Fractal dimensionality of clusters formed by coagulation

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The problem of the coagulation of small particles into large aggregates is shown to have a highest critical dimensionality $d_c = 10$. A new self-consistent approximation, analogous to the Flory approximation, has been developed. This approximation can be used to find the index ν, which relates the average size of an aggregate to its mass, for $d < d_c$. The results are compared with experimental data.

The problem of coagulation, i.e., of the formation of bound clusters from originally free single particles, arises in a wide variety of situations: polymerization reactions resulting in the formation of a gel, the coagulation of colloids, the coagulation of soot particles, etc. We wish to analyze this problem in its most general formulation: The space initially contains small particles of unit size, which diffuse; if they collide, they become irreversibly attached. The resulting clusters also diffuse as rigid bodies, and they adhere to each other if they come into contact at even a single point; etc. We are interested in the structure of the large clusters which are formed as a result of this process. Different functional dependences of the diffusion coefficients on the cluster mass correspond to different physical situations. In the numerical simulations by Meakin[1] and Kolb *et al.*,[2] the diffusion coefficient was independent of the number of particles in the cluster, $N(D = 1)$; or there was a functional dependence $D = N^{-1}$; or only the lightest clusters moved. There can also be physical problems in which the particles do not diffuse but instead move along linear trajectories with some random velocity distribution. We will use the superscripts "dif" and "lin" to distinguish between quantities which correspond to a diffusive motion and to a linear motion of the particles during the coagulation.

We will show that the coagulation problem has an upper critical dimensionality, i.e., that above a certain dimensionality of the space the structure of the aggregates can be described in a simple approximation. This approximation will generally vary with the type of diffusion or linear motion. We will show that this approximation is nearly or exactly the same as the tree approximation. We will then use the self-consistent approximation to analyze the structure of clusters for $d < d_c$.

We assume that the dimensionality of the space in which the coagulation is occurring is large enough that in the collision of two clusters an arbitrary point of one can touch an arbitrary point of the other with a probability which does not depend on the positions of these points on the clusters. We also assume that the clusters move with diffusion coefficients (or linear velocities) which are independent of their mass. The probability for the linkup of two clusters of masses N_1 and N_2 is then simply proportional to $N_1 N_2$. We know quite well that the structures formed in this case are the same as those which result from a random branching process (see Refs. 3 and 4, for example). The size of these structures depends on their mass in accordance with $R \propto N^{1/4}$, and their size distribution is $f(N) \propto N^{-5/2}$. Knowing which clusters arise in the course of the coagulation, we can then find the critical dimensionality above which there can be a mutual penetration of the clusters such that an arbitrary point of one can touch an arbitrary point of the other. Here one of the cluster must be able to diffuse into the other without ever grazing it. We treat the motion of a cluster as a sequence of random elementary displacements of unit length (we recall that we are also assuming that the elementary particles forming a cluster are of unit size). The probability for a collision at each instant is $\rho_1 \rho_2 V$, where ρ_1 and ρ_2 are the densities of particles in the clusters, and V is the volume of the space in which they intersect. We assume that the numbers of particles in the clusters are comparable in magnitude; we then have $\rho_1 \sim \rho_2 \sim N/R^d \sim N^{1-d\nu}$ and $V \sim R^d \sim N^{\nu d}$ ($R \propto N^{\nu}$). We multiply this probability by the total number of displacements of one cluster in the other. For a random walk, this quantity would be on the order of R^2. The total probability for one cluster to penetrate deeply into the other without ever grazing it is then

$$W \sim N^{2+2\nu-d\nu}, \tag{1}$$

and we have $d_c^{\text{dif}} = 10$ with $\nu = 1/4$. If the clusters move along linear trajectories instead of diffusing, the length of the path traced out by one cluster in the other is on the order of R, and we have $d_c^{\text{lin}} = 9$.

We assumed above that the diffusion coefficients (or linear velocities) of the different clusters do not depend on their masses. More realistically, the cluster mobility would fall off with increasing cluster mass. The small clusters would then coagulate more rapidly than the large clusters. In this case the size distribution of the clusters changes, so that there may be changes in the structure of the large clusters which arise during the coagulation. We therefore consider the other limiting case in which the mobility of the small clusters is much higher than that of the large clusters, so that the small clusters quickly "become extinct." The size distribution of the clusters is then comparatively narrow and can be characterized at any instant by an average cluster mass. We assume that when two clusters collide they have nearly the same mass. We call the large cluster resulting from this repeated enlargement process (a doubling in this case) the "limiting" cluster. We find the structural properties of this limiting cluster by using a recurrence relation.

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Let us assume that in some stage of the coagulation, when the average mass of the clusters is N_0, the resulting clusters can be described as the structures which result from branching processes (trees) with a radius $R \sim N_0^{1/4}$ and with the following correlation function for any two points:

$$G_{N_0}(\mathbf{r}) = N_0^{-1} \sum_{\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}} \overline{\mathcal{G}_{N_0}(\mathbf{r}_1, \mathbf{r}_2)}. \tag{2}$$

Here $\mathcal{G}_{N_0}(\mathbf{r}_1, \mathbf{r}_2)$ is the connectedness function of the cluster, defined by

$$\mathcal{G}_{N_0}(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} 1 \text{ if the points } \mathbf{r}_1 \text{ and } \mathbf{r}_2 \text{ belong to the given cluster,} \\ 0 \text{ otherwise.} \end{cases}$$

The superior bar means an average over the ensemble of all possible clusters, in contrast with the angle brackets $\langle \cdots \rangle$, which we will use to denote the average over a cluster.

For the tree problem we would have

$$G_{N_0}(\mathbf{k}) = \frac{N_0^{1/2}}{k^2 + N_0^{-1/2}} \quad \left(G(\mathbf{k}) = \int G(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} d\mathbf{r} \right). \tag{3}$$

The normalization is chosen such that

$$\int G_{N_0}(\mathbf{r})\, d\mathbf{r} = N_0.$$

If the process by which two clusters, with N_1 and N_2 particles, join together occurs in such a way that an arbitrary point of one connects with an arbitrary point of the other, then the connectivity function of the resulting cluster is

$$\mathcal{G}_{N_1+N_2}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{G}_{N_1}(\mathbf{r}_1, \mathbf{r}_2) + \mathcal{G}_{N_2}(\mathbf{r}_1, \mathbf{r}_2) + \mathcal{G}_{N_1}(\mathbf{r}_1, \mathbf{r}^*)\mathcal{G}_{N_2}(\mathbf{r}^*, \mathbf{r}_2). \tag{4a}$$

Taking an average over all possible connection points r^* and also over all possible clusters with N_1 and N_2, we find the following expression for the correlation function of the resulting cluster:

$$G_{N_1+N_2}(\mathbf{r}) = \frac{N_1}{N_1+N_2} G_{N_1}(\mathbf{r}) + \frac{N_2}{N_1+N_2} G_{N_2}(\mathbf{r}) + \frac{2}{N_1+N_2} \int G_{N_1}(\mathbf{r}-\mathbf{r}^*) G_{N_2}(\mathbf{r}^*)\, d\mathbf{r}^*. \tag{4b}$$

We now switch to the normalization $\tilde{G}_N = G_N/N$; with $N_1 = N_2$, in the momentum representation, we find the recurrence relation

$$\tilde{G}_{2N}(\mathbf{k}) = {}^1/_2[\tilde{G}_N(\mathbf{k}) + \tilde{G}_N^2(\mathbf{k})]. \tag{5}$$

Let us calculate

$$\langle R^2 \rangle = -\frac{\partial^2}{\partial k^2} \tilde{G}(\mathbf{k})\,|_{\mathbf{k}=0}, \quad \langle R^4 \rangle = \frac{\partial^4}{\partial k^4} \tilde{G}(\mathbf{k})\,|_{\mathbf{k}=0}$$

for the limiting cluster as $N/N_0 \to \infty$:

$$\langle R^2 \rangle = 2N_0^{1/4} (N/N_0)^{(\ln 3 - \ln 2)/\ln 2}, \quad \langle R^4 \rangle = 16 N_0 (N/N_0)^{(\ln 3 - \ln 2)/\ln 2}. \tag{6}$$

We thus find the index value $\nu = 0.295$ ($R \propto N^\nu$), which is close to the value for the tree problem, $\nu = 1/4$. The internal structure of the limiting cluster which results from this process is generally different from the structure of trees. For example, the dimensionless ratio of $\langle R^4 \rangle$ and $\langle R^2 \rangle^2$ is

$$\frac{\langle R^4 \rangle}{\langle R^2 \rangle^2} = \begin{cases} 2 \text{ for the tree problem,} \\ 4 \text{ for the limiting cluster,} \end{cases} \tag{7}$$

i.e., the limiting cluster is slightly denser at the periphery.

If the masses of the clusters which join are not equal and are instead distributed in accordance with

$$N_1/(N_1+N_2) = {}^1/_2 + \sigma, \quad N_2/(N_1+N_2) = {}^1/_2 - \sigma,$$

where σ is a small random quantity, then by repeating the calculations above we find the corrections to ν:

$$\delta\nu = -\overline{2\sigma^2}/3 \ln 2 = -0.961\overline{\sigma^2}. \tag{8}$$

The two extreme cases of the distributions thus yield similar values, $\nu = 0.295$ and $\nu = 0.250$. Taking the sign of correction (5) into account, we could reasonably assume that the index ν for intermediate types of cluster mass distributions will lie between these two values.

Since we will be comparing our calculations with the results of numerical simulations with $D = 1$ and $D = N^{-1}$, we set $\nu = 1/4$.

For $d < d_c$ we calculate the index by a method similar to that used by Flory.[5] Flory's method, despite its simplicity, yields good estimates of the indices for spaces of low dimensionality, although near d_c it disagrees with the results found by the ϵ-expansion method. This approximation has been used previously to estimate the size of the coil formed by a linear polymer. The idea of this approximation is to estimate the minimum of the free energy of the coil as a function of its size. The free energy consists of the two terms F_{el} and F_{rep}. The first component F_{el}, is the energy required to stretch out a coil of free size $R_0 = N^{1/2}$ to a size R:

$$F_{el} \sim R^2/N. \tag{9}$$

The second component is the repulsive energy of the monomers forming the polymer:

$$F_{rep} \sim \rho^2 R^d \sim N^2/R^d. \tag{10}$$

Here ρ is the average density of monomers in the coil.

Minimizing the sum of (9) and (10) with respect to R, we find[6]

$$\nu = \begin{cases} 3/(2+d), & d<4, \\ {}^1/_2, & d \geqslant 4. \end{cases} \tag{11}$$

Although this formula was derived as a very crude approximation (in terms of the spirit of its derivation, it might be compared with the formulas for the indices in the theory of phase transitions ignoring the small indices α and η; Ref. 7), it yields surprisingly good estimates of ν for $d = 3$ and 2: The errors are only 1.5% and 0.3%. At $d = 4$ and 1, this formula is exact (see also the discussion in Ref. 8 of whether this formula is exact for $d = 2$).

The arguments in the case of a branching polymer are analogous. The only difference is the F_{el} is written[9,10]

$$F_{el} \sim R^2/N^{1/2}. \tag{12}$$

We find[9]

$$\nu = \begin{cases} 5/2(d+2), & d<8, \\ {}^1/_4, & d \geqslant 8, \end{cases} \tag{13}$$

in excellent agreement with the results of the numerical simu-

lations for $2 \leqslant d \leqslant 8$. The sum of F_{el} and F_{rep} has a simple physical meaning. The "elastic energy" is none other than

$$-\ln\left[K(R)\Big/\sum_{R} K(R)\right],$$

where $K(R)$ is the total number of configurations of size R (including self-intersecting configurations). The "repulsion energy" can be written as $-\ln W(R)$, where

$$W(R)=\prod_{\mathbf{r}}(1-\rho^2)\propto\exp\left(-\int\rho^2\,d\mathbf{r}\right) \tag{14}$$

is the probability that there will be no self-intersections in configurations of N monomers. The minimum of the sum of (9) and (10) as a function of R corresponds to the maximum of the product $K(R)W(R)$, which is the number of nonself-intersecting configurations of size R. The minimum of the sum of the "energies" in (9) and (10) thus determines the most probable size of a nonself-intersecting coil.

An important distinction in our case is that the formation of a branching cluster results from an irreversible process, but we can still write estimates for the "free energy." In contrast with Flory's method and also in contrast with Refs. 9 and 10, we will write an expression not for the total free energy but for the change in free energy upon the connection of two clusters:

$$\Delta F=R^2(N)/N^{1/2}-R^2(N_1)/N_1^{1/2}-R^2(N-N_1)/(N-N_1)^{1/2}+N^2 l(N,\ d)/R^d. \tag{15}$$

The sum of the first three terms is the change in the configurational entropy upon the attachment of two clusters at some single point. Since the clusters are assumed rigid, this change in entropy can be understood as $-\ln\widetilde{K}(R)$, where $\widetilde{K}(R)$ is the number of different ways to form a cluster of size $R(N)$ from two clusters $R(N_1)$ and $R(N-N_1)$. The last term in (15) differs from the ordinary term describing the potential energy, N^2/R^d, by a factor (in the diffusion case)

$$l^{dif}(N,\ d)=[R(N)\alpha^{dif}(d)]^2,$$

which is the average number of configurations assumed by overlapping clusters before they connect; $\alpha^{dif}(d)$ is the relative depth to which the clusters penetrate into each other. It is clear from similarity considerations that $\alpha(d)$ does not depend on N; it can depend on only the dimensionality of the space, $1 \geqslant \alpha(d) \geqslant 0$. If the colliding clusters move along linear trajectories, the factor $l^{dif}(N, d)$ must be replaced by

$$l^{lin}(N,\ d)=R(N)\alpha^{lin}(d).$$

The last term in sum (15) can be written as $-\ln\widetilde{W}(R)$, where $W(R)$ is the probability for one cluster to move to a relative depth $\alpha(d)$ into the other without any linkup on the way. The minimum of free energy (15) with respect to R thus determines the saddle point of the product $\widetilde{K}(R)\widetilde{W}(R)$, i.e., the number of real methods for forming a cluster of size R. Minimizing the free energy, we find

$$R^{dif}(N)\propto N^{5/2d}\quad R^{lin}(N)\propto N^{5/2(d+1)}. \tag{16}$$

These formulas change only very slightly if ν is not exactly $1/4$ at $d > d_c$: The terms $R^2(N)/N^{1/2}$ in (15) must be replaced by $R^2(N)/R_0^2(N)$, where $R_0(N)$ is the functional dependence of R on N at $d > d_c$. The 5/2 in (16) must then be replaced by $2 + 2\nu$, and since we have $0.250 \leqslant \nu < 0.295$ at $d > d_c$, there will be only a very slight (less than 4%) change in the final answer: the exponent on N in (16). With $d^{dif} = 10/3$ and also with $d^{lin} = 7/3$ the index is $\nu = 3/4$, and the sum of the first three terms vanishes. The fact that the entropy does not change when two clusters attach means that they do not "mix." This case is possible if $\alpha(d) = 0$, i.e., if the clusters penetrate no further into each other upon connection.

At $d^{dif} = 10/3$ and $d^{lin} = 7/3$ there is accordingly a transition from a region of volume penetration of clusters into each other to a region of surface connection. The total free energy of a cluster is linear in the number of constituent particles. In order to compare our results with experiment, we write the final expressions for the quantity $\mathscr{D} \equiv 1/\nu$, the fractal dimensionality of the clusters:

$$\mathscr{D}^{dif}=\begin{cases}2d/5, & d>{}^{10}/_{3}\\ {}^{4}/_{3}, & d<{}^{10}/_{3}\end{cases},\quad \mathscr{D}^{lin}=\begin{cases}2(d+1)/5, & d>{}^{7}/_{3},\\ {}^{4}/_{3}, & d<{}^{7}/_{3}.\end{cases} \tag{17}$$

Let us look at the experimental results available. The diffusion-controlled coagulation has been simulated numerically for various functional dependences of the diffusion coefficient on the cluster mass. The results imply that the fractal dimensionality of large clusters is insensitive to the functional dependence $D(N)$, in agreement with our general conclusion that the structure of the limiting cluster depends only weakly on the particular distribution in the mass of the colliding clusters. The results found for the fractal dimensionality in the simulations of Refs. 11 and 12 are compared with the theoretical predictions of (17) in Table I. We see that the values of $\mathscr{D}$ found in the simulations are 10–20% higher than those predicted here.[1)] There are two possible reasons for the discrepancy. First, there is the uncontrollable error of Flory's approximation. In all the simulations carried out, the clusters which arise for $d = 2$ and 3 are greatly stretched out in one direction, so that for spaces of low dimensionality the approximation of the clusters as random branching structures char-

TABLE I.

d	$\mathscr{D}^{dif}_{exp}$	$\mathscr{D}^{dif}$	$\mathscr{D}^{lin}_{exp}$	$\mathscr{D}^{lin}$	$2(d+2)/5$
2	1,46±0,04	1,33	1,55±0,04	1,33	1,6
3	1,82±0,10	1,33	1,91±0,10	1,60	2,0
4	2,10±0,15	1,60	2,25±0,15	2,00	2,4
5	2,35±0,15	2,00	⩾2,50±0,06	2,40	2,8
6	2,65±0,25	2,40	⩾2,64±0,05	2,80	3,2

acterized by only a single dimension is not really successful. Second, the scaling behavior sets in very slowly. Expression (15) contains, in addition to the terms shown, a term which is the same as (10) and which is responsible for the absence of self-intersections in the final state. This term was discarded since at large R it is small in comparison with the term $N^2 l(N, d)/R$. At $R < \alpha^{-1}(d)$, however, it is the leading term! Since $\alpha(d)$ is equal to one at $d = 10$ and vanishes at $d^{\text{dif}} = 10/3$ and $d^{\text{lin}} = 7/3$, it should be small at low dimensionalities of the space. It is thus quite possible that the numerical simulations have covered only a transition region between the behavior typical of branching polymers, (13) (see the last column in Table I), with $R < \alpha^{-1}(d)$, and the true asymptotic behavior in the limit of large R.

[1)]While this paper was being written, only the data on $\mathscr{D}^{\text{dif}}$ for $d = 2$ were available.[1,2] The data from Refs. 11 and 12 shown in Table I were added in a revision of this paper.

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