty} [K(s,j)c(s)c(j) - F(s,j)c(s+j)] \tag{1}$$

where $c(s)$ is the number of clusters of mass s per unit volume, $K(i,j)$ the rate of aggregation of two clusters of mass i and j, and $F(i,j)$ the rate of fragmentation of a cluster of mass $i + j$ into two clusters of mass i and j. The aggregation and fragmentation rates are the averages over all configurations.

A detailed balance condition [9]

$$F(i,j)c(i+j) = K(i,j)c(i)c(j) \tag{2}$$

is consistent with a stationary, $c(s)$, and with (1). A cluster of mass s may occur in many configurations, labelled A, B or α, β. Let $P_s(A)$ be the probability for a cluster of mass s to be in configuration A, $k(i,\alpha,j,\beta,A)$ the rate of aggregation of two clusters of mass and configuration (i,α) and (j,β) into $(i+j, A = \alpha \oplus \beta)$, and $f(A,i,\alpha,j,\beta)$ the rate of fragmentation of a cluster of mass and configuration $(i+j, A = \alpha \oplus \beta)$ into two clusters (i,α) and (j,β). The existence of a stationary structure is consistent with a detailed balance condition on the configurations

$$f(A,i,\alpha,j,\beta)c(i+j)P_{i+j}(A) = k(i,\alpha,j,\beta,A)c(i)P_i(\alpha)c(j)P_j(\beta) \tag{3}$$

and with (2) we substitute the cluster-mass distribution by the average aggregation and fragmentation rates:

$$P_{i+j}(A) = \frac{F(i,j)}{K(i,j)} \frac{k(i,\alpha,j,\beta,A)}{f(A,i,\alpha,j,\beta)} P_i(\alpha) P_j(\beta) \,. \tag{4}$$

For a cluster in configuration A there is exactly one particular bond to be broken for fragmentation into α and β with $A = \alpha \oplus \beta$. Thus for *random* bond breaking with rate $1/\tau$ it is $f(A,i,\alpha,j,\beta) = 1/\tau$ and the average fragmentation rate is $F(i,j) = N(i,j)(1/\tau)$ where $N(i,j)$ is the number of ways a cluster of size $(i+j)$ can break into two clusters of size i and j, averaged over all configurations.

Similarly for two clusters (i,α) and (j,β) there is exactly one particular bond to be made to aggregate into $(i+j, A = \alpha \oplus \beta)$. In the *reaction-limited* regime the sticking rate, k, between particles is sufficiently small to let two clusters explore all possible configurations, and assuming that during this exploration no breaking can occur, until they finally stick at random into one of them with rate $k(i,\alpha,j,\beta,A) = k$ and the average aggregation rate is $K(i,j) = N(i,j)k$. Thus for reaction-limited cluster–cluster aggregation with random bond breaking we find with (4)

$$P_{i+j}(\alpha \oplus \beta) = P_i(\alpha) P_j(\beta) \,. \tag{5}$$

All i,j decomposable configurations $(A, B, \ldots) = \alpha \oplus \beta$ occur with equal probability. Starting with $i = j = 1$ for which there is only one configuration, $P_i(\alpha) = P_i$, and since for each (i,j) pair there is exactly one (α,β) pair to form A, we find recursively

$$P_s(A) = \frac{1}{2} \sum_{i+j=s} \sum_{\alpha \oplus \beta = A} P_i(\alpha) P_j(\beta) = \frac{1}{2} \sum_{i+j=s} P_i P_j = P_s \tag{6}$$

that all configurations of the same mass are equally likely to occur.

In contrast in the *diffusion-limited* regime the rate of aggregation depends on the configurations. Equation (4), derived fom detailed balance conditions, still holds, but due to $k(i,\alpha,j,\beta,A)$ the probabilities $P_{i+j}(A)$ are biased towards more tenuous configurations. However, with the key assumption that a cluster typically breaks bonds and aggregates with its own fragments many times before the cluster or its fragments, which are assumed to be stable, aggregate with other clusters, we will argue that due to multiple random bond breaking and aggregation with its own fragments a cluster relaxes towards equilibrium. The validity of our key assumption is difficult to check, since it is not obvious how to estimate the number of necessary fragmentation and aggregation events of a single cluster to reach equilibrium.

Let us consider a *single* cluster of $b = s - 1$ bonds which can occur in many configurations, for instance the configurations A and B (see figure 1). Configuration A can evolve out of B by breaking the appropriate bond, letting the fragments undergo a random walk (or equivalently keeping one stationary and the other doing the random walk), and finally letting the fragments stick together at the appropriate site. The transition probability from A to B is
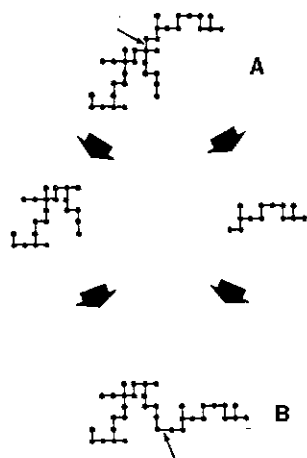
$$T(A, B) = \frac{1}{b} w_{ij} \frac{1}{z} \tag{7}$$

Figure 1. The transition from configuration A to B.

where $1/b$ gives the probability to choose the appropriate bond to break, w_{ij} is the fraction of all walks from site i which reach site j without any particle of the fragment landing on the remaining cluster first, multiple visits to site j allowed and counted multiplicatively, and $1/z$ is the fraction of these which immediately form a bond with the neighbouring fragment site, where z is the coordination number of the lattice.

An ambiguity arises on a lattice in the case of more than one pair of particles colliding simultaneously. While forming all possible bonds leads to loops, choosing one of the pairs at random to form a bond leads to loopless clusters. In the simulation [6] both possibilities have been investigated and have led to indistinguishable results; furthermore multiple contact events are seen to be rare (see figure 1 in [6]). From the theoretical point of view, there is a problem that the different ways to bond appear to be in competition and thus to reduce each other's probability of occuring. This would violate the requirement that each be in detailed balance with the corresponding constant probability to break it once made. In RLCA this problem is resolved by the low sticking probability, each sticking probability then representing a negligible perturbation on the probability of others. In DLCA there appears, however, to be a more severe problem which can only be solved by more drastic means. The simplest is to keep the low sticking probability per time step as per RLCA but also to set the probability of a diffusion move per time step correspondingly small. Over the typical time to make a diffusion move the sticking probability is then high, corresponding to DLCA, but conflicts between events are eliminated, as per RLCA. The above resolution of difficulties in DLCA is equivalent to approaching a continuous time limit. Loops can also be resolved by recourse to continuous (i.e. real) space coordinates, wherein loops have negligible statistical weight to occur.

Since for every walk from i to j in N steps there is exactly one corresponding time-reversed walk from j to i in N steps, the symmetry $w_{ij} = w_{ji}$ holds. Thus the transition probabilities in both directions are identical $T(A, B) = T(B, A)$ and the master equation for the configurational probabilities $P_s(A)$

$$\frac{\mathrm{d}P_s(A)}{\mathrm{d}t} = \sum_B [P_s(B)T(B, A) - P_s(A)T(A, B)] \tag{8}$$

has detailed balance solutions $P_s(A)$ = constant. For a single cluster all configurations of b bonds have the same probability to occur. Thus for DLCA with random bond breaking in the non-gelling regime two clusters may aggregate into a biased configuration but the new cluster relaxes towards equilibrium before aggregating with other clusters.

A special feature of the reversible aggregation models considered above is that they have multiple contacts weighted in at most a linearly additive way. In a simple binary phase equilibrium model one would expect the Boltzmann factors to break a multiple contact to combine multiplicatively, thus favouring compact droplets when the energy of dissociation per contact is large compared to $k_B T$. The aggregation models thus correspond to a marginal case where the energies are weak, and hence to critical equlibrium-branched polymers. The aggregation models could readily be modified to incorporate Boltzmann weighting of dissociation events with energies related to the number of contacts, and we could expect the corresponding droplet equilibrium to be obtained.

In conclusion, within the assumption of stable clusters during the exploration of mutual configurations, cluster–cluster aggregation in the reaction-limited regime with random bond breaking leads to an ensemble in which all configurations with the same number of bonds have equal probability to occur. The same is true for the diffusion-limited regime, provided that single clusters break into stable fragments and aggregate sufficiently often to reach an unbiased structure before aggregating with other clusters. In this case the structure is independent of the cluster-mass distribution. This is in accord with simulations [6], which yield fractal dimensions equal to those of lattice animals, independent of the cluster-mass distribution which had been changed via the diffusivity parameter or a sticking probability.

References

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