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## LETTER TO THE EDITOR

# Fluctuation-induced kinetics of reversible coagulation

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**Abstract.** The influence of spatial fluctuations in the density of monomeric units on the long-time kinetics of reversible coagulation is investigated. It is shown that the long-time approach to the equilibrium cluster size distribution is determined by relaxation of the spatial fluctuation spectrum and described by a power-law dependence.

For a wide variety of kinetic behaviour in diverse physical, chemical and biological systems, including applied problems such as colloidal and aerosol physics (Friedlander 1977), studies of antigen-antibody aggregation (Johnston and Benedek 1984), the kinetics of reversible polymerisation (van Dongen and Ernst 1984) and gelation phenomena (Leyvraz and Tschudi 1981, 1982), there arises the problem of describing coagulation/fragmentation processes.

As usual, this problem was investigated in the limit of infinite velocity of monomer or cluster transport. In particular, such investigations were carried out by van Dongen and Ernst (1984). They extended the kinetic mean-field theory of polymerisation by including fragmentation of clusters in such a way that the results of Flory (1936) or Stockmayer (1943) appear as a limiting case for large times.

However, the consideration of finite diffusive transport of reagents is essential for the investigation of the kinetics of bimolecular processes. On the one hand, the consideration of diffusive motion leads to the renormalisation of direct and backward rate constants as was shown by Smoluchowsky. On the other hand, the existence of spatial fluctuations in reagent distributions results in a crucial difference between the mean-field approximations and long-time fluctuation-induced kinetics. For instance, the long-time kinetics of the bimolecular irreversible reaction  $A + B \rightarrow \text{Inert}$  in the case of equal initial mean densities of  $A$  and  $B$  is governed by diffusive smoothing of initial density fluctuations which leads to the dependence  $C(t) \sim t^{-d/4}$  (Ovchinnikov and Zeldovich 1978, Burlatsky 1978, Toussaint and Wilczek 1983), where  $d$  is the space dimensionality. An essential deviation from the exponential mean-field law for the long-time approach to equilibrium was observed by Zeldovich and Ovchinnikov 1977, 1978, Kang and Redner 1985; Burlatsky *et al* 1989, for reversible bimolecular diffusion-controlled reactions. For instance, for the reversible reaction  $A + A \leftrightarrow B$ , which is a special case of the coagulation/fragmentation process, the existence of initial Gaussian fluctuations of the densities of the reagents leads to the power-law approach to equilibrium,  $C(t) - C(\infty) \sim (Dt)^{-d/2}$ , where  $D$  is the diffusion coefficient.

For irreversible coagulation, the influence of spatial fluctuations was investigated by Kang and Redner (1984) and Kang *et al* (1986). For special cases of direct rate constant they deduced that for spatial dimension  $d$  less than  $d_c = 2$  the fluctuation

effects can be relatively important and give rise to dimension-dependent kinetic exponents and a novel non-monotonic cluster size distribution. For  $d > d_c$  the solution of the Smoluchowsky mean-field equation is still valid.

In this letter we investigate the influence of initial spatial fluctuations on the long-time approach to the equilibrium cluster size distribution in coagulation/fragmentation processes.

A coagulation/fragmentation process can generally be written in terms of the following infinite set of reversible reactions:



Here  $A_m$  denotes a cluster ( $m$ -mer) containing  $m$  monomeric units  $A_1$ . Neglecting terms connected with noise of diffusive fluxes (Gardiner 1983) the time evolution of (1) is given by an infinite set of coupled non-linear rate equations

$$\dot{C}_k = \frac{1}{2} \sum_{i+j=k} (K_{ij}C_iC_j - F_{ij}C_{i+j}) - \sum_{j=1} (K_{kj}C_kC_j - F_{kj}C_{k+j}) + D\Delta_r C_k \quad (2)$$

$$C_k = C_k(r, t)$$

where  $\Delta_r$  is the  $d$ -dimensional Laplacian. The direct rate constant  $K_{ij}$  describes the bimolecular coagulation process. The unimolecular fragmentation process is described by the backward rate constant  $F_{ij}$ . Other reactions, such as triple collisions and break-up into many particles are assumed to be absent. We consider only one kind of rate constants:

$$K_{ij} = 2p[(f-2)i+2][(f-2)j+2]$$

$f$  is a parameter of Flory's polymer model  $RA_f$ , where  $RA_f$  units carry  $f$   $A$  groups forming  $A$ - $A$  bonds; and a constant fragmentation kernel  $F_{ij} = Q$ . Besides, we assume  $Q$  to be large enough that a sol-gel transition would not exist.

Let us denote the moments of  $C_k(r, t)$  distribution

$$\mu_n(r, t) = \sum_{k=1} k^n C_k(r, t)$$

where, for instance,  $\mu_0$  is a prescribed number of clusters and  $\mu_1$  is a prescribed number of monomeric units. By summing (2) over all  $k$  we obtain:

$$\dot{\mu}_0(r, t) = -p(2\mu_0(r, t) + (f-2)\mu_1(r, t))^2 + Q(\mu_1(r, t) - \mu_0(r, t)) + D\Delta_r \mu_0(r, t) \quad (3a)$$

for the zeroth moment and for moments of  $n$ th order

$$\begin{aligned} \dot{\mu}_n = p \left( \sum_{j=1}^{n-1} C_{nj} \{ (f-2)^2 \mu_{j+1} \mu_{n+1-j} + 2[(f-2)(n+1)/(n+1-j)] \mu_j \mu_{n+1-j} + 4\mu_j \mu_{n-j} \} \right. \\ \left. + 2(f-2)(n-1)\mu_1 \mu_n \right) \\ + Q \left( [2/(n+1)] \sum_{j=0}^n C_{n+1,j} B_j \mu_{n-j+1} - \mu_{n+1} + \mu_n \right) + D\Delta_r \mu_n \quad (3b) \end{aligned}$$

where  $\mu_n = \mu_n(r, t)$  and  $C_{nj}$  are the binomial coefficients, and  $B_j$  are Bernoulli numbers.

For  $\mu_1$  it follows that

$$\dot{\mu}_1 = D\Delta_r \mu_1. \quad (4)$$

This equation was recently obtained with field theoretical techniques by Elderfield (1987). The moments can be represented in the following form:

$$\mu_n(r, t) = \mu_n(t) + \mu_n^*(r, t) \quad \langle \mu_n^*(r, t) \rangle = 0$$

where  $\mu_n(t)$  is the mean value,  $\mu_n^*(r, t)$  is a local deviation from  $\mu_n(t)$  and angle brackets represent volume average. Averaging (3a) we obtain the equation which governs time evolution of the zeroth mean moment

$$\dot{\mu}_0(t) = -p[2\mu_0(t) + (f-2)M]^2 - 4p[G_{00}(0, t) + (f-2)G_{01}(0, t) + (f-2)^2G_{11}(0, t)] + Q(M - \mu_0(t)) \quad (5)$$

where  $M$  is the mean density of monomeric units,  $G_{ij}$  are the pair correlation functions

$$G_{ij}(R, t) = \langle \mu_i^*(r, t) \mu_j^*(r+R, t) \rangle$$

and  $R$  is the  $d$ -dimensional correlation parameter. Using (3)–(5) and neglecting terms with  $\mu_i^* \mu_j^{*2}$  we obtain the following system of linear rate equations for  $G_{ij}$ :

$$\begin{aligned} \dot{G}_{11} &= 2D\Delta_R G_{11} \\ \dot{G}_{01} &= 2D\Delta_R G_{01} - 4p(f-2)(MG_{01} + \mu_0(t)G_{11}) + Q(G_{11} - G_{10}) \\ \dot{G}_{00} &= 2D\Delta_R G_{00} - 8p(f-2)(MG_{00} + \mu_0(t)G_{01}) + 2Q(G_{01} - G_{00}). \end{aligned}$$

For the monodisperse initial distribution

$$C_k(r, 0) = \delta_{k1} \mu_1(r, 0)$$

where  $\delta_{k1}$  is a Kroneker delta and  $\mu_1$  we assume to be a random function with Gaussian  $\delta$ -correlated distribution and mean value  $\langle \mu_1(r, 0) \rangle = M$ , we obtain the following long-time dependences for  $G_{ij}(R=0, t)$

$$\begin{aligned} G_{11}(0, t) &= M(2Dt)^{-d/2} & G_{01}(0, t) &= -\frac{1}{2}M[f-2-f/(1+8fpM/Q)](2Dt)^{-d/2} \\ G_{00}(0, t) &= \frac{1}{4}M[f-2-f/(1+8fpM/Q)](2Dt)^{-d/2}. \end{aligned}$$

At the large- $t$  limit we can represent the mean zeroth moment in the following form:

$$\mu_0(t) = \mu_0(\infty) + \delta\mu_0(t) \quad \delta\mu_0(t)/\mu_0(\infty) \ll 1$$

where  $\mu_0(\infty)$  is an equilibrium value and  $\delta\mu_0(t)$  is a small deviation from the equilibrium state. Linearising (5) near the equilibrium we get the leading terms of  $\delta\mu_0(t)$  at large  $t$ :

$$\delta\mu_0(t) = -[pQ^{1/2}/(Q+8fpM)^{3/2}]M(2Dt)^{-d/2}$$

and, hence, the long-time approach to the equilibrium cluster size distribution is described by the power-law dependence

$$C_k(t) = C_k(\infty) - \text{constant} \times (2Dt)^{-d/2}.$$

To summarise, we have shown that the long-time kinetics of reversible coagulation is determined by fluctuation effects and described by a power-law dependence on time as compared to the exponential laws predicted by mean-field approximations. Thus, we affirm that the upper critical dimension of the considered system is equal to infinity,  $d_c = \infty$ .

The long-time peculiarities of coagulation/fragmentation processes are determined by the existence of a pure diffusive mode associated with the conserved density  $M$  (the fact that  $\mu_1$  is a pure diffusive mode was recently pointed out by Elderfield (1987)). This conservation law is, however, only valid as long as no gelation occurs. We expect that the power law for the long-time approach to equilibrium would be valid even if the system exceeds the sol-gel point, because we would then have a new diffusive

mode—a prescribed value of monomeric units contained both in the sol and the gel phases. This is, however, an open problem of detailed investigation.

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