RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 36, NUMBER 1 JULY 1, 1987

Scaling laws in aggregation: Fragmentation models with detailed balance

M. H. Ernst
Physics Department, University of Florida, Gainesville, Florida 32611
and Institute for Theoretical Physics, University of Utrecht,
Postbus 80006, 3508 TA Utrecht, The Netherlands

P. G. J. van Dongen
Institute for Theoretical Physics, University of Utrecht,
Postbus 80006, 3508 TA Utrecht, The Netherlands
(Received 30 March 1987)

Coagulation processes may be balanced by very slow breakup reactions that lead to a self-similar stationary cluster size distribution, as recently described by Family, Meakin, and Deutch (FMD) [Phys. Rev. Lett. **57**, 727 (1986); **57**, 2332 (1986)]. Here, a class of reversible coagulation-fragmentation models is presented that satisfies detailed balance, for which the scaling functions can be calculated explicitly. The FMD models do not have the property of detailed balance in general.

Recently Family, Meakin, and Deutch[1] (referred to as FMD) have proposed a scaling description of an aggregation process, balanced by breakup reactions, that reaches a steady state after a sufficiently long time. If the average cluster size becomes sufficiently large, scaling or self-similar behavior can be observed. For this to happen, the overall rate of breakup reactions must be sufficiently slow.

Suppose that the total fragmentation rate for any breakup reaction is proportional to a small parameter k, then FMD propose that the average cluster size in this steady state scales as a power of k, viz. $S(k)\sim k^{-y}$, and that the size distribution scales as

$$N_s(k)\sim s^{-2}f(s/S(k))\sim s^{-2}f(sk^{y}) .$$

By applying scaling arguments to Smoluchowski's coagulation equation with fragmentation terms included (coupled system of chemical rate equations), FMD show that the exponent y is simply related to the degrees of homogeneity of the coagulation and fragmentation rate constants. Their scaling ideas and exponent relations were supported by convincing computer simulations of diffusion-limited aggregation of clusters, showing that a mean-field theory is adequate to describe the observed phenomena.

The purpose of this Rapid Communication is to show that one can construct classes of coagulation-fragmentation models for which scaling functions, exponents, and constants can be evaluated explicitly for reversible reactions obeying detailed balance. We refer to these models as detailed-balance models.

Steady-state distributions obeying detailed balance are of course a special type of stationary solution of the chemical rate equations. Our reversible aggregation models are closely related, but not identical, to the aggregation-fragmentation models of FMD. The latter models violate the detailed-balance condition. However, detailed balance is not a necessary requirement for the existence of an equilibrium state.

If aggregation and breakup reactions occur simultaneously the distribution of clusters over different sizes may reach a stationary value N_s. The assumption that this stationary state obeys detailed balance enables us to determine N_s for a given coagulation-fragmentation model, defined through (i) given coagulation kernel $K(i,j)$, and (ii) given *total* breakup rate $F^{(s)}$ of an s-cluster.

Here the rate for the coagulation reaction of an i-cluster and a j-cluster into an s-cluster $(s=i+j)$ is $K(i,j)N_iN_j$. The total breakup rate, $F^{(s)}N_s$, is the sum of all possible rates $F(i,j)N_{i+j}$ for breakup of an s-cluster into an i- and j-cluster with $i+j=s$, so that

$$F^{(s)}=\tfrac{1}{2}\sum_{\substack{i,j\\(i+j=s)}}F(i,j) . \tag{1}$$

The factor $\frac{1}{2}$ corrects for double-counting configurations. The fragmentation kernel $F(i,j)$ cannot be specified *a priori*. As we shall see, the detailed-balance condition combined with the above requirements determines both the stationary size distribution N_s as well as the kernel $F(i,j)$.[2] The detailed-balance condition reads

$$K(i,j)N_iN_j=F(i,j)N_{i+j},\quad (i,j=1,2,\ldots) . \tag{2}$$

A stationary solution satisfying detailed balance is in fact a special solution of Smoluchowski's mean-field kinetic equation for coagulation and fragmentation processes. Of course, Eq. (2) with arbitrarily prescribed $K(i,j)$ and $F(i,j)$ does not have a solution in general. The detailed-balance condition, therefore, imposes a restriction on the possible combinations of coagulation and fragmentation rates in Smoluchowski's mean-field equation. Summing Eq. (2) with $i+j=s=$const yields, in combination with (1), a recursion relation for N_s $(s=1,2,\ldots)$, viz.,

$$\tfrac{1}{2}\sum_{\substack{i,j\\(i+j=s)}}K(i,j)N_iN_j=F^{(s)}N_s , \tag{3a}$$

that can be solved for a given $K(i,j)$ and $F^{(s)}$. Here we assume that the total fragmentation rate $F^{(s)}$ of a *large*

cluster is proportional to some power of the cluster size,

$$F^{(s)}=ks^a(s-1) \ , \tag{3b}$$

and the factor $(s-1)$ guarantees that $F^{(1)}$ vanishes. The constants k and a are the parameters of the model. In the FMD model $F(i,j)=k(i+j)^a$, so that the total breakup rate of an s cluster is the same as in (3b), but it will appear that $F(i,j)$ is very different in the two classes of models. To be more explicit, we assume that the coagulation process can be modeled by a homogeneous kernel, specified by two exponents μ and ν:

$$\begin{aligned} &K(bi,bj)=b^{\lambda}K(i,j) \ , \\ &K(i,j)\sim i^{\mu}j^{\nu}, \ (j\gg i,\lambda\equiv\mu+\nu) \ . \end{aligned} \tag{4}$$

To solve the recursion relation, we make the substitution

$$N_s=ks^{-a}n_sC^s, \ (n_1=1) \ . \tag{5}$$

This transforms (3) into the well-known recursion relation

$$\begin{aligned} (s-1)n_s &= \tfrac{1}{2}\sum_{\substack{i,j\\(i+j=s)}} K(i,j)(ij)^{-a}n_in_j \\ &\equiv \tfrac{1}{2}\sum_{\substack{i,j\\(i+j=s)}} K'(i,j)n_in_j \ , \end{aligned} \tag{6}$$

where $\lambda'=\lambda-2a$ is the degree of homogeneity of K'. This equation has been used extensively to study the short-time behavior of the solutions of Smoluchowski's coagulation equation.[3-5] The arbitrary constant C can be determined from mass conservation $\sum_s sN_s=1$.

For the time being, we assume (later on we return to this point again) that the asymptotic solution of Eq. (6) at large s is given by $n_s\sim Bs^{-\theta'}R^{-s}$. Thus,

$$\begin{aligned} &N_s\sim\kappa s^{-\tau}e^{-\zeta s} \ , \\ &\tau=a+\theta' \ , \end{aligned} \tag{7}$$

where κ is a new fragmentation constant (proportional to k) and $\exp(-\zeta)\equiv C/R$. The exponents τ and θ' are still undetermined.

The explicit form of the fragmentation kernel is now given by Eq. (2) in combination with the solution of Eq. (6). This would yield an asymptotic form for $F(i,j)$:

$$F(i,j)=\kappa K(i,j)(i^{-1}+j^{-1})^{\tau} \ , \tag{8}$$

which is a homogeneous kernel of degree $\alpha=\lambda-\tau=\lambda-\theta'-a$. Here we choose to define the fragmentation model for all i,j through this relation, where κ and τ or α are the important parameters of the fragmentation model.

In view of possible *scaling laws* we are interested in the occurrence of large cluster sizes. This can only happen if the breakup constant κ is small. In that case ζ, appearing in Eq. (7), can be determined explicitly from mass conservation $1\sim\kappa\sum_s s^{1-\tau}\exp(-s\zeta)$. Since $\kappa\to 0$, this equation can only be satisfied if the sum at $\zeta\to 0$ is divergent; thus, $\tau<2$.

Using the relation

$$\sum_s s^{p-1}\exp(-s\zeta)\sim\zeta^{-p}\Gamma(p)$$

for $\zeta\to 0$ (valid for $p<0$), it follows from mass conservation that

$$\begin{aligned} &\zeta\sim[\kappa\Gamma(1/y)]^y, \ (\text{as } \kappa\to 0) \ , \\ &y=1/(2-\tau)=1/(2-a-\theta') \ . \end{aligned} \tag{9}$$

The size distribution (7) in combination with (9) enables us to calculate the moments $M_n=\sum_s s^nN_s$ with the result:

$$M_n\sim\begin{cases} \zeta^{1-n}\Gamma(n+1-\tau)/\Gamma(2-\tau)\propto\kappa^{(1-n)y}, & (n>\tau-1) \ , \\ -\zeta^{2-\tau}\ln\zeta/\Gamma(2-\tau)\propto-\kappa\ln\kappa, & (n=\tau-1) \ , \\ \kappa\times\text{const}, & (n<\tau-1) \ , \end{cases} \tag{10}$$

where $\tau<2$. This yields in particular for the average cluster size as $\kappa\to 0$:

$$S=M_2\sim(y\zeta)^{-1}\sim[\kappa\Gamma(1/y)]^{-y}/y \ . \tag{11}$$

The result for the total number of clusters $N=M_0$ follows by setting $n=0$ in (10) and the total mass $M_1=1$. The scaling of the size distribution N_s as $s\to\infty$ and $\kappa\to 0$ follows from Eqs. (7) and (9):

$$\begin{aligned} &s^2N_s\sim f(\zeta s) \ , \\ &f(x)=x^{2-\tau}e^{-x}/\Gamma(2-\tau) \ . \end{aligned} \tag{12}$$

Here, $f(x)$ is the Γ distribution, normalized as $\int dx\, x^{-1}f(x)=1$.

In the previous discussion, we have assumed that the solution of the recursion relation (6) was of the form $n_s\sim Bs^{-\theta'}R^{-s}$. If we define exponents for the kernel $K'(i,j)$ with the help of Eq. (4) as $\lambda'=\lambda-2a$ and $\nu'=\nu-a$, then the solution of Eq. (6) always has the above form if $\nu'<1$. In that case the θ' exponent is given by $\theta'=\lambda'$.[4] Hence, for coagulation kernels $K(i,j)$ with $\nu<1+a$ and fragmentation kernels with homogeneity index $\alpha=\lambda-\lambda'-a=a$, we find from (7) and (9) the exponent relations

$$\tau=\lambda-a, \ y=(a-\lambda+2)^{-1} \ . \tag{13}$$

Here the τ exponent describes the small-x behavior of the scaling form $f(x)\propto x^{2-\tau}$ and the y exponent the growth of the average cluster size $S\propto k^{-y}$. Furthermore, $K(bi,bj)=b^{\lambda}K(i,j)$ and $F(bi,bj)=b^aF(i,j)$.

If $\nu'=1$, the solution of the recursion relation (6) has either an algebraic form $n_s\sim Bs^{-\theta'}R^{-s}$ or a stretched-exponential form.[6] For $\nu'>1$ the solutions increase faster than exponentially. In the context of scaling behavior we may restrict ourselves to the algebraic forms and refer to the literature[6] for a determination of θ'. As an illustration, we briefly sketch an example with $\nu'=1$, namely $K(i,j)=(ij)^{\omega}$ and $K'(i,j)=ij$ so that $a=\omega-1$. The exact solution of the recursion relation (6) is now

$$n_s=s^{s-2}/s!\sim(\sqrt{2\pi})^{-1}s^{-5/2}e^s$$

and $\theta'=\frac{5}{2}$ (see Ref. 4), yielding

$$N_s\sim\kappa s^{-\omega-3/2}\exp(-\zeta s)$$

for $s\to\infty$. The undetermined constant ζ follows from

mass conservation, $\sum_s sN_s = 1$. As $\kappa \to 0$ (divergent sum), a consistent solution for ζ can only be found provided $\omega < \frac{1}{2}$. This yields ζ, as in Eq. (9), with exponents $\tau = \omega + \frac{3}{2}$ and $y = (\frac{1}{2} - \omega)^{-1}$. Detailed balance (2) gives, for the fragmentation kernel,

$$F(i,j) = \kappa(i+j)^{\omega}(i^{-1}+j^{-1})^{3/2}, \quad (\omega < \tfrac{1}{2}) , \qquad (14)$$

with a degree of homogeneity $a = \omega - \frac{3}{2}$ and one verifies that the exponent relation (13) of FMD is again satisfied. This particular example with $\nu' = 1$ differs from the general case with $\nu' < 1$ only in that the total breakup rate $F^{(s)}$ in (3b) has an exponent $a = \alpha + \frac{1}{2}$, whereas the general case $\nu' < 1$ has $a = \alpha$.

In summary: For coagulation-fragmentation models with homogeneous coagulation and fragmentation kernels $K(i,j)$ and $F(i,j)$ that satisfy *detailed balance* we have derived the scaling relations proposed by FMD. The average cluster size $S \sim k^{-y}$ and the size distribution $s^2 N_s \sim f(sk^y)$ for large cluster size s and small fragmentation constant k where $f(x) \sim x^{2-\tau}$ as $x \to 0$. The exponents are simply expressed in the degrees of homogeneity λ and α of $K(i,j)$ and $F(i,j)$, respectively, and given by $y = (\alpha - \lambda + 2)^{-1}$ and $\tau = \lambda - \alpha$. The explicit form of the scaling size distribution is the Γ distribution $f(x) \sim x^{2-\tau} e^{-x}$. All constants are calculated explicitly. The results derived here are mean-field results based on Smoluchowski's rate equations.

The exponent relation $\tau = \lambda - \alpha$, describing the small-x behavior of the scaling form $f(x) \sim x^{2-\tau}$, is a new result, which has only been derived for the restricted class of detailed balance models. The expression for the y exponent has been derived before by FMD, using *only the homogeneity properties* of $K(i,j)$ and $F(i,j)$ and has, therefore, a more general validity.

It is of interest to compare the size distribution obtained in the computer simulations of Family, Meakin, and Deutch,[1] with the theoretical predictions for the detailed balance models. FMD have simulated diffusion-limited aggregation for the particle coalescence model,[7] where the radius of gyration of a cluster is mass independent, $R_s = 1$, and they have taken a mass-independent diffusion coefficient $D_s = 1$. The corresponding mean-field description is therefore given by Smoluchowski's equation for Brownian coagulation with a coagulation kernel $K(i,j) = DR = 1$ with exponents $\lambda = \nu = 0$ [see Eq. (4)]. Unfortunately, FMD's fragmentation model, $F(i,j) = k(i+j)^{\alpha}$, is not a detailed balance model, and the comparison will therefore be more of a qualitative nature.

TABLE I. Homogeneity index and τ exponents.

$F^{(s)}$ in Eq. (3) a	F in Eq. (8) α	FMD model τ_{sim}	DB model τ_{theor}
1	1	0	-1
0	0	0	0
-1	$-\frac{3}{2}$	0.7	$\frac{3}{2}$

We compare the FMD-simulation results with those for the detailed balance (DB) model at the same total fragmentation rate, viz. $F^{(s)} = ks^a(s-1)$ and at the same coagulation rate $K(i,j) = 1$. Table I shows the τ exponent obtained from the simulations at different a values with the corresponding results for the detailed-balance model.

We first note that at the special value $\alpha = 0$, the FMD model does satisfy the detailed-balance condition and there is perfect agreement. The result for this special case, $K = 1$ and $F = k$, was of course known for a long time.[8] The results of the detailed-balance model for $\alpha > -1$ are contained in Eq. (9). The results for $\alpha = -1$ are contained in the example treated above Eq. (13).

The big difference in τ values, as seen in Table I, between both models may be understood from the differences in the fragmentation kernels. In the FMD model one has $F(i,j) = k(i+j)^{\alpha}$ and in the detailed balance model $F(i,j) = k(i^{-1}+j^{-1})^{-\alpha}$ for $\alpha > -1$, and $F(i,j) = k(i^{-1}+j^{-1})^{3/2}$ for $\alpha = -1$. In the former model, small and large fragments are equally likely. However, in the detailed-balance model $F(j,j)/F(1,2j-1) \sim j^{\alpha}$ for $\alpha > -1$. Hence, in the detailed-balance model large (small) fragments are more likely for $\alpha > 0$ ($\alpha < 0$), leading to a depletion (excess) of small clusters or, equivalently, to a lower (higher) τ value in the DB model as compared to the FMD model.

The work of one of us (P.v.D.) is part of a research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO). One of us (M.H.E.) thanks the Physics Department of the University of Florida for its hospitality during his stay. This research was supported in part by National Science Foundation under Grant No. CHE-8411932.

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