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LETTER TO THE EDITOR

Critical kinetics near the gelation transition

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Abstract. Smoluchowski's equation for rapid coagulation is used to describe the kinetics of gelation, in which the coagulation kernel K_{ij} models the bonding mechanism. For different classes of kernels we derive criteria for the occurrence of a gelation transition, and obtain critical exponents in the pre- and post-gelation stages in terms of the model parameters.

In recent papers by Leyvraz and Tschudi (1982) and Ziff *et al* (1982, hereinafter referred to as I) a kinetic model of polymerisation has been discussed in which bonding between polymers takes place only at their surface. The time-dependent concentrations of k-mers $c_k(t)$ satisfy Smoluchowski's equation

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \tag{1}$$

with coagulation kernel $K_{ij} = s_i s_j$, in which s_k represents the effective surface area of a k-mer. At large k, $s_k \sim k^{\omega}$ (e.g. for compact clusters $\omega = \frac{2}{3}$). For $\omega > \frac{1}{2}$, *gelation* occurs, i.e. a transition at a specific time t_c, manifesting itself through the sudden violation of the conservation of mass, $M_1(t) = \Sigma_{k=1}^{\infty} k c_k(t)$, contained in finite clusters. The formerly constant $M_1(t)$—chosen equal to unity—decreases after t_c as the finite clusters lose mass to the gel (infinite cluster). *At* and *past* t_c the size distribution satisfies

$$c_k(t) \sim A(t) k^{-\tau'} \qquad (t \geq t_c,\ k \to \infty) \tag{2}$$

with $\tau' = \omega + \frac{3}{2}$ and $A(t)$ a smooth function of $(t - t_c)$. Leyvraz and Tschudi (1982) have conjectured that the scaling postulate holds,

$$c_k(t) \sim k^{-\tau} \Phi[k(t_c - t)^{1/\sigma}], \tag{3}$$

in the limit $t \uparrow t_c$, $k \to \infty$ with $x = k(t_c - t)^{1/\sigma}$ fixed. Consistency of (1) and (3) requires $\tau = \tau' = \omega + \frac{3}{2}$, $\sigma = \omega - \frac{1}{2}$ and $\Phi(x) \sim \exp(-Cx^{\omega})$ as $x \to 0$.

All other critical exponents depend only on σ and τ (see e.g. Essam (1980) and Stauffer (1979)). Scaling does not hold in the post-gelation stage, due to the absence of sol–gel interactions in (1) (see I).

Here we report new results on the more general questions: what properties of coagulation kernels K_{ij} cause gelation and what type of singularities—critical

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exponents—do they induce? A detailed account will be published elsewhere in a paper (1982) to be referred to as II.

This letter consists of three parts: (i) an investigation of the possibility of post-gelation solutions for kernels of the general form $K_{ij} = s_i r_j + r_i s_j$; (ii) derivations of criteria for the occurrence of gelation, using moment equations; (iii) a discussion of the scaling postulate.

(i) Does the coagulation equation (1) with $K_{ij} = s_i r_j + r_i s_j$ admit post-gelation solutions (where $\dot{M}_1(t) \neq 0$) and if so, what is their large k-dependence? Suppose first that $s_k \sim k^{\mu}$ and $r_k \sim k^{\nu}$ as $k \to \infty$ so that

$$K_{ij} = i^{\mu} j^{\nu} + i^{\nu} j^{\mu} \tag{4}$$

at large i, j (constants being absorbed in the unit of time). For kernels (4) gelation does not occur for $\nu \leq \mu \leq \frac{1}{2}$, as shown by White (1980) (note $K_{ij} \leq 2(ij)^{1/2}$). We expect gelation for $\nu + \mu > 1$. For post-gelation solutions to be possible more conditions are required, however. To see this we introduce generating functions $f_\rho(x, t)$, $\rho = 0, \mu, \nu$ as

$$f_\rho(x, t) = \sum_{k=1}^{\infty} k^{\rho} c_k(t)\, \mathrm{e}^{kx} \simeq M_\rho(t) + a_\rho(t)(-x)^{\alpha_\rho} \qquad (x \uparrow 0). \tag{5}$$

The moments $M_\rho(t) \equiv \sum_{k=1}^{\infty} k^{\rho} c_k(t)$ with $\rho = 1, \mu, \nu$ should be *finite* since M_1 represents the total sol mass, and M_μ and M_ν appear in the coagulation equation (1) for model (4), which is supposedly well defined in the pre- and post-gelation stages. This yields

$$\dot{f}_0 - \dot{M}_0 = (f_\mu - M_\mu)(f_\nu - M_\nu). \tag{6}$$

Since $M_1(t)$ is bounded for all t, we must have $a_0(t) = -M_1(t)$ and $\alpha_0 = 1$ in (5). If (6) admits solutions with $\dot{M}_1 \neq 0$, we find

$$\dot{M}_1 x = a_\mu a_\nu (-x)^{\alpha_\mu + \alpha_\nu} \qquad (x \uparrow 0). \tag{7}$$

Consequently $\alpha_\mu + \alpha_\nu = 1$ and $\dot{M}_1 = -a_\mu a_\nu$. Non-integral values of α_μ and α_ν in (5) imply an asymptotic behaviour of the form (2) with $\tau' = \frac{1}{2}(\mu + \nu + 3)$ and yield an expression for $A(t)$ in terms of $\dot{M}_1(t)$. From a further analysis of (6) and (7) it can be deduced that post-gelation solutions are excluded, unless

$$\mu, \nu > 0, \qquad \mu + \nu > 1, \qquad |\mu - \nu| < 1. \tag{8}$$

Similarly one shows that kernels $K_{ij} = r_i s_j + r_j s_i$ with $r_k = \exp(\alpha k)$ and $s_k \sim k^{\mu}$ or $s_k \sim \exp(\beta k)$ do not admit post-gelation solutions. For $s_k = r_k = \exp(\alpha k)$, $\alpha > 0$ and $r_k = s_k = k^{\lambda}$, $\lambda > \frac{1}{2}$ explicit post-gelation solutions will be given in II. No post-gelation solutions exist for $K_{ij} = s_i + s_j$, irrespective of the functional form of s_k.

(ii) In the pre-gelation stage, moment equations are an important tool when investigating gelation. White (1980) has derived exact rate equations for the partial moments $M_{\alpha,L}(t) \equiv \sum_{k=1}^{\infty} k^{\alpha} c_k(t)$. If for all j

$$\Lambda_{\alpha,j} \equiv \lim_{L \to \infty} \sum_{k=1}^{L} c_k K_{ij} k^{\alpha} < \infty, \tag{9}$$

these equations reduce to the limiting form (with $M_\alpha \equiv M_{\alpha,\infty}$)

$$\dot{M}_\alpha = \tfrac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} c_i c_j K_{ij} [(i+j)^{\alpha} - i^{\alpha} - j^{\alpha}]. \tag{10}$$

For some kernels the right-hand side can be expressed in terms of moments and the set is closed. The equation with $\alpha = 1$ implies that no gelation occurs as long as $\Lambda_{1,j} < \infty$; when at some point t_c this quantity becomes infinite, $\dot{M}_1(t)$ becomes non-vanishing and gelation sets in. In principle, some $\Lambda_{\alpha,j}$ with $\alpha \geq 2$ might become infinite at earlier times t_α. The equations (10) would then only be valid for $t < \min_\alpha t_\alpha$ (possibly zero). Here we assume that this is *not* the case and that all $\Lambda_{\alpha,j}$ diverge simultaneously at $t = t_c$ (a heuristic argument will be given in II) so that the moment equations are valid up to t_c. The divergence of a single moment then suffices to decide whether and when gelation will occur.

We consider the general class of kernels $K_{ij} = \Psi(i, j)$ where $\Psi(i, j)$ is a positive, homogeneous function of degree λ, i.e. $\Psi(si, sj) = s^\lambda \Psi(i, j)$, as discussed by Lushnikov (1973), Silk and White (1978). When $\Psi(i, j)$ is either convex or concave in both its variables, we can formulate a general result: for convex $\Psi(i, j)$ and $\lambda > 1$, gelation occurs and for concave $\Psi(i, j)$ and $\lambda \leq 1$, gelation is excluded. In deriving these criteria we need Jensen's inequality: given a convex function $\Psi(x)$ and a set of positive numbers $\{a_k\}$ from which for any set $\{b_k\}$ expectation values are calculated as $E(b) = \Sigma\, b_k a_k / \Sigma\, a_k$, the inequality $E[\Psi(b)] \geq \Psi[E(b)]$ holds and is strict unless $\Psi(x) = x$. For concave $\Psi(x)$ the inequality is reversed.

We consider (10) with $\alpha = 2$, namely

$$\dot{M}_2 = \sum_{i,j} c_i c_j ij \Psi(i, j) \qquad (t < t_c). \tag{11}$$

First, take $\Psi(i, j)$ *convex* and apply Jensen's inequality twice with $a_k = kc_k$, $b_k = k$ (so that $E(k) = M_2$ as $M_1 = 1$), yielding $\dot{M}_2 > \Psi(1, 1) M_2^\lambda$. Integrating this result yields

$$M_2(t) > M_2(0)(1 - t/t_2)^{-1/(\lambda - 1)} \tag{12}$$

with $t_2 = [\Psi(1, 1)(\lambda - 1) M_2^{\lambda-1}(0)]^{-1}$. For $\lambda > 1$, t_2 is positive and the second moment diverges at some point, before or at t_2. Hence, gelation occurs and we find the upper bound t_2 for t_c.

For *concave* $\Psi(i, j)$ the inequality sign in (12) is reversed and if also $\lambda \leq 1$, the moment M_2 remains finite for all times. This is sufficient to *exclude* gelation as in the concave case $\Psi(i, j) < A_j i$ ($i \to \infty$, fixed j), implying $\Lambda_{1,j} < A_j M_2 < \infty$.

(iii) In view of the fundamental importance of scaling, we investigate (pre-gelation) similarity solutions to (1) for homogeneous kernels $K_{ij} = \Psi(i, j)$, following Lushnikov, Silk and White. Since the scaling property is formulated for large k, we may consider the continuous version of (1) where the size distribution is represented by a continuous function $c(k, t)$. This equation is invariant under the group of similarity transformations (with $s > 0$)

$$\bar{k} = sk, \qquad \bar{t} = s^{-\sigma} t, \qquad \bar{c}(\bar{k}, \bar{t}) = s^{-\tau} c(k, t), \tag{13a}$$

provided the exponents σ and τ are related by

$$\sigma + \tau = \lambda + 1. \tag{13b}$$

This can be verified by direct substitution into the continuous version of (1). A similarity solution remains itself invariant under (13), and must have the property $c(k, t) = s^\tau c(sk, s^{-\sigma} t)$ for all $s > 0$. As (1) is also invariant under time translations, we may replace t by $t_c - t$, so that the similarity solution has the form (3), where σ and τ satisfy (13*b*). If we have an *exact* solution to (1) of this form it should satisfy mass conservation, imposing the further restrictions $\tau = 2$ and $\sigma = \lambda - 1$ (see Lushnikov, White and Silk). However, on the basis of the scaling postulate one expects the general solution only to *approach* this similarity form in the limit defined below (3). Therefore, mass conservation should not be imposed on (3) and we expect that the invariance properties (13) of the coagulation equation imply the exponent relation, $\tau+\sigma=\lambda+1$, whenever the general solution approaches the scaling form (3).

This supports the conjecture (3) of Leyvraz and Tschudi and is in agreement with the classical Flory–Stockmayer theory, where $K_{ij}\sim ij$ as $i,j\to\infty$ (see Ziff and Stell (1980) and Leyvraz and Tschudi (1981)). In the latter case one has for $t\uparrow t_c$ the behaviour $c_k\sim(2\pi)^{-1/2}k^{-5/2}\exp[-\frac{1}{2}k(t-t_c)^2]$, so that $\tau=\frac{5}{2}$ and $\sigma=\frac{1}{2}$.

A more direct verification of the exponent relation (13*b*) is possible for the kernels in (4). Under the assumption that the general solution approaches the scaling form (3), the singular part of $M_n(t)$ behaves as

$$M_n(t)\simeq B_n(t_c-t)^{-(n+1-\tau)/\sigma} \qquad (t\uparrow t_c), \tag{14}$$

where B_n are positive constants. The equations (12) become

$$\dot{M}_n=\sum_{l=1}^{n-1}\binom{n}{l}M_{l+\lambda}M_{n-l+\mu}. \tag{15}$$

A dominant behaviour (14) is only consistent with (15) if the exponent relation (13*b*) is satisfied.

We conclude this note with a number of remarks.

(a) The scaling property (3) or (14) cannot be valid in the pre-gelation stage for *all* kernels, that allow gelation according to the above discussed criteria. A counter-example is provided by $K_{ij}=(ij)^2$. One finds that always some B_n become negative (unphysical). We have not been able to determine more restrictive conditions on the kernels for the validity of scaling.

(b) For certain kernels the conclusions of (i) and (ii) are paradoxical. For example, for $K_{ij}=i^\lambda+j^\lambda$, $\lambda>1$ gelation should occur but post-gelation solutions do not exist. A tentative explanation of this is that solutions exist up to t_c, where $\Lambda_{1,j}(t_c)\sim\sum k^{1+\lambda}c_k(t_c)$ diverges (gelation), but at the same time also $M_\lambda(t_c)=\sum k^\lambda c_k(t_c)$ diverges, since $c_k(t_c)\sim k^{-\tau}$ and $\lambda-\tau=\sigma-1>-1$. Therefore, the coagulation equation is no longer well defined for $t>t_c$, as it explicitly contains M_λ. The kernels (4) with $|\mu-\nu|>1$ and $\mu,\nu>1$ lead to a similar paradox.

(c) Rigorous results for the coagulation equation are scarce. As far as existence and uniqueness of solutions to the initial value problem is concerned, the following has been proved: for $K_{ij}<Cij$, unique solutions satisfying the conditions of normalisation and positivity exist in a finite time interval (McLeod 1962). Leyvraz and Tschudi (1981) proved global existence but not uniqueness for $K_{ij}=s_is_j$ with $s_i<Ci$. For $K_{ij}<C(i+j)$, White (1980) proved that initial solutions exist and are unique, for which all moments are bounded on bounded time intervals. In all other cases existence proofs are lacking to our knowledge. Here we have tentatively assumed that in all cases considered the initial solutions exist and are unique, but rigorous proofs are very much desired. It would be of particular interest to prove (or disprove) existence and uniqueness for cases where $K_{ij}\sim A_ji^\lambda$ ($i\to\infty$, j fixed, $\lambda>1$, A_j positive). Here the formal Taylor series expansion of the solution suggests a singularity in $c_k(t)$ at $t=0$ (for details, see II). The existence of such a singularity might invalidate the conclusions of (ii) for the kernels (4) with μ or $\nu>1$. It is therefore desirable to have a rigorous proof showing when the limiting form (12) of the moment equations is valid for all $t\leqslant t_c$.

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