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On Lushnikov's Model of Gelation

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We characterize gelation for models of polymers built up as infinite-volume limits of finite systems. We establish rigorously the occurrence of gelation in Lushnikov's model with reaction rate $R_{jk} = jk$. We obtain bounds on the size of the largest polymer in the system at time t.

KEY WORDS: Polymers; gelation; Markov chain; large-deviation bound.

1. INTRODUCTION

Many recent studies[1-7] have been devoted to systems of interacting polymers evolving through the irreversible aggregation reaction

$$(j) + (k) \xrightarrow{R_{jk}} (j+k) \tag{1}$$

whereby polymers of lengths j and k link themselves together to form a polymer of length $j+k$; the number R_{jk} denotes the corresponding reaction rate. The standard approach to such a system is through Smoluchlovski's equations for the density $x_j(t)$ of polymers made up of j units in an infinite-volume homogeneous system,[2,6]

$$\begin{aligned} \dot{x}_1 &= -\sum_{k=1}^{\infty} R_{1k} x_1 x_k \\ \dot{x}_j &= \frac{1}{2} \sum_{k=1}^{j-1} R_{kj-k} x_k x_{j-k} - \sum_{k=1}^{\infty} R_{jk} x_j x_k, \qquad j \geqslant 2 \end{aligned} \tag{2}$$

An alternative approach allowing a more detailed description has been

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pioneered by Marcus[8] and studied in detail by Lushnikov[9]: the state of a finite homogeneous system of polymers of lengths 1, 2, 3,..., N in a volume V is described by a vector $\mathbf{n} \in \mathbf{N}^N$, the jth component of which is the number of j-mers. The only allowed transitions are of the form $\mathbf{n} \to \mathbf{n}_{jk}^+$ and $\mathbf{n}_{jk}^- \to \mathbf{n}$, where

$$\mathbf{n}_{jk}^+ = \begin{cases} (n_1, n_2,..., n_j - 1,..., n_k - 1,..., n_{j+k} + 1,..., n_N) & \text{if } j \neq k \\ (n_1, n_2,..., n_j - 2,..., n_{2j} + 1,..., n_N) & \text{if } j = k \end{cases} \tag{3}$$

and

$$\mathbf{n}_{jk}^- = \begin{cases} (n_1, n_2,..., n_j + 1,..., n_k + 1,..., n_{j+k} - 1,..., n_N) & \text{if } j \neq k \\ (n_1, n_2,..., n_j + 2,..., n_{2j} - 1,..., n_N) & \text{if } j = k \end{cases} \tag{4}$$

The evolution of the system is modeled by the Markov chain with forward equation

$$\dot{p}_t(\mathbf{n}) = \sum_{\substack{j,k=1 \\ n_{j+k} \neq 0}}^{N} Q_{jk}(\mathbf{n}_{jk}^-)\, p_t(\mathbf{n}_{jk}^-) - \sum_{\substack{j,k=1 \\ n_j n_k \neq 0}}^{N} Q_{jk}(\mathbf{n})\, p_t(\mathbf{n}) \tag{5}$$

where $p_t(\mathbf{n})$ is the probability for the system to be in state $\mathbf{n}$ at time t [for some initial distribution $p_0(\mathbf{n})$] and the transition function is proportional to the reaction rate and to the density of pairs of reacting polymers:

$$Q_{jk}(\mathbf{n}) = \begin{cases} \dfrac{1}{2V} R_{jk} n_j n_k & \text{if } \ j \neq k \\[2ex] \dfrac{1}{2V} R_{jj} n_j (n_j - 1) & \text{if } \ j = k \end{cases} \tag{6}$$

The connection between the two models is as follows: let $N_1(t)$, $N_2(t)$,..., $N_N(t)$ be the random variables denoting the numbers of monomers, dimers,..., N-mers at time t in Lushnikov's model; then the expected values $(1/V)\, E[N_j(t)]$ should coincide in the thermodynamic limit $N \to \infty$, $V \to \infty$, $N/V = \rho$ with the densities x_j of Smoluchovski's model; see ref. 7. Lushnikov's description is obviously the more complete of the two, in the sense that it allows the investigation of finite-size effects and fluctuations; for instance, see ref. 4. Nevertheless, it is still not fully microscopic; it is an instance of the mesoscopic level of description in the sense of ref. 10. Both models ignore diffusion effects and are thus restricted to homogeneous systems.

What makes the two models both interesting and difficult is the possibility that within a finite time a polymer of macroscopic length has formed. In the Smoluchovski scheme this manifests itself by an apparent lack of conservation of the density of units:

$$\sum_{j=1}^{\infty} jx_j(t) < \sum_{j=1}^{\infty} jx_j(0) \qquad \text{for} \quad t > t_g \tag{7}$$

This depletion phenomenon seems to contradict the fact that all reactions (1) conserve the number of units, but the contradiction is resolved once one realizes that the left-hand side of (7) represents only the contribution of all polymers of *finite length* to the total density of units.

The characterization of gelation in Lushnikov's model is necessarily different, since we start with a finite system. We propose the following definition: let $N_1(t)$, $N_2(t)$,..., $N_N(t)$ be as above; we will say that *there is no gelation* at time t if the random variable

$$V^{-1} \sum_{\alpha N \leqslant j \leqslant N} jN_j(t) \tag{8}$$

(which gives the contribution to the total density of units by polymers of length larger than αN, $0 < \alpha \leqslant 1$) is asymptotically concentrated at zero for all values of α; in other words, for all $\alpha > 0$, $x > 0$:

$$\lim_{\substack{N \to \infty \\ V \to \infty \\ N/V = \rho}} P\left[V^{-1} \sum_{\alpha N \leqslant j \leqslant N} jN_j(t) \geqslant x \right] = 0 \tag{9}$$

If condition (9) is violated, this means that a macroscopic fraction of the total density of units is tied up in polymers of macroscopic length, and this is the essence of the phenomenon of gelation.

A complete characterization of the reaction rates R_{jk} leading to gelation is still an open problem in Smoluchovski's scheme (see, however, refs. 3, 5, and 11) and *a fortiori* in the stochastic approach; in fact, the latter problem remains largely unexplored as far as rigorous results are concerned. In this paper we study the gelation problem in Lushnikov's model with reaction rate $R_{jk} = jk$. The corresponding deterministic problem is the earliest known example of gelation.[2,12,13]

We have gathered in Section 2 the main properties of Lushnikov's model for a whole class of reaction rates. This is largely a review of known results, although the previously published proofs are often incorrect or unduly convoluted. An explicit solution of Eq. (5) can be obtained for suitable initial conditions, but this solution is too complicated to be really useful. In Section 3 we use simple bounds to prove that gelation occurs in the model with reaction rate $R_{jk} = jk$. We use the method of *large deviations* to obtain a describtion of the asymptotic distribution which replaces (9) beyond the gelation time. We conclude the paper with a conjecture.

2. BASIC PROPERTIES OF LUSHNIKOV'S MODEL IN FINITE VOLUME

Consider the Markov chain defined by (3)–(6). A remarkable simplification occurs for a certain class of initial conditions when the reaction rate is of the form

$$R_{jk} = jf(k) + kf(j) \tag{10}$$

for some positive function f. If $p_0(\mathbf{n})$ is of the form

$$p_0(\mathbf{n}) = \begin{cases} \prod_{j=1}^{N} \dfrac{a_j^{n_j}}{n_j!} & \text{if } \sum_{j=1}^{N} jn_j = N \\ 0 & \text{otherwise} \end{cases} \tag{11}$$

where $a_1, a_2,..., a_N$ are nonnegative numbers such that

$$\sum_{\mathbf{n}:\sum jn_j = N} \prod_{j=1}^{N} \frac{a_j^{n_j}}{n_j!} = 1 \tag{12}$$

then the time-dependent probability $p_t(\mathbf{n})$ retains the form (11) with time-dependent numbers a_j.

More precisely:

Theorem 1. (i) Consider the diffential equation

$$\begin{aligned} V\dot{a}_{N,1}(t) &= -(N-1)\, f(1)\, a_{N,1}(t) \\ V\dot{a}_{N,j}(t) &= \sum_{r=1}^{j-1} rf(j-r)\, a_{N,r}(t)\, a_{N,j-r}(t) \\ &\quad - (N-j)\, f(j)\, a_{N,j}(t), \qquad j \geqslant 2 \end{aligned} \tag{13}$$

with initial condition $a_{N,j}(0) = a_j$. It admits a unique solution $\{a_{N,j}(t), j = 1, 2,..., N\}$. This solution exists globally and is nonnegative for nonnegative initial conditions. Moreover,

$$\sum_{\mathbf{n}:\sum jn_j = N} \prod_{j=1}^{N} \frac{a_{N,j}^{n_j}(t)}{n_j!} = \sum_{\mathbf{n}:\sum jn_j = N} \prod_{j=1}^{N} \frac{a_j^{n_j}}{n_j!} \tag{14}$$

(ii) The solution of Eq. (5) with initial condition (11) is

$$p_t(\mathbf{n}) = \begin{cases} \prod_{j=1}^{N} \dfrac{a_{N,j}^{n_j}(t)}{n_j!} & \text{if } \sum_{j=1}^{N} jn_j = N \\ 0 & \text{otherwise} \end{cases} \tag{15}$$

where the functions $a_{N,j}(t)$ obey the differential equation and initial condition in (i).

Proof. (i) Let

$$b_{N,j}(t) = V^{-1} e^{(N-j)f(j)t/V} a_{N,j}(t) \tag{16}$$

The new functions obey the equation

$$\begin{aligned} \dot{b}_{N,1}(t) &= 0 \\ \dot{b}_{N,j}(t) &= \sum_{r=1}^{j-1} rf(j-r)\, b_{N,r}(t)\, b_{N,j-r}(t) \\ &\quad \times (\exp\{[(N-j)\, f(j) - (N-r)\, f(r) - (N-j+r) \\ &\quad \times f(j-r)]\, t/v\}), \qquad j \geqslant 2 \end{aligned} \tag{17}$$

which can be rewritten as the integral equation

$$\begin{aligned} b_{N,j}(t) = \frac{a_j}{V} + \int_0^t ds \sum_{r=1}^{j-1} rf(j-r)\, b_{N,r}(s)\, b_{N,j-r}(s) \\ \times (\exp\{[(N-j)\, f(j) - (N-r)\, f(r) \\ -(N-j+r)\, f(j-r)]\, s/V\}) \end{aligned} \tag{18}$$

The right-hand side of (18) involves only functions $b_{N,k}$, $k<j$; hence (18) is really a recursion relation with initial condition $b_{N,1}(t) = a_1/V$, and this makes both the uniqueness and the positivity of the solution obvious. Global existence follows from the continuity of the integrand. The proof of the normalization property (14) is straightforward.

(ii) Insert the proposed solution (15) into the right-hand side of Eq. (5) to get

$$\begin{aligned} \frac{1}{2V} \prod_{l=1}^{N} \frac{a_{N,l}^{n_l}(t)}{n_l!} \Bigg\{ \sum_{j \neq k : n_{j+k} \neq 0} [jf(k) + kf(j)]\, n_{j+k} \\ \times \frac{a_{N,j}(t)\, a_{N,k}(t)}{a_{N,j+k}(t)} + \sum_{j : n_{2j} \neq 0} 2jf(j)\, n_{2j} \frac{a_{N,j}^2(t)}{a_{N,2j}(t)} \\ - \sum_{j \neq k : n_j n_k \neq 0} [jf(k) + kf(j)]\, n_j n_k - \sum_{j : n_j \neq 0} 2jf(j)\, n_j(n_j - 1) \Bigg\} \end{aligned}$$

Next use the obvious symmetry properties of the summands together with the fact that n_{j+k} vanishes if $j+k>N$ to rewrite the above expression as

$$\begin{aligned}
&\frac{1}{V}\prod_{l=1}^{N}\frac{a_{N,l}^{n_l}(t)}{n_l!}\left\{\sum_{j=1}^{N-1}\sum_{k=1}^{N-j} jf(k)\frac{a_{N,j}(t)\,a_{N,k}(t)}{a_{N,j+k}(t)}\right.\\
&\qquad\left.-\sum_{k=1}^{N} kn_k\sum_{j=1}^{N} f(j)n_j+\sum_{j=1}^{N} jf(j)n_j\right\}\\
&=\frac{1}{V}\prod_{l=1}^{N}\frac{a_{N,l}^{n_l}(t)}{n_l!}\left\{\sum_{j=1}^{N-1}\sum_{q=j+1}^{N} jf(q-j)\frac{a_{N,j}(t)\,a_{N,q-j}(t)}{a_{N,q}(t)}\right.\\
&\qquad\left.-\sum_{j=1}^{N}(N-j)\,f(j)n_j\right\}\\
&=\frac{1}{V}\prod_{l=1}^{N}\frac{a_{N,l}^{n_l}(t)}{n_l!}\left\{\sum_{q=2}^{N}\sum_{j=1}^{q-1} jf(q-j)\frac{a_{N,j}(t)\,a_{N,q-j}(t)}{a_{N,q}(t)}\right.\\
&\qquad\left.-\sum_{j=1}^{N}(N-j)\,f(j)n_j\right\}\\
&=\dot{p}_n(t)\quad\blacksquare
\end{aligned}$$

Remarks. (i) Initial conditions of the form (11) contain as special cases probability distributions concentrated on any given q-mer; it suffices to take

$$a_j=\begin{cases}[(N/q)!]^{q/N} & \text{if } j=q\\ 0 & \text{otherwise}\end{cases}\tag{19}$$

(note that N must be a multiple of q if the whole system is made up of q-mers initially). Not every probability distribution concentrated on a given configuration is in the class (11).

(ii) Formula (11) resembles the multinomial distribution. Note, however, that the support condition $\sum jn_j=N$ is not the usual one.

The differential equations (13) are not easy to handle in general. However, the solution can be computed exactly in the special case $f(j)=j/2$; this corresponds to the reaction rate $R_{jk}=jk$, which is also the easiest nontrivial case in Smoluchovski's scheme.[2,12,13]

Theorem 2. When $f(j)=j/2$, the solution of Eq. (13) is

$$\begin{aligned}
a_{N,k}(t)=e^{-(kN/2V)t}\sum_{j=1}^{k}\frac{(-1)^{j-1}}{j}\\
\times\sum_{\substack{n_1,n_2,\dots,n_j\geq 1\\ n_1+n_2+\cdots+n_j=k}}\beta_{n_1}\beta_{n_2}\cdots\beta_{n_j}e^{(n_1^2+n_2^2+\cdots+n_j^2)t/2V}
\end{aligned}\tag{20}$$

where

$$\beta_n = \sum_{m=[n/N]}^{n} \frac{1}{m!} \sum_{\substack{l_1, l_2, \ldots, l_m \geqslant 1 \\ l_1 + l_2 + \cdots + l_m = n}} a_{l_1} a_{l_2} \cdots a_{l_m}, \qquad n > 0, \quad \beta_0 = 1 \tag{21}$$

Proof. For fixed N, define the functions $A_j(t)$, $j = 1, 2, 3, \ldots$, to be the solutions of the equation

$$\begin{aligned} 2V\dot{A}_1(t) &= (N-1)\, A_1(t) \\ 2V\dot{A}_j(t) &= -\sum_{r=1}^{j-1} r(j-r)\, A_r(t)\, A_{j-r}(t) + (N-j)\, jA_j(t) \end{aligned} \tag{22}$$

with initial conditions

$$A_j(0) = \begin{cases} a_j, & j \leqslant N \\ 0, & j > N \end{cases} \tag{23}$$

Obviously $A_j(t) = a_{N,j}(-t)$ whenever $j \leqslant N$.

The generating function

$$G(x, t) = \sum_{k=1}^{\infty} A_k(2Vt)\, e^{k(x - Nt)}, \qquad t \geqslant 0 \tag{24}$$

is easily seen to obey the partial differential equation

$$\frac{\partial G}{\partial t} = -\left(\frac{\partial G}{\partial x}\right)^2 - \frac{\partial^2 G}{\partial x^2}, \qquad t \geqslant 0 \tag{25}$$

This can be transformed into a linear equation: the function

$$H(x, t) = e^{G(x, t)} \tag{26}$$

obeys the equation

$$\frac{\partial H}{\partial t} = -\frac{\partial^2 H}{\partial x^2}, \qquad t \geqslant 0, \quad x \in \mathbf{R} \tag{27}$$

with initial condition

$$H(x, 0) = \exp\left(\sum_{k=1}^{N} a_k e^{kx}\right) \tag{28}$$

This has the solution

$$H(x, t) = \sum_{n=0}^{\infty} \beta_n e^{nx - n^2 t} \tag{29}$$

where the coefficients β_n are as in (21). The series (29) converges because by (28), $H(x, 0)$ is an entire function of e^x and by (29) so is $H(x, t)$ for every t. Next, for fixed $t \geqslant 0$, choose R such that when $|e^x| < R$

$$|H(x, t) - 1| = \left| \sum_{n=1}^{\infty} \beta_n e^{nx - n^2 t} \right| < 1 \tag{30}$$

Then $\log H(x, t)$ is analytic in $H(x, t)$, and thus in e^x, so that

$$\begin{aligned} G(x, t) &= \log H(x, t) \\ &= \log\left(1 + \sum_{n=1}^{\infty} \beta_n e^{nx - n^2 t}\right) \\ &= \sum_{j=1}^{\infty} \frac{(-1)^{j-1}}{j} \\ &\quad \times \sum_{n_1, n_2, \ldots, n_j = 1}^{\infty} \beta_{n_1} \beta_{n_2} \cdots \beta_{n_j} e^{(n_1 + n_2 + \cdots + n_j)x - (n_1^2 + n_2^2 + \cdots + n_j^2)t} \end{aligned}$$

implying by comparison with (24)

$$\begin{aligned} A_k(2Vt) e^{-kNt} = \sum_{j=1}^{k} \frac{(-1)^{j-1}}{j} \\ \times \sum_{\substack{n_1, n_2, \ldots, n_j \geqslant 1 \\ n_1 + n_2 + \cdots + n_j = k}} \beta_{n_1} \beta_{n_2} \cdots \beta_{n_j} e^{-(n_1^2 + n_2^2 + \cdots + n_j^2)t} \end{aligned}$$

and thus for $t \geqslant 0$

$$\begin{aligned} A_k(t) = e^{kNt/2V} \sum_{j=1}^{k} \frac{(-1)^{j-1}}{j} \\ \times \sum_{\substack{n_1, n_2, \ldots, n_j \geqslant 1 \\ n_1 + n_2 + \cdots + n_j = k}} \beta_{n_1} \beta_{n_2} \cdots \beta_{n_j} e^{-(n_1^2 + n_2^2 + \cdots + n_j^2)t/2V} \end{aligned} \tag{31}$$

Finally, since both (31) and the right-hand side of (22) are analytic functions of t, formula (31) can be extended to $t < 0$, giving the result (20) for $a_{N,k}(t) = A_k(-t)$. ∎

Remarks. (i) The above proof is a rigorous version of those appearing in refs. 4 and 9.

(ii) For an initial distribution concentrated on q-mers (i.e., $a_j = [(N/q)!]^{q/N}\,\delta_{jq}$) the coefficients β_n take the form

$$\beta_n = \begin{cases} \dfrac{[(N/q)!]^{n/N}}{(n/q)!} & \text{if} \quad n \text{ is a multiple of } q \\ 0 & \text{otherwise} \end{cases} \tag{32}$$

so that

$$a_{N,kq}(t) = e^{-kNt/2V}\left[\left(\frac{N}{q}\right)!\right]^{kq/N} \times \sum_{j=1}^{k} \frac{(-1)^{j-1}}{j} \times \sum_{\substack{m_1, m_2, \ldots, m_j \geq 1 \\ m_1 + m_2 + \cdots + m_j = k}} \frac{e^{q^2(m_1^2 + m_2^2 + \cdots + m_j^2)t/2V}}{m_1!\, m_2! \cdots m_j!} \tag{33}$$

and $a_{N,j}(t)$ vanishes when j is not a multiple of q.

Although formulas (15) and (20) give the full time-dependent probability distribution, most of our subsequent study is based on the mean number of polymers.

Proposition 1. Let $N_r(t)$ be the random variable denoting the number of r-mers at time t in the model defined by Eq. (4)–(6) with $f(j) = j/2$ and initial condition (11). Then

$$\mathbf{E}[N_r(t)] = a_{N,r}(t)\, e^{-r(N-r)t/2V} \sum_{\mathbf{n}:\sum jn_j = N-r} \prod_{j=1}^{N-r} \frac{a_j^{n_j}}{n_j!}, \qquad r < N$$

$$\mathbf{E}[N_N(t)] = a_{N,N}(t)$$

Proof. From theorem 1(ii),

$$\mathbf{E}[N_r(t)] = \sum_{\mathbf{n}:\sum jn_j = N} n_r \prod_{j=1}^{N} \frac{a_{N,j}^{n_j}(t)}{n_j!} = a_{N,r}(t) \sum_{\mathbf{n}:\sum jn_j = N-r} \prod_{j=1}^{N-r} \frac{a_{N,j}^{n_j}(t)}{n_j!}$$

But the factor of $a_{N,r}(t)$ in the above expression can be computed exactly because the equations for $a_{N,j}(t)$ and $a_{N-r,j}(t)$ differ only by a linear term; see (13). Hence, with $f(j) = j/2$,

$$a_{N,j}(t) = e^{-rjt/2V} a_{N-r,j}(t)$$

and by Theorem 1(i),

$$\mathbf{E}[N_r(t)] = a_{N,r}(t)\, e^{-r(N-r)t/2V} \sum_{\mathbf{n}:\sum jn_j = N-r} \prod_{j=1}^{N-r} \frac{a_{N-r,j}^{n_j}(t)}{n_j!}$$

$$= a_{N,r}(t)\, e^{-r(N-r)t/2V} \sum_{\mathbf{n}:\sum jn_j = N-r} \prod_{j=1}^{N-r} \frac{a_j^{n_j}}{n_j!} \quad \blacksquare$$

Remark. With a monomer initial condition we get

$$\mathbf{E}[N_r(t)] = \frac{(N!)^{(N-r)/N}}{(N-r)!}\, e^{-r(N-r)t/2V} a_{N,r}(t) \tag{34}$$

$$= \frac{N!}{(N-r)!}\, e^{-r(2N-r)t/2V} \sum_{j=1}^{r} \frac{(-1)^{j-1}}{j} \times \sum_{\substack{m_1, m_2, \ldots, m_j \geqslant 1 \\ m_1 + m_2 + \cdots + m_j = r}} \frac{e^{(m_1^2 + \cdots + m_j^2)t/2V}}{m_1!\, m_2! \cdots m_j!} \tag{35}$$

3. GELATION

The proper characterization of gelation in a model constructed as the infinite-volume limit of a sequence of finite systems has been discussed in Section 1; see (8), (9). However, one can also use a weaker criterion imitated from (7), namely

$$\sum_{j=1}^{\infty} \lim_{\substack{N \to \infty \\ V \to \infty \\ N/V = \rho}} \frac{j\mathbf{E}[N_j(t)]}{V} < \sum_{j=1}^{\infty} \lim_{\substack{N \to \infty \\ V \to \infty \\ N/V = \rho}} \frac{j\mathbf{E}[N_j(0)]}{V} = \rho \tag{36}$$

For simplicity, we restrict ourselves to a monomer initial condition and fix the initial density to be $\rho = 1$, so that we can take

$$N = V \tag{37}$$

With this choice the equations (17) for the functions $b_{N,j}$ defined in (16) become [recall $f(j) = j/2$]

$$\dot{b}_{N,1}(t) = 0$$

$$\dot{b}_{N,j}(t) = \frac{1}{2} \sum_{r=1}^{j-1} r(j-r)\, e^{-r(j-r)t/N} \times b_{N,r}(t)\, b_{N,j-r}(t), \qquad j \geqslant 2 \tag{38}$$

with initial conditions [see (19)]

$$b_{N,1}(0) = \frac{1}{N}(N!)^{1/N}$$
$$b_{N,j}(0) = 0, \qquad j \geqslant 2 \tag{39}$$

It turns out that sufficient bounds to prove gelation can be obtained very simply from (38).

Lemma 1. The solution of the differential equation (38) with initial condition (39) obeys the bound

$$b_{N,j}(t) \leqslant \frac{1}{N^j}(N!)^{j/N}\frac{j^{j-2}}{j!}t^{j-1}$$

Proof. Obviously, $b_{N,j}(t) \leqslant C_j(t)$, where $C_j(t)$ obeys the equation

$$\dot{C}_1(t) = 0$$
$$\dot{C}_j(t) = \frac{1}{2}\sum_{r=1}^{j-1} r(j-r)\, C_r(t)\, C_{j-r}(t) \tag{40}$$

with the same initial condition as $b_{N,j}$. But the solution of (40) is easily found (see ref. 2) to be

$$C_j(t) = \frac{1}{N^j}(N!)^{j/N}\frac{j^{j-2}}{j!}t^{j-1}$$

so that the lemma follows. ∎

The next lemma is used several times in the sequel (see formula 5.13.20, p. 64, in ref. 14).

Lemma 2. The power series

$$\sum_{j=1}^{\infty} \frac{j^{j-1}}{j!} z^j$$

has radius of convergence e^{-1}. Moreover, for $z \geqslant 0$ the sum of the series is the smallest root of the equation $xe^{-x} = z$.

Proposition 2. For a pure monomer initial condition, the following estimate holds:

$$\sum_{j=1}^{\infty} \lim_{N\to\infty} \frac{j\mathbf{E}[N_j(t)]}{N} \leqslant \frac{1}{t}$$

so that gelation takes place in the sense of criterion (36) at or before $t = 1$.

Proof. Using (34), (16), and Lemma 1, we get

$$\frac{j}{N}\mathbf{E}[N_j(t)] \leqslant \frac{N!}{N^j(N-j)!}\, e^{-j(N-j)t/N}\frac{j^{j-1}}{j!}\, t^{j-1}$$
$$\leqslant e^{-jt}e^{j^2t/N}\frac{j^{j-1}}{j!}\, t^{j-1} \tag{41}$$

Hence

$$\sum_{j=1}^{\infty} \lim_{N\to\infty} \frac{j\mathbf{E}[N_j(t)]}{N} \leqslant \sum_{j=1}^{\infty} e^{-jt}\frac{j^{j-1}}{j!}\, t^{j-1}$$
$$= \frac{1}{t}\sum_{j=1}^{\infty} \frac{j^{j-1}}{j!}\,(te^{-t})^j$$
$$= \frac{1}{t}\quad (\text{smallest root of } xe^{-x} = te^{-t}) \leqslant \frac{1}{t} \quad \blacksquare$$

We turn now to stronger criterion (9). We state our result in terms of expectations first.

Theorem 3. For a monomer initial condition, the following limits hold:

(i) For any $t < \log 2$, $0 < \alpha < 1$,

$$\lim_{N\to\infty} \sum_{\alpha N \leqslant j \leqslant N} \frac{j\mathbf{E}[N_j(t)]}{N} = 0 \tag{42}$$

(ii) For any $\varepsilon > 0$, $\delta > 0$, and $t > t_\varepsilon$,

$$\lim_{N\to\infty} \sum_{(\beta(t)-\delta)N \leqslant j \leqslant N} \frac{j\mathbf{E}[N_j(t)]}{N} \geqslant 1 - \frac{x_\varepsilon(t)}{t} \tag{43}$$

where $t_\varepsilon > 1$ is the largest solution of

$$te^{-(1-\varepsilon)t} = e^{-1} \tag{44}$$

$x_\varepsilon(t)$ is the smallest nonnegative solution of

$$xe^{-x} = te^{-(1-\varepsilon)t} \tag{45}$$

and $\beta(t)$ is the only positive root $(t > 1)$ of the function $I_t(\cdot)$: $[0, 1] \to \mathbf{R}$ defined by

$$I_t(x) = (1-x)\log(1-x) - x\log t + x(1-x)t \tag{46}$$

These functions have the following properties:

$$\text{(a)} \qquad x_\varepsilon(t) \leqslant 1 \qquad \text{and} \qquad \lim_{t \to \infty} x_\varepsilon(t) = 0$$

$$\text{(b)} \qquad \beta(t) = 1 - \frac{\log t}{t} + o\left(\frac{\log t}{t}\right) \qquad \text{as} \quad t \to \infty$$

Remarks. (i) The result (42) is equivalent to the criterion (9) for absence of gelation because, since

$$\sum_{\alpha N \leqslant j \leqslant N} N^{-1} j N_j(t)$$

is a nonnegative random variable,

$$\mathbf{P}\left[\sum_{\alpha N \leqslant j \leqslant N} N^{-1} j N_j(t) \geqslant x\right] \leqslant x^{-1} \mathbf{E}\left[\sum_{\alpha N \leqslant j \leqslant N} N^{-1} j N_j(t)\right]$$

(ii) Formula (43) says that a macroscopic fraction of the total density of units is tied up in polymers of size $N\beta(t)$ or more. This is gelation with an explicit lower bound on the size of the largest polymer formed at time t. In view of property (a), gelation is asymptotically complete as $t \to \infty$.

(iii) In the Smoluchovski scheme, the blowup of the second moment

$$\sum_{j=1}^{\infty} j^2 x_j(t)$$

is often taken as an indication that gelation has occurred.[1,2] We have this property here as a simple consequence of (43):

$$\begin{aligned} \sum_{j=1}^{N} \frac{j^2 \mathbf{E}[N_j(t)]}{N} &\geqslant \sum_{(\beta(t) - \delta) N \leqslant j \leqslant N} \frac{j^2 \mathbf{E}[N_j(t)]}{N} \\ &\geqslant N(\beta(t) - \delta)\left(1 - \frac{x_\varepsilon(t)}{t}\right) \end{aligned}$$

This tends to infinity as $N \to \infty$ for any $t > 1$.

In order to prove the theorem, define the following family of measures on the Borel subsets of $[0, 1]$:

$$m_{N,t}(A) = \sum_{j: j/N \in A} \frac{j \mathbf{E}[N_j(t)]}{N} \tag{47}$$

Using the inequality (41), we see that

$$m_{N,t}(A) \leqslant \sum_{j:\, j/N \in A} C_j^N \frac{t^{j-1}}{N^j} j^{j-1} e^{-j(N-j)t/N} \tag{48}$$

The right-hand side of (48) can be rewritten as the integral

$$2^N \int_A e^{-Nx\log N} e^{-Nx(1-x)t} e^{(Nx-1)\log(Nxt)} \mu_N(dx) \tag{49}$$

with the probability measure on [0, 1]:

$$\mu_N(A) = \sum_{j:\, j/N \in A} 2^{-N} C_j^N \tag{50}$$

But the sequence μ_N has well-known properties; see ref. 15.

Lemma 3. The sequence of probability measures defined by (50) has the large-deviation property with rate function

$$J(x) = x \log x + (1-x)\log(1-x) + \log 2 \tag{51}$$

namely,

$$\limsup_{N \to \infty} \frac{1}{N} \log \mu_N(A) \leqslant -\inf_{x \in A} J(x), \qquad A \text{ closed} \tag{52}$$

$$\liminf_{N \to \infty} \frac{1}{N} \log \mu_N(A) \geqslant -\inf_{x \in A} J(x), \qquad A \text{ open} \tag{53}$$

Our bound (48) reads

$$m_{N,t}(A) \leqslant \int_A e^{NG_{N,t}(x)} \mu_N(dx) \tag{54}$$

with

$$G_{N,t}(x) = \begin{cases} \left(x - \dfrac{1}{N}\right) \log(xt) - x(1-x)t + \log 2 - \dfrac{1}{N}\log N, & x \geqslant \dfrac{1}{N} \\ -x(1-x)t + \log 2 - \dfrac{1}{N}\log N, & x < \dfrac{1}{N} \end{cases} \tag{55}$$

As $N \to \infty$, $G_{N,t}(x)$ converges uniformly in x to

$$G_t(x) = x\log(xt) - x(1-x)t + \log 2 \tag{56}$$

Using this fact and Theorem 3.5 in ref. 15, we get the following estimate.

Proposition 3.

$$\limsup_{N \to \infty} \frac{1}{N} \log m_{N,t}(\bar{A}) \leqslant -\inf_{x \in \bar{A}} \{J(x) - G_t(x)\}$$
$$= -\inf_{x \in A} I_t(x)$$

with $I_t(x)$ as in (46).

It follows from Proposition 3 that the measure $m_{N,t}(A)$ of any set A where $I_t(x)$ is strictly positive tends to zero exponentially fast as $N \to \infty$. The properties of the rate function I_t: $[0, 1] \to \mathbf{R}$ are summarized in the following proposition.

Proposition 4. (i) For $0 < t \leqslant \log 2$, $I_t(x)$ is an increasing function of x vanishing only at the origin.

(ii) For $t > 1$, $I_t(x)$ has a single positive root $\beta(t)$; I_t is positive on $(0, \beta(t))$ and negative on $(\beta(t), 1]$ (see Fig. 1).

Remarks. (i) One would expect $I_t(x)$ to remain nonnegative all the way to $t = 1$; our bound is not good enough for this.

(ii) In order to prove the property (b) of Theorem 3, we check that

$$\lim_{t \to \infty} \frac{I_t(1 - \delta(\log t)/t)}{\log t} = \delta - 1$$

We can now complete the proof of Theorem 3. Part (i) follows immediately from Proposition 3 and Proposition 4(i). For part (ii) we note that

$$\sum_{(\beta(t) - \delta) N \leqslant j \leqslant N} \frac{j\mathbf{E}[N_j(t)]}{N} = 1 - m_{N,t}([0, \beta(t) - \delta))$$
$$= 1 - m_{N,t}([0, \varepsilon)) - m_{N,t}([\varepsilon, \beta(t) - \delta)) \qquad (57)$$

The last term on the right-hand side of (57) tends to zero as $N \to \infty$ by Proposition 3 and Proposition 4(ii). It remains to bound the second term using (41):

$$m_{N,t}([0, \varepsilon)) = \sum_{j \leqslant \varepsilon N} \frac{j\mathbf{E}[N_j(t)]}{N}$$
$$\leqslant \sum_{j \leqslant \varepsilon N} e^{-jt} e^{j\varepsilon t} \frac{j^{j-1}}{j!} t^{j-1}$$
$$\leqslant \frac{1}{t} \sum_{j=1}^{\infty} \frac{j^{j-1}}{j!} (te^{-(1-\varepsilon)t})^j = x_\varepsilon(t)$$

This completes the proof of Theorem 3.

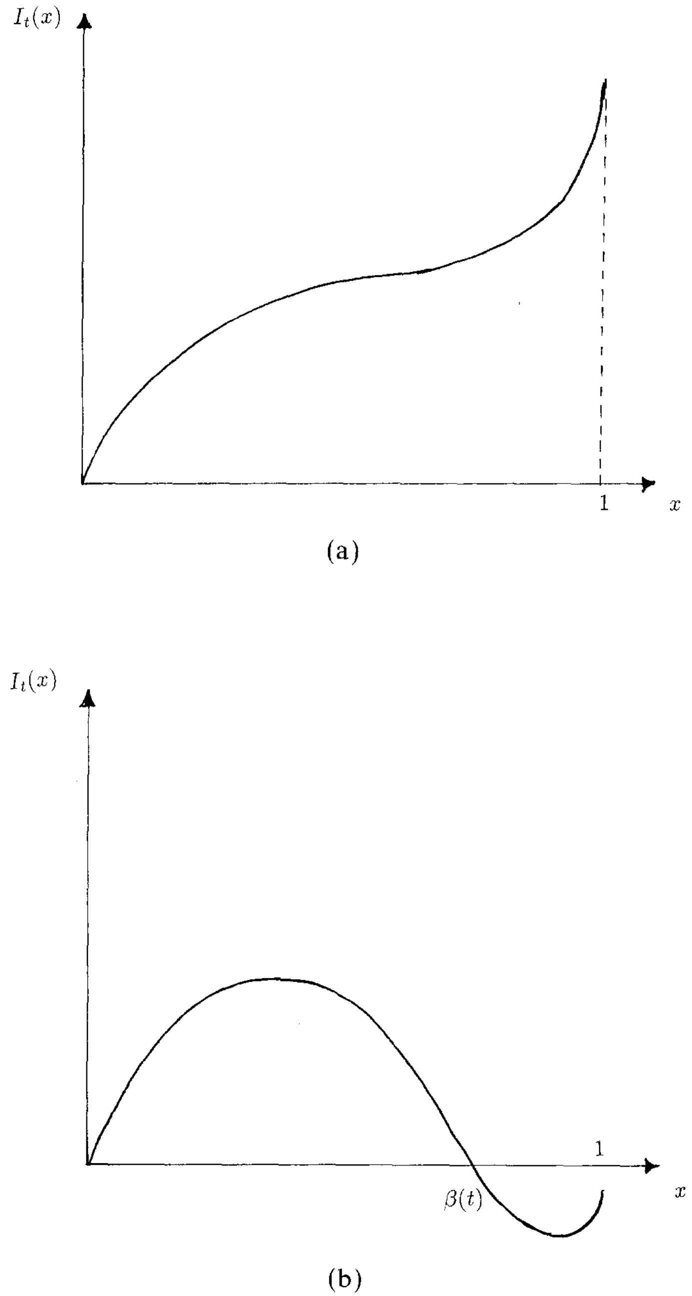

Fig. 1. (a) The function $I_t(x)$ for $t \leqslant \log 2$. (b) The function $I_t(x)$ for $t > 1$.

Remarks. (i) The proof of the properties of $x_\varepsilon(t)$ stated in Theorem 3a is straightforward.

(ii) We conjecture the following improvement of the bound of Lemma 1:

$$b_{N,j}(t) \leqslant \frac{1}{j!\,N}(N!)^{j/N}\left(1-e^{-t(j-1)/N}\right)^{j-1}$$

We can check this up to arbitrary order, but we could not find a general proof (induction will definitely not give this result). If this conjecture is correct, it implies the inequality

$$\frac{j\mathbf{E}[N_j(t)]}{N} \leqslant \frac{j}{N} C_j^N e^{-j(N-j)t/N}\left(1-e^{-(j-1)t/N}\right)^{j-1}$$

so that Proposition 3 holds with the following improved rate function in place of $I_t(x)$:

$$K_t(x) = (1-x)\log(1-x) + x\log\left(\frac{x}{1-e^{-xt}}\right) + x(1-x)t$$

The graph of this function has the shape shown in Fig. 2 for $t > 1$, where the roots $r(t)$ and $R(t)$ have the behavior

$$r(t) = 1 - e^{1-t} + o(e^{-t}), \qquad t \to \infty$$

$$R(t) = 1 - \frac{e^{-2t}}{t} + o\left(\frac{e^{-2t}}{t}\right), \qquad t \to \infty$$

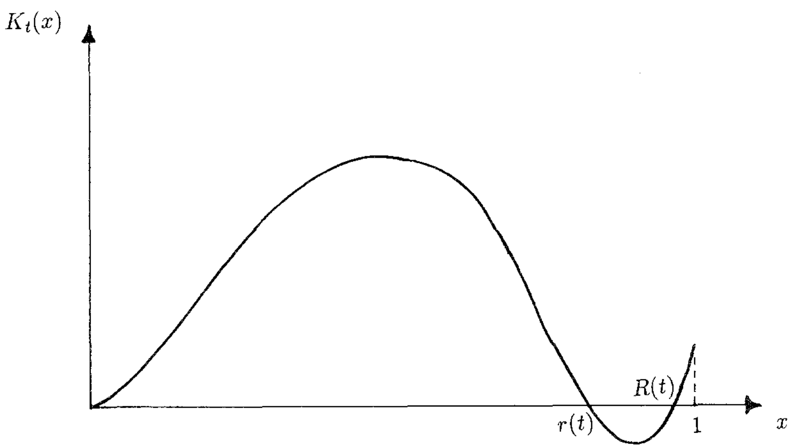

Fig. 2. The conjectured bound $K_t(x)$ for $t > 1$.

This leads to the following improved version of Theorem 3(ii): for every $\delta > 0$, $\Delta > 0$, $\varepsilon > 0$, and $t > t_\varepsilon$,

$$\lim_{N \to \infty} \sum_{(r(t)-\delta)N \leqslant j \leqslant (R(t)+\Delta)N} \frac{j\mathbf{E}[N_j(t)]}{N} \geqslant 1 - \frac{x_\varepsilon(t)}{t}$$

showing that at time t the size of the largest polymer is between $N(1-e^{1-t})$ and $N(1-e^{-2t}/t)$.

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