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A necessary and sufficient condition for gelation of a reversible Markov process of polymerization

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Abstract

A reversible Markov process as a chemical polymerization model which permits the coagulation and fragmentation reactions is considered. We present a necessary and sufficient condition for the occurrence of a gelation in the process. We show that a gelation transition may or may not occur, depending on the value of the fragmentation strength, and, in the case that gelation takes place, a critical value for the occurrence of the gelation and the mass of the gel can be determined by close forms.

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1. Introduction

For systems of interacting polymers evolving through the irreversible aggregation reaction

$$(j) + (k) \overset{R(j,k)}{\rightarrow} (j + k)$$

whereby polymers of lengths j and k link themselves together to form a polymer of length $j + k$ (the number $R(j, k)$ denotes the corresponding reaction rate), the standard approach is through Smoluchlovski's coagulation equations to describe the coupled evolution of the densities $c_j(t)$ of polymers made up of j units ($j = 1, 2, 3, \ldots$) in an infinite-volume homogeneous system [5, 49]:

$$C_j'(t) = \frac{1}{2}\sum_{i+k=j} K(i,k)C_i(t)C_j(t) - C_j(t)\sum_{l=1}^{\infty} K(j,l)C_l(t).$$

An alternative approach allowing a more detailed description has been pioneered by Marcus [29] and studied in detail by Lushnikov [27], which is the stochastic counterpart of Smoluchlovski's coagulation equations, namely the Marcus–Lushnikov coagulation model or process.

The connection between the two models is as follows: let $N_1(t), N_2(t), \ldots, N_N(t)$ be the random variables denoting the numbers of monomers, dimers, …, N-mers at time t, respectively, in the Marcus–Lushnikov process, then the expected values $(1/V)E[N_j(t)]$ should coincide in the thermodynamic limit $N \to \infty$, $V \to \infty$ and $N/V = \rho$ with the densities $c_j(t)$ of Smoluchlovski's model (see [21]). Various aspects of the two models have been extensively studied by many authors (see [3, 5, 8, 12, 15, 19, 21, 25, 27, 29–30, 42–46]). Recently, rigorous mathematics was brought to bear on the two models making the cooperation between mathematics and physics more fruitful. For readers who are interested in the mathematical aspects of the models, we recommend the survey paper of Aldous [1].

Perhaps what makes the two models both interesting and difficult is the possible occurrence of a gelation, the density dropping phenomenon, within a finite time. In Smoluchlovski's model this manifests by an apparent lack of conservation of the density of units:

$$\sum_{j=1}^{\infty} jc_j(t) < \sum_{j=1}^{\infty} jc_j(0) \tag{1}$$

for $t > t_c$, where t_c is the critical time of gelation transition. This density dropping phenomenon seems to contradict the fact that particles are neither created nor destroyed, but the contradiction is resolved once one realizes that the left-hand side of (1) represents only the contribution of all polymers of finite length to the total density of units. This is also interpreted as an indication of the formation of gel, or an infinite size cluster (see [7, 9, 20, 24, 26, 34, 39, 47–49]). Gelation in the case $R(j,k) = jk$ is known to be equivalent to the emergence of a giant component in the random graph theory, a result which was initiated by Erdös and Rényi [13] and extensively studied by many authors [2, 6, 22, 31–32].

For Smoluchlovski's model the kinetic theory of polymerization does not contain the equilibrium theory of Flory [14] and Stockmayer [37] as a limiting case for large values of time, due to the absence of fragmentation effects. In fact, as clusters grow in size, break-up processes become more important, and the irreversible coagulation reaction should be replaced by a coagulation–fragmentation reaction. Van Dongen and Ernst [40, 41] and Spouge [36] were the first to extend Smoluchlovski's coagulation equations by including the fragmentation reaction. Since then, many studies of the kinetic equations and their stochastic counterparts containing the combined effects of coagulation and fragmentation have been done (see [4, 10, 11, 16–18, 23, 36, 40–41, 44]).

Although there are many studies devoted to the deterministic and stochastic models based on the coagulation–fragmentation reaction of polymerization, the kinetic model of reversible polymerization proposed by Van Dongen and Ernst [41] and its stochastic counterpart have received minimal attention. It is worthwhile to study the kinetic model of reversible polymerization in order to predict the occurrence of a gelation transition, depending on the value of the fragmentation strength, in the equilibrium theory of Flory and Stockmayer.

This paper investigates the gelation problem in a stochastic counterpart of the kinetic model of reversible polymerization. The main objective of this paper is to present a necessary and sufficient condition for the occurrence of a gelation. Section 2 gives the description of a reversible Markov process of polymerization considered in the paper. A necessary and sufficient condition for the occurrence of a gelation is proved in section 3. Some applications, including two examples and a proposition, are contained in section 4. The paper concludes in section 5, with some discussions on the gelation.

2. A reversible Markov process of polymerization

As in [8, 41], we restrict our discussion to homogeneous systems of polymers where diffusion effects are ignored. We also assume that intramolecular reactions do not occur, and therefore only branched-chain (non-cyclic) polymers are formed and all unreacted functional groups are equally reactive. A state of a finite homogeneous system of polymers of lengths $1, 2, 3, \ldots, N$ in the volume V is described by a vector $\underline{n} = (n_1, n_2, \ldots, n_k, \ldots, n_N)$, the kth component of which is the number of k-mers. Now define, as in [17], a Markov process of polymerization as follows: the process, denoted by $\{M_N(t), t \geqslant 0\}$, is a continuous-time Markov process on the state space

$$\Omega_N = \left\{ \underline{n} \in \{0, 1, 2, \ldots, N\}^N : \sum_{k=1}^{N} k n_k = N \right\} \tag{2}$$

with transition rates

$$Q_{\underline{n}\,\underline{n}'} = \begin{cases} \frac{R(k,l)}{N^2} n_k n_l & \underline{n}' = n^+_{kl} \quad k \neq l \\ \frac{R(k,l)}{N^2} n_k (n_k - 1) & \underline{n}' = n^+_{kl} \quad k = l \\ \frac{F(k,l)}{N} n_{k+l} & \underline{n}' = n^-_{kl} \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

where

$$\begin{aligned} n^+_{kl} &= \{n_1, \ldots, n_k - 1, \ldots, n_l - 1, \ldots, n_{k+l} + 1, \ldots, n_N\} && \text{if} \quad k \neq l \\ n^+_{kl} &= \{n_1, \ldots, n_k - 2, \ldots, n_{2k} + 1, \ldots, n_N\} && \text{if} \quad k = l \\ n^-_{kl} &= \{n_1, \ldots, n_k + 1, \ldots, n_l + 1, \ldots, n_{k+l} - 1, \ldots, n_N\} && \text{if} \quad k \neq l \\ n^-_{kl} &= \{n_1, \ldots, n_k + 2, \ldots, n_{2k} - 1, \ldots, n_N\} && \text{if} \quad k = l. \end{aligned}$$

In (3), $R(k, l)$ represents the coagulation rate which describes the congelation process linking k-mers and l-mers to form $(k + l)$-mers, $F(k, l)$ represents the fragmentation rate which describes the fragmentation process from $(k + l)$-mers to k-mers and l-mers, and $R(k, l)$ and $F(k, l)$ satisfy the following detailed balance condition (see [41]):

$$R(k, l) f(k) f(l) = \lambda F(k, l) f(k + l) \tag{4}$$

where $\frac{1}{\lambda}$ $(\lambda > 0)$ represents the fragmentation strength and $k!\, f(k)$ denotes the number of distinct ways of forming a k-mer from k distinguishable units. Equation (4) states that the number of distinct ways for $(k + l)$-mers to break up into k-mer and l-mers $(\lambda F(k, l) f(k + l))$ equals the number of bonds between (k) and (l) clusters in $(k + l)$-mer configurations $(R(k, l) f(k) f(l))$. The choice of $Q_{\underline{n}\,\underline{n}'}$ reflects the fact that in the homogeneous system (ignoring diffusion effects), reaction occurs with a probability proportional to the number of reactants and inversely proportional to the volume; here the density is taken to be equal to 1, so that the volume coincides with the total number of units N.

As has been shown in [17] the Markov process $\{M_N(t), t \geqslant 0\}$ is a reversible Markov chain and has a unique stationary distribution:

$$P_N(\underline{n}) = \frac{1}{\pi_N} \prod_{k \geqslant 1} \frac{\left[\frac{N}{\lambda} f(k)\right]^{n_k}}{n_k!} \qquad \underline{n} \in \Omega_N \tag{5}$$

where

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \sum_{\underline{n} \in \Omega_N} \prod_{k \geqslant 1} \frac{\left[\frac{N}{\lambda} f(k)\right]^{n_k}}{n_k!}. \tag{6}$$

$\pi(N)$ is usually called the partition function of the process. It has an integral formula

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \frac{1}{2\pi \mathrm{i}} \int_\Gamma \exp\left\{\frac{N}{\lambda} F(x) - N \log x\right\} x^{-1}\, \mathrm{d}x \tag{7}$$

where Γ denotes a contour surrounding the origin $x = 0$ and the series $F(x)$

$$F(x) = \sum_{k=1}^{\infty} f(k)x^k \tag{8}$$

has a positive radius, r, of convergence, that is $F(x) < \infty$ for $0 \leqslant x < r$.

3. A necessary and sufficient condition for gelation

In this section we first give a definition of a gelation in the reversible Markov process of polymerization.

Definition 1. *Let N_k be a random number of k-mers and $E(\cdot)$ denote the expectation corresponding to the stationary probability distribution $P_N(\cdot)$ in (5). We say that there is a gelation in the reversible polymerization process, or the reversible polymerization process has a gelation, if and only if there is a critical value $\lambda_c > 0$ such that*

$$\lim_{N\to\infty} \frac{1}{N} \sum_{k=1}^{N} kE(N_k) = 1 \tag{9}$$

for $\lambda \leqslant \lambda_c$ and

$$\lim_{N\to\infty} \frac{1}{N} \sum_{k=1}^{N} kE(N_k) < 1 \tag{10}$$

for $\lambda > \lambda_c$.

Note that the definition above is the same as usually used in physical literature. Other definitions of gelation can be found in [1, 7, 23]. If we denote the mass of the sol and gel by $S(\lambda)$ and $G(\lambda)$, respectively, then

$$S(\lambda) + G(\lambda) = 1$$

and

$$G(\lambda) = 1 - S(\lambda) = 1 - \lim_{N\to\infty} \frac{1}{N} \sum_{k=1}^{N} kE(N_k). \tag{11}$$

Thus, $G(\infty) = \lim_{\lambda\to\infty} G(\lambda)$ can be defined as the maximum mass of the gel.

Theorem 1. *If there exists a gelation in the reversible polymerization process, then*

$$F'(r) < \infty \qquad F''(r) = \infty \tag{12}$$

and the critical value λ_c satisfies

$$\lambda_c \geqslant rF'(r). \tag{13}$$

Proof. Let $F'(r) = \infty$. Then, for any $\lambda > \lambda_c$ we can choose $r_0 < r$ such that $r_0 F'(r_0) = \lambda$. It follows from (5) and (6) that

$$\begin{aligned} E(N_k) &= \sum_{\underline{n}\in\Omega_N} n_k P_N(\underline{n}) \\ &= \frac{Nf(k)}{\lambda\pi_N} \sum_{\underline{n}\in\Omega_N} \frac{\left[\frac{N}{\lambda} f(k)\right]^{n_k-1}}{(n_k-1)!} \prod_{j\neq k}^{N} \frac{\left[\frac{N}{\lambda} f(j)\right]^{n_j}}{n_j!} \\ &= \frac{Nf(k)}{\lambda\pi_N} \sum_{\underline{n}\in\Omega_{N-k}} \prod_{j=1}^{N-k} \frac{\left[\frac{N}{\lambda} f(j)\right]^{n_j}}{n_j!} \\ &= \frac{Nf(k)}{\lambda} \frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)}. \end{aligned} \tag{14}$$

By (7) and (8) we have

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \frac{1}{2\pi\mathrm{i}}\int_\Gamma \exp\left\{\frac{N}{\lambda}F(x) - N\log x\right\}x^{-1}\,\mathrm{d}x$$

where Γ is a contour with its radius equal to r_0 surrounding the origin $x = 0$. Let $D_N(x) = \frac{N}{\lambda}F(x) - N\log x$, then $D'_N(r_0) = 0$. Obviously, the root r_0 is unique in $[0, r)$, since $xF'(x)$ is a strictly monotone increasing function on $[0, r)$. Such a root is a saddle point of $\mathrm{e}^{D_N(x)}$. By a standard saddle-point-type argument (see [33], p 96) we can obtain

$$\pi_N\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{1}{\sqrt{2\pi A(r_0)N}}\exp\left\{\frac{N}{\lambda}F(r_0) - N\log r_0\right\}$$

where

$$A(r_0) = \frac{r_0^2F''(r_0) + r_0F'(r_0)}{r_0F'(r_0)}.$$

Note that

$$\int_{-\infty}^{+\infty}\exp\{\mathrm{i}bx - a^2x^2\}\,\mathrm{d}x = \frac{\sqrt{\pi}}{a}\exp\left\{-\frac{b^2}{4a^2}\right\} \tag{15}$$

where $a > 0$ and $\mathrm{i} = \sqrt{-1}$. Thus, we also have

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{r_0^k}{\sqrt{2\pi A(r_0)N}}\exp\left\{-\frac{k^2}{2A(r_0)N}\right\}\exp\left\{\frac{N}{\lambda}F(r_0) - N\log r_0\right\}.$$

Substituting the above two formulae into (14), immediately yields

$$E(N_k) = \frac{Nf(k)}{\lambda}\frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} = (1 + o(1))\frac{Nf(k)}{\lambda}r_0^k\exp\left\{-\frac{k^2}{2A(r_0)N}\right\}$$

and therefore

$$\frac{1}{N}\sum_{k=1}^{N}kE(N_k) = (1 + o(1))\frac{1}{\lambda}\sum_{k=1}^{N}kf(k)r_0^k\exp\left\{-\frac{k^2}{2A(r_0)N}\right\}.$$

Note that $\frac{1}{N}\sum_{k=1}^{N}kE(N_k) \leqslant 1$ and $r_0F'(r_0) = \lambda$. For any small $\varepsilon > 0$ we can choose two large numbers n_0 and n_1 with $n_0 < n_1$ such that

$$(1 + o(1))\frac{1}{\lambda}\sum_{k=1}^{n_0}kf(k)r_0^k\exp\left\{-\frac{k^2}{2A(r_0)N}\right\} > 1 - \varepsilon$$

for $N > n_1$. Thus

$$\frac{1}{N}\sum_{k=1}^{N}kE(N_k) \to 1$$

as $N \to \infty$. This is a contradiction to the definition of a gelation. That is, the number $F'(r)$ satisfies $F'(r) < \infty$.

If $\lambda_c < rF'(r)$, then we can choose two numbers λ_1 and r_1 such that $\lambda_c < \lambda_1 < rF'(r)$ and $\lambda_1 = r_1F'(r_1)$. Note that $r_1 < r$. By the same method used above we can obtain $\frac{1}{N}\sum_{k=1}^{N}kE(N_k) \to 1$ for $\lambda_c < \lambda_1$. This is a contradiction to (10). Thus, we have $\lambda_c \geqslant rF'(r)$.

Assume now that $F''(r) < \infty$. Let $x = r\,\mathrm{e}^{\mathrm{i}\theta}$, $-\pi \leqslant \theta \leqslant \pi$. Then we have the following Taylor series near $x = r$:

$$\begin{aligned}F(r\,\mathrm{e}^{\mathrm{i}\theta}) &= F(r) + rF'(r)(\mathrm{e}^{\mathrm{i}\theta} - 1) + \tfrac{1}{2}r^2F''(r)(\mathrm{e}^{\mathrm{i}\theta} - 1)^2 + o(\theta^2)\\ &= F(r) + \mathrm{i}rF'(r)\theta - \tfrac{1}{2}[rF'(r) + r^2F''(r)]\theta^2 + o(\theta^2).\end{aligned}$$

It follows that

$$\pi_N = \frac{1}{2\pi\mathrm{i}}\int_{©} \exp\left\{\frac{N}{\lambda}F(x) - N\log x\right\} x^{-1}\,\mathrm{d}x$$
$$= \frac{1}{2\pi}\int_{-\pi}^{\pi} \exp\left\{\frac{N}{\lambda}F(r\,\mathrm{e}^{\mathrm{i}\theta}) - N\log r\,\mathrm{e}^{\mathrm{i}\theta}\right\}\mathrm{d}\theta$$
$$= \frac{D_N(r)}{2\pi}\int_{-\pi}^{\pi} \exp\left\{-\mathrm{i}\left[1-\frac{rF'(r)}{\lambda}\right]N\theta - \frac{rF'(r)A(r)}{2\lambda}N\theta^2 + o(\theta^2)\right\}\mathrm{d}\theta$$
$$= \frac{D_N(r)}{2\pi\sqrt{N}}\int_{-\pi\sqrt{N}}^{\pi\sqrt{N}} \exp\left\{-\mathrm{i}\left[1-\frac{rF'(r)}{\lambda}\right]\sqrt{N}t - \frac{rF'(r)A(r)}{2\lambda}t^2 + o\left(\frac{t^2}{N}\right)\right\}\mathrm{d}t$$

where © is a contour with its radius equal to r. By (15) we have

$$\pi_N\left(\frac{N}{\lambda}\right) = (1+o(1))\frac{\sqrt{\lambda}D_N(r)}{\sqrt{2\pi rF'(r)A(r)}}\exp\left\{-\frac{N\left[1-\frac{rF'(r)}{\lambda}\right]^2}{2rF'(r)A(r)/\lambda}\right\}.$$

Similarly,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))\frac{\sqrt{\lambda}D_N(r)r^k}{\sqrt{2\pi rF'(r)A(r)}}\exp\left\{-\frac{N\left[1-\frac{rF'(r)}{\lambda}-\frac{k}{N}\right]^2}{2rF'(r)A(r)/\lambda}\right\}.$$

Then

$$\frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} = (1+o(1))r^k\exp\left\{\frac{k\left[2\left(1-\frac{rF'(r)}{\lambda}\right)-\frac{k}{N}\right]}{2rF'(r)A(r)/\lambda}\right\}.$$

Choose $\lambda > 2rF'(r)$ such that

$$\frac{2\left(1-\frac{rF'(r)}{\lambda}\right)-\frac{k}{N}}{2rF'(r)A(r)/\lambda} \geqslant \frac{1-\frac{2rF'(r)}{\lambda}}{2rF'(r)A(r)/\lambda} = d_\lambda > 0.$$

Thus

$$1 \geqslant \frac{1}{N}\sum_{k=1}^{N} kE(N_k) = (1+o(1))\frac{1}{\lambda}\sum_{k=1}^{N} kf(k)r^k\exp\left\{\frac{k\left[2\left(1-\frac{rF'(r)}{\lambda}\right)-\frac{k}{N}\right]}{2rF'(r)A(r)/\lambda}\right\}$$
$$\geqslant (1+o(1))\frac{1}{\lambda}\sum_{k=1}^{N} kf(k)(r\,\mathrm{e}^{d_\lambda})^k.$$

Obviously,

$$\frac{1}{\lambda}\sum_{k=1}^{N} kf(k)(r\,\mathrm{e}^{d_\lambda})^k \to \infty$$

as $N \to \infty$, since r is the radius of convergence for the series $F'(x)$. It is contradictory to $\frac{1}{N}\sum_{k=1}^{N} kE(N_k) \leqslant 1$ for every $N \geqslant 1$. This means that $F''(r) = \infty$. □

Next, we prove a lemma which is a slightly modified one given by Leyvraz [25].

Lemma 1. *Let the a_j be positive numbers such that*

$$F(z) = \sum_{j=1}^{\infty} a_j z^j$$

has convergence radius 1. Define $S_k = \sum_{j=1}^{k} a_j$. If there exists a positive number λ such that

$$S_k \sim k^\lambda \qquad (k \to \infty)$$

then

$$F(z) \sim (1-z)^{-\lambda} \qquad (z \to 1).$$

where $x \sim y$ *means that* $x/y \to 1$.

Proof. Since $k^{\lambda} \sim \left|\binom{-\lambda-1}{k}\right|$, we can choose M so large that

$$\begin{aligned}\sum_{j=1}^{\infty} a_j z^j &= (1-z)\sum_{j=1}^{M-1} S_j z^j + (1-z)\sum_{j=M}^{\infty} S_j z^j \\ &= (1-z)\sum_{j=1}^{M-1} S_j z^j + (1+o(1))(1-z)\sum_{j=M}^{\infty}\left|\binom{-\lambda-1}{k}\right| z^j \\ &= (1-z)\sum_{j=1}^{M-1} S_j z^j + (1+o(1))(1-z)\left[(1-z)^{-\lambda-1} + \sum_{j=1}^{M-1}\left|\binom{-\lambda-1}{k}\right| z^j\right].\end{aligned}$$

From this it follows that

$$(1-z)^{\lambda} F(z) \to 1$$

as $z \to 1$. □

We now mention our main results in the following theorem.

Theorem 2. *Let* $f(k) = c_k r^{-k} k^{-\beta}$, *where* $c_k > 0$ *and* $c_k \to c > 0$ *as* $k \to \infty$. *Then a necessary and sufficient condition for the occurrence of a gelation in the process is that the number* β *satisfies*

$$2 < \beta < 3. \tag{16}$$

Moreover, the critical value λ_c *of gelation satisfies* $\lambda_c = rF'(r)$ *and*

$$S(\lambda) = \lim_{N\to\infty} \frac{1}{N}\sum_{k=1}^{N} kE(N_k) = 1$$

for $\lambda \leqslant \lambda_c$ *and*

$$S(\lambda) = \lim_{N\to\infty} \frac{1}{N}\sum_{k=1}^{N} kE(N_k) = \frac{\lambda_c}{\lambda} + \left[1 - \frac{\lambda_c}{\lambda}\right](3-\beta)\Gamma(3-\beta) < 1 \tag{17}$$

for $\lambda > \lambda_c$.

Proof. *Sufficiency*. Since $rF'(r) = \sum_{k=1}^{\infty} c_k k k^{-\beta} < \infty$ for $2 < \beta < 3$, for any $\lambda < rF'(r)$ we can choose a number r_0 such that $r_0 F'(r_0) = \lambda$. By the same method used for proving theorem 1 we can prove that $\frac{1}{N}\sum_{k=1}^{N} kE(N_k) \to 1$ for $2 < \beta \leqslant 3$ and $\lambda < rF'(r)$ as $N \to \infty$. Let $\lambda \geqslant rF'(r)$. It follows from lemma 1 that

$$F''(x) \sim \frac{r^{-(\beta-1)}c}{(3-\beta)}(r-x)^{-(3-\beta)} \qquad (x \to r)$$

since $\sum_{k=1}^{j} c_k k^{2-\beta} \sim c j^{3-\beta}/(3-\beta)$ as $j \to \infty$. Let

$$B(x) = \frac{F(x) - F(r) - F'(r)(x-r)}{F''(x)(r-x)^2/2}.$$

It can be checked that, as $x \to r$,

$$B(x) \to \frac{2}{(\beta-1)(\beta-2)}.$$

Hence

$$F(r\,e^{i\theta}) - F(r) = F'(r)(r\,e^{i\theta} - r) + \frac{1}{2}B(r\,e^{i\theta})F''(r\,e^{i\theta})(r - r\,e^{i\theta})^2$$
$$= irF'(r)\theta + \frac{c}{(\beta-1)(\beta-2)(3-\beta)}(-i\theta)^{\beta-1} + o((\theta)^{\beta-1}).$$

Let $\alpha = \beta - 1$, $b = 1 - rF'(r)/\lambda$ and

$$\gamma = \frac{c}{(\beta-1)(\beta-2)(3-\beta)}.$$

Since $e^{\pm i\pi} = -1$ and $e^{-i\pi/2} = -i$, we have

$$F(r\,e^{i\theta}) - F(r) = irF'(r)\theta - \gamma|\theta|^\alpha \exp\left\{-i\frac{(\alpha-2)\pi}{2}\mathrm{sign}(\theta)\right\} + o(|\theta|^\alpha) \tag{18}$$

where $\mathrm{sign}(\theta) = 1$ for $\theta > 0$, $\mathrm{sign}(\theta) = -1$ for $\theta < 0$ and $\mathrm{sign}(\theta) = 0$ for $\theta = 0$. It follows from (7) and (18) that

$$\pi_N\left(\frac{N}{\lambda}\right) = \frac{1}{2\pi i}\int_\Gamma \exp\left\{\frac{N}{\lambda}F(x) - N\log x\right\} x^{-1}\,dx$$
$$= \frac{D_N(r)}{2\pi}\int_{-\pi}^{\pi}\exp\left\{-ibN\theta - \frac{\gamma}{\lambda}N|\theta|^\alpha \exp\left\{-i\frac{(\alpha-2)\pi}{2}\mathrm{sign}(\theta)\right\} + o(N|\theta|^\alpha)\right\} d\theta$$
$$= \frac{D_N(r)}{2\pi(\gamma N/\lambda)^{1/\alpha}}\int_{-\pi(\gamma N/\lambda)^{1/\alpha}}^{\pi(\gamma N/\lambda)^{1/\alpha}}\exp\left\{-ib\frac{N^{(\alpha-1)/\alpha}}{(\gamma/\lambda)^{1/\alpha}}t\right.$$
$$\left. - |t|^\alpha \exp\left\{-i\frac{(\alpha-2)\pi}{2}\mathrm{sign}(t)\right\} + o(|t|)\right\} dt.$$

Comparing this with the stable density $q(x;\alpha,\delta)$, where $\delta = \alpha - 2$ (see [38], p 131), we have

$$\pi_N\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{D_N(r)}{(\gamma N/\lambda)^{1/\alpha}}q(0;\alpha,\alpha-2)$$

for $\lambda = rF'(r)$, i.e. $b = 0$, and

$$\pi_N\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{\gamma D_N(r)}{\lambda N^\alpha}b^{-(\alpha+1)}q(0;1/\alpha,(2\alpha-3)/\alpha)$$

for $\lambda > rF'(r)$, since $q(x;\alpha,\delta) = x^{-1-\alpha}q(x^{-\alpha};1/\alpha,1+(\delta-1)/\alpha)$. Let $l_N = bN - N^{1/\alpha}\log N$, $L_N = bN + N^{1/\alpha}\log N$ and

$$x_{k,N} = \left[b - \frac{k}{N}\right]\frac{N^{(\alpha-1)/\alpha}}{(\gamma/\lambda)^{1/\alpha}}.$$

Similarly, we have

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{D_N(r)r^k}{(\gamma N/\lambda)^{1/\alpha}}q(-k(\gamma N/\lambda)^{-1/\alpha};\alpha,\alpha-2)$$

for $\lambda = rF'(r)$,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{\gamma D_N(r)r^k}{\lambda N^\alpha}\left[b - \frac{k}{N}\right]^{-(\alpha+1)}q(0;1/\alpha,(2\alpha-3)/\alpha)$$

for $\lambda > rF'(r)$ and $k < l_N$,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{D_N(r)r^k}{(\gamma N/\lambda)^{1/\alpha}}q(x_{k,N};\alpha,\alpha-2)$$

for $\lambda > rF'(r)$ and $l_N \leqslant k \leqslant L_N$, and

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))\frac{\gamma D_N(r)r^k}{\lambda N^\alpha}\left[\frac{k}{N} - b\right]^{-(\alpha+1)} q(0; 1/\alpha, -(2\alpha-3)/\alpha)$$

for $\lambda > rF'(r)$ and $L_N < k \leqslant N$. Note that $q(x;\alpha,\delta) = q(-x;\alpha,-\delta)$,

$$q(0;\alpha,\alpha-2) = \pi^{-1}\Gamma(1+1/\alpha)\cos\left[\frac{(\alpha-2)\pi}{2\alpha}\right] > 0$$

$$\begin{aligned} q(0; 1/\alpha, \pm(2\alpha-3)/\alpha) &= \pi^{-1}\Gamma(1+\alpha)\cos\left[\frac{(2\alpha-3)\pi}{2}\right] \\ &= \pi^{-1}\Gamma(1+\alpha)\sin[(\alpha-1)\pi] > 0 \end{aligned} \tag{19}$$

and for any x, there exists a constant $M > 0$ (only depending on α) such that

$$q(x;\alpha,\alpha-2) \leqslant M$$

Thus, for $\lambda = rF'(r)$,

$$\begin{aligned} \frac{1}{N}\sum_{k=1}^{N} kE(N_k) &= \sum_{k=1}^{N} \frac{kf(k)}{\lambda}\frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} \\ &= (1+o(1))\frac{1}{\lambda}\sum_{k=1}^{N} kf(k)r^k \frac{q(-k(\gamma N/\lambda)^{-1/\alpha};\alpha,\alpha-2)}{q(0;\alpha,\alpha-2)} \to 1 \end{aligned}$$

as $N \to \infty$. For $\lambda > rF'(r)$ we have

$$\begin{aligned} \frac{1}{N}\sum_{k=1}^{N} kE(N_k) &= (1+o(1))\frac{b^{\alpha+1}}{\lambda}\sum_{k=1}^{N/\log N} kf(k)r^k \frac{1}{\left[b-\frac{k}{N}\right]^{\alpha+1}} \\ &\quad + (1+o(1))\frac{b^{\alpha+1}}{\lambda}\sum_{k>N/\log N}^{l_N-1} kf(k)r^k \frac{1}{\left[b-\frac{k}{N}\right]^{\alpha+1}} \\ &\quad + (1+o(1))\frac{b^{\alpha+1}N^{\alpha-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\sum_{k=l_N}^{L_N} kf(k)r^k \frac{q(x_{k,N};\alpha,\alpha-2)}{q(0;1/\alpha,(2\alpha-3)/\alpha)} \\ &\quad \times (1+o(1))\frac{b^{\alpha+1}}{\lambda}\sum_{k>L_N}^{N} kf(k)r^k \frac{1}{\left[\frac{k}{N}-b\right]^{\alpha+1}} \\ &\to \frac{rF'(r)}{\lambda} + \left[1-\frac{rF'(r)}{\lambda}\right](3-\beta)\Gamma(3-\beta). \end{aligned}$$

Obviously,

$$\frac{1}{\lambda}\sum_{k=1}^{N/\log N} kf(k)r^k \frac{b^{\alpha+1}}{\left[b-\frac{k}{N}\right]^{\alpha+1}} \to \frac{rF'(r)}{\lambda}$$

as $N \to \infty$. Furthermore,

$$\begin{aligned} \sum_{k>N/\log N}^{l_N-1} kf(k)r^k \frac{1}{\left[b-\frac{k}{N}\right]^{\alpha+1}} &= \sum_{k>N/\log N}^{l_N-1} \frac{c_k}{k^\alpha\left[b-\frac{k}{N}\right]^{\alpha+1}} \\ &= (1+o(1))cN^{-(\alpha-1)}\int_{1/\log N}^{b-N^{-(1-1/\alpha)}\log N} \frac{\mathrm{d}x}{x^\alpha(b-x)^{\alpha+1}} \end{aligned}$$

$$= (1+o(1))cN^{-(\alpha-1)}\int_{1/\log N}^{b/2}\frac{\mathrm{d}x}{x^\alpha(b-x)^{\alpha+1}}$$
$$+ (1+o(1))cN^{-(\alpha-1)}\int_{b/2}^{b-N^{-(1-1/\alpha)}\log N}\frac{\mathrm{d}x}{x^\alpha(b-x)^{\alpha+1}}$$
$$\to 0$$

and

$$\sum_{k>L_N}^{N} kf(k)r^k\frac{1}{\left[\frac{k}{N}-b\right]^{\alpha+1}} = (1+o(1))cN^{-(\alpha-1)}\int_{b+N^{-(1-1/\alpha)}\log N}^{1}\frac{\mathrm{d}x}{x^\alpha(x-b)^{\alpha+1}} \to 0$$

as $N\to\infty$. Since $\Gamma(s+1)=s\Gamma(s)$, $\Gamma(s)\Gamma(1-s)=\pi/\sin(s\pi)$ for $0<s<1$ and

$$\frac{b^{\alpha+1}N^{\alpha-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\sum_{k=l_N}^{L_N} kf(k)r^k q(x_{k,N};\alpha,\alpha-2)$$
$$= (1+o(1))\frac{cb^{\alpha+1}N^{1-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\int_{b-N^{-(1-1/\alpha)}\log N}^{b+N^{-(1-1/\alpha)}\log N}\frac{q(x_{k,N};\alpha,\alpha-2)}{x^\alpha}\,\mathrm{d}x$$
$$= (1+o(1))\frac{cbN^{1-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\int_{b-N^{-(1-1/\alpha)}\log N}^{b} q(x_{k,N};\alpha,\alpha-2)\,\mathrm{d}x$$
$$+ (1+o(1))\frac{cbN^{1-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\int_{b}^{b+N^{-(1-1/\alpha)}\log N} q(x_{k,N};\alpha,\alpha-2)\,\mathrm{d}x$$
$$= (1+o(1))\frac{cb}{\gamma}\int_{-\log N}^{\log N} q(x_{k,N};\alpha,\alpha-2)\,\mathrm{d}(x_{k,N})$$
$$\to b(\beta-1)(\beta-2)(3-\beta)$$

as $N\to\infty$, it follows from (19) that

$$\frac{b^{\alpha+1}N^{\alpha-\frac{1}{\alpha}}}{\lambda(\gamma/\lambda)^{\frac{\alpha+1}{\alpha}}}\sum_{k=l_N}^{L_N} kf(k)r^k\frac{q(x_{k,N};\alpha,\alpha-2)}{q(0;1/\alpha,(2\alpha-3)/\alpha)} \to b(3-\beta)\Gamma(3-\beta).$$

Thus,

$$\lim_{N\to\infty}\frac{1}{N}\sum_{k=1}^{N} kE(N_k) = \frac{rF'(r)}{\lambda} + \left[1-\frac{rF'(r)}{\lambda}\right](3-\beta)\Gamma(3-\beta) < 1$$

for $\lambda > rF'(r)$, since $(3-\beta)\Gamma(3-\beta)<1$ for $2<\beta<3$. This also shows that $\lambda_c = rF'(r)$.

Necessary. Assume that there exists a gelation in the process. Since $rF'(r) = \sum_{k=1}^{\infty} c_k k k^{-\beta}$, it follows from theorem 1 that $2<\beta\leqslant 3$. Let $\beta=3$ and $\lambda>\lambda_c$. Note that $\lambda_c \geqslant rF'(r)$ and $\sum_{k=1}^{j} c_k \sim cj$ as $j\to\infty$. By lemma 1 we know that $F'''(x)\sim cr^{-2}(r-x)^{-1}$ $(x\to r)$, and therefore $F''(x)\sim -cr^{-2}\log(r-x)$ $(x\nearrow r)$. Moreover, taking $x = r\,\mathrm{e}^{\mathrm{i}\theta}$ we have $F''(r\,\mathrm{e}^{\mathrm{i}\theta})\sim 2cr^{-2}|\log|\theta/\sqrt{2}\|$ $(\theta\to 0)$. Let

$$B(x) = \frac{F(x)-F(r)-F'(r)(x-r)}{F''(x)(x-r)^2/2}.$$

It can be checked that $B(r\,\mathrm{e}^{\mathrm{i}\theta})\sim (1+O(|\log|\theta\|)^{-1})$ $(\theta\to 0)$. Hence

$$F(r\,\mathrm{e}^{\mathrm{i}\theta}) - F(r) = F'(r)(r\,\mathrm{e}^{\mathrm{i}\theta}-r) + \tfrac{1}{2}B(r\,\mathrm{e}^{\mathrm{i}\theta})F''(r\,\mathrm{e}^{\mathrm{i}\theta})(r\,\mathrm{e}^{\mathrm{i}\theta}-r)^2$$
$$= \mathrm{i}rF'(r)\theta - c|\log|\theta\|\theta^2 + O(\theta^2).$$

It follows from (7) and (15) that

$$\begin{aligned}
\pi_N\left(\frac{N}{\lambda}\right) &= \frac{1}{2\pi\mathrm{i}}\int_\Gamma \exp\left\{\frac{N}{\lambda}F(x) - N\log x\right\} x^{-1}\,\mathrm{d}x \\
&= \frac{D_N(r)}{2\pi}\int_{-\pi}^{\pi} \exp\left\{-\mathrm{i}bN\theta - \frac{c|\log|\theta\|}{\lambda}N\theta^2 + O(\theta^2)\right\}\mathrm{d}\theta \\
&= \frac{D_N(r)}{2\pi\sqrt{N\log\sqrt{N}}}\int_{-\pi\sqrt{N\log\pi}}^{\pi\sqrt{N\log\pi}} \exp\left\{-\mathrm{i}b\frac{\sqrt{N}}{\sqrt{\log\sqrt{N}}}t\right. \\
&\quad \left. - \frac{c}{\lambda}t^2 + O\left(\frac{\log|t|}{\log\sqrt{N}} + \frac{t^2}{N}\right)\right\}\left(1 + O\left(\frac{\log|t|}{\log\sqrt{N}}\right)\right)\mathrm{d}t \\
&= (1 + o(1))\frac{\sqrt{\lambda}D_N(r)}{2\sqrt{\pi c}}\exp\left\{-\frac{\frac{N}{\log\sqrt{N}}b^2}{4c/\lambda}\right\}.
\end{aligned}$$

Similarly,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1 + o(1))\frac{\sqrt{\lambda}D_N(r)}{2\sqrt{\pi c}}r^k\exp\left\{-\frac{\frac{N}{\log\sqrt{N}}\left[b - \frac{k}{N}\right]^2}{4c/\lambda}\right\}.$$

Hence, for $\lambda > \lambda_c \geqslant rF'(r)$,

$$\begin{aligned}
1 \geqslant \frac{1}{N}\sum_{k=1}^{N} kE(N_k) &= \sum_{k=1}^{N}\frac{kf(k)}{\lambda}\frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} \\
&= (1 + o(1))\frac{1}{\lambda}\sum_{k=1}^{N} kf(k)r^k\exp\left\{\frac{k\left(2b - \frac{k}{N}\right)}{4(c/\lambda)\log\sqrt{N}}\right\} \\
&> \frac{c}{\lambda N}\left(\frac{5b}{3}\right)^{-2}\int_{4b/3}^{5b/3}\exp\left\{\frac{Nx(2b - x)}{4(c/\lambda)\log\sqrt{N}}\right\}\mathrm{d}x \\
&= \frac{c\,\exp\left\{\frac{Nb^2}{4(c/\lambda)\log\sqrt{N}}\right\}}{\lambda N}\int_{4b/3}^{5b/3}\exp\left\{-\frac{N(x - b)^2}{4(c/\lambda)\log\sqrt{N}}\right\}\mathrm{d}x \\
&> \frac{c\,\exp\left\{\frac{5Nb^2}{36(c/\lambda)\log\sqrt{N}}\right\}}{\lambda N} \to +\infty
\end{aligned}$$

as $N \to \infty$. The contradiction means that $\beta \neq 3$, i.e. $\beta < 3$. If $\lambda_c > rF'(r)$, then we can choose λ_1 such that $\lambda_c > \lambda_1 > rF'(r)$. By (17) we know

$$\lim_{N\to\infty}\frac{1}{N}\sum_{k=1}^{N} kE(N_k) = \frac{\lambda_c}{\lambda_1} + \left[1 - \frac{\lambda_c}{\lambda_1}\right](3 - \beta)\Gamma(3 - \beta) < 1.$$

This contradict the definition of critical value of gelation. That is, we have $\lambda_c = rF'(r)$. □

Remark 1. For $\lambda > \lambda_c$, we have

$$\begin{aligned}
G(\lambda) = 1 - S(\lambda) &= 1 - \lim_{N\to\infty}\frac{1}{N}\sum_{k=1}^{N} kE(N_k) \\
&= \left[1 - \frac{rF'(r)}{\lambda}\right][1 - (3 - \beta)\Gamma(3 - \beta)].
\end{aligned}$$

Moreover, the function $S(\lambda)$ is continuous on $[0, \infty)$ and $M'(\lambda)$ is discontinuous at $\lambda = \lambda_c$. In particular, $G(\infty) = \lim_{\lambda\to\infty} G(\lambda) = 1 - (3-\beta)\Gamma(3-\beta)$, which is the maximum mass of the gel and only depends on β.

Remark 2. With no rigorous argument we can see from (17) that there is no gelation when $\beta = 2$ or $\beta = 3$ since $\Gamma(1) = 1$ and $\lim_{\beta\to 3}(3-\beta)\Gamma(3-\beta) = 1$.

4. Applications

In this section we show two examples and a proposition.

Example 1. RA_a model ($a \geqslant 3$).

The numbers $f(k)$ for the RA_a model have already been calculated by Stockmayer:

$$f(k) = \frac{a^k[(a-1)k]!}{k![(a-2)k+2]!}.$$

Since the coagulation coefficients

$$R(i, j) = [(a-2)i+2][(a-2)j+2]$$

the fragmentation coefficients $F(i, j)$ can be taken as in Van Dongen and Ernst [41]:

$$\sum_{i+j=k} F(i, j) = \frac{2}{\lambda}(k-1).$$

Hence

$$2(k-1)f(k) = \sum_{i+j=k} R(i, j)f(i)f(j).$$

We can calculate (see [17]) that $\beta = 5/2$, $c_k \to \sqrt{(a-1)/[2\pi(a-2)^5]}$,

$$r = \lim_{k\to\infty} \frac{f(k)}{f(k+1)} = \frac{(a-2)^{(a-2)}}{a(a-1)^{(a-1)}}$$

and $\lambda_c = rF'(r) = (a-1)/[a(a-2)^2]$. Thus the mass of gelation for $\lambda > \lambda_c$ is

$$G(\lambda) = \left[1 - \frac{(a-1)}{\lambda a(a-2)^2}\right]\left[1 - \frac{\sqrt{\pi}}{2}\right]$$

and the maximum mass of gelation is $G(\infty) = 1 - \frac{\sqrt{\pi}}{2}$.

Example 2. RA_∞ model.

For the RA_∞ model we have $f(k) = k^{k-2}/k!$ and $R_{ij} = ij$. It can be checked (see [17]) that $\beta = 5/2$, $r = e^{-1}$, $c_k \to 1/\sqrt{2\pi}$ and $\lambda_c = rF'(r) = 1$. Thus

$$G(\lambda) = \left[1 - \frac{1}{\lambda}\right]\left[1 - \frac{\sqrt{\pi}}{2}\right]$$

for $\lambda > \lambda_c$ and $G(\infty) = 1 - \frac{\sqrt{\pi}}{2}$.

To model surface interactions, the coagulation and fragmentation coefficients can be taken as

$$R(i, j) = i^\sigma j^\sigma$$

and

$$\sum_{i+j=k} F(i,j) = \frac{2}{\lambda}(k-1)^{\sigma} \tag{20}$$

where $\sigma \geqslant 0$. Note that $k^{\sigma} - 1$ proposed by van Dongen and Ernst [41] has been replaced by $(k-1)^{\sigma}$. When $\sigma = 1$, the model has been well studied by van Dongen and Ernst [41].

Assume that the positive numbers $f(k)$ satisfy (4), and therefore

$$2(k-1)^{\sigma} f(k) = \sum_{i+j=k} i^{\sigma} j^{\sigma} f(i) f(j). \tag{21}$$

We now present a proposition in the following.

Proposition 1. *If the numbers $f(k)$ satisfy (21) and their convergence radius r is positive, then a necessary and sufficient condition for the occurrence of a gelation is*

$$\tfrac{1}{2} < \sigma < \tfrac{3}{2} \tag{22}$$

and

$$\sum_{k=1}^{\infty} k^{1+\sigma} f(k) r^k = \infty. \tag{23}$$

Moreover, the critical value of the gelation satisfies $\lambda_c = rF'(r)$ and

$$G(\lambda) = \left[1 - \frac{\lambda_c}{\lambda}\right]\left[1 - \left(\frac{3}{2} - \sigma\right)\Gamma\left(\frac{3}{2} - \sigma\right)\right] \tag{24}$$

for $\lambda > \lambda_c$ and $\frac{1}{2} < \sigma < \frac{3}{2}$.

Proof. Let $f_{\sigma}(k) = k^{\sigma-1} f(k)$, $F_{\sigma}(x) = \sum_{k=1}^{\infty} f_{\sigma}(k) x^k$, $U(x) = xF'_{\sigma}(x)$ and $V(x) = \sum_{k=1}^{\infty} [1 - (1 - 1/k)^{\sigma}] k f_{\sigma}(k) x^k$. It follows from (21) that

$$2U(x) - 2V(x) = [U(x)]^2$$

for $0 \leqslant x < r$, and therefore

$$U(x) = 1 \pm \sqrt{1 - 2V(x)}.$$

Obviously, $V(r) = \lim_{x\to r} V(x) \leqslant 1/2$ and $U(r) = \lim_{x\to r} U(x) < \infty$. Furthermore, we have $U^{(n)}(r) < \infty$ if and only if $V^{(n+1)}(r) < \infty$, and in particular

$$0 < \lim_{x\to r} \frac{V''(x)}{U'(x)} = \frac{V''(r)}{U'(r)} < \infty \tag{25}$$

since $[1 - (1 - 1/k)^{\sigma}] = \sigma/k + o(1/k)$. Note that $U'(x) > 0$ and $V'(x) > 0$ for $0 \leqslant x < r$. It follows that

$$U'(x) = \frac{V'(x)}{\sqrt{1 - 2V(x)}} \tag{26}$$

for $0 \leqslant x < r$.

Let the process have a gelation. We prove that $U'(r) = \lim_{x\to r} U'(x) = \infty$, that is, (23) holds. If $U'(r) < \infty$, then $1 - 2V(r) > 0$, $V''(r) < \infty$. From (26) it follows that

$$U''(r) = \frac{V''(r)(1 - 2V(r)) + (V'(r))^2}{(1 - 2V(r))\sqrt{1 - 2V(r)}} < \infty. \tag{27}$$

From $U''(r)$ we know $V^{(3)}(r) < \infty$. Repeating the calculation for $U^{(n)}(r)$ we can obtain $U^{(n)}(r) < \infty$ for every $n \geqslant 0$. Hence $F''(r) < \infty$. This contradicts the results of theorem 1. Obviously, $U'(r) = \infty$ means that $1 - 2V(r) = 0$ and $\sum_{k=1}^{\infty} k^{1+\sigma} f(k) r^k = \infty$.

Since $V'(r) < \infty$ and $1-2V(r) = 0$, by (25), (26) and (27) we have $U'(r)\sqrt{1-2V(r)} < \infty$, $U'(r)(1-2V(r)) = 0$ and

$$\frac{U''(r)}{[U'(r)]^3} = \lim_{x\to r} \frac{U''(x)}{[U'(x)]^3} = 1.$$

Let $W(x) = xF'_\sigma(x) - F_\sigma(x)$. Then the function $y = W(x)$ is monotone increasing and analytic on $[0, r)$, and $W'(x) = xF''_\sigma(x)$. Furthermore, its inverse function $x = w(y), 0 \leqslant y < \overline{y}$, is also monotone increasing, analytic and left continuous at $y = \overline{y}$, where $\overline{y} = W(r)$. By Cauchy's integral formula we have

$$\begin{aligned} k(k-1)f_\sigma(k) &= (2\pi\mathrm{i})^{-1} \int_{©} xF''_\sigma(x)x^{-k}\,\mathrm{d}x \\ &= (2\pi\mathrm{i})^{-1} \int_{©'} \exp\{-k\log w(y)\}\,\mathrm{d}y \end{aligned}$$

where © and ©′ are two contours with their radii being respectively less than r and equal to $\overline{y}$ surrounding the origin 0. Since

$$w'(\overline{y}) = \frac{1}{W'(r)} = \frac{1}{U'(r) - U(r)/r} = 0$$

and

$$w''(\overline{y}) = -\frac{W''(r)}{[W'(r)]^3} = -\frac{U''(r) - U'(r)/r + U(r)/r^2}{[U'(r) - U(r)/r]^3} = -1$$

$\log w(y)$ can be expanded in a Taylor series near $y = \overline{y}$ as follows:

$$\log w(y) = \log r - \frac{1}{2r}(y-\overline{y})^2 + o((y-\overline{y})^2).$$

Thus

$$\begin{aligned} k(k-1)f_\sigma(k) &= \frac{\overline{y}}{2\pi}\int_{-\pi}^{\pi} \exp\{\mathrm{i}\theta - k\log w(\overline{y}\,\mathrm{e}^{\mathrm{i}\theta})\}\,\mathrm{d}\theta \\ &= \frac{\overline{y}r^{-k}}{2\pi}\int_{-\pi}^{\pi} \exp\left\{\mathrm{i}\theta - k\frac{\overline{y}^2}{2r}\theta^2 + O(k\theta^3)\right\}\mathrm{d}\theta \\ &= \frac{\overline{y}r^{-k}}{2\pi\sqrt{k}}\int_{-\pi\sqrt{k}}^{\pi\sqrt{k}} \exp\left\{\mathrm{i}t/\sqrt{k} - \frac{\overline{y}^2}{2r}t^2 + O(t^3/\sqrt{k})\right\}\mathrm{d}\theta \\ &= (1+o(1))\left(\frac{r}{2\pi}\right)^{1/2} r^{-k}k^{-1/2} \end{aligned}$$

and therefore

$$f(k) = k^{1-\sigma} f_\sigma(k) = c_k r^{-k} k^{-(1+\sigma+1/2)} \tag{28}$$

where $c_k = (1+o(1))k/(k-1)(r/2\pi)^{1/2}$ for $k \geqslant 2$. By theorem 2 we have $2 < 1+\sigma+1/2 < 3$, i.e. $1/2 < \sigma < 3/2$.

If (22) and (23) hold, then (28) can be obtained by the same approach. By theorem 2 we see that the process has a gelation, $\lambda_c = rF'(r)$ and (24) holds. □

It is known that the expected values $(1/V)E[N_j(t)]$ coincide in the thermodynamic limit $N \to \infty$, $V \to \infty$ and $N/V = \rho$ with the densities $c_j(t)$ of Smoluchlovski's model. If we have $(1/V)E[N_j(t)] \sim \text{const} \times k^{-\tau}$ $(V > k \to \infty)$ at the critical value of the gelation, then the exponent τ characterizes the size distribution at the gel point. Thus it is interesting to study the asymptotic behaviour of $(1/V)E[N_j(t)]$. The asymptotic estimates for $(1/N)E[N_j(t)]$ with $\rho = 1$ will be given in the following proposition.

Proposition 2. *Suppose that* $1/2 < \sigma < 3/2$, *the numbers* $f(k)$ *satisfy (21), the convergence radius* $r > 0$ *and* $\sum_{k=1}^{\infty} k^{1+\sigma} f(k) r^k = \infty$. *Then* $\lambda_c = rF'(r)$ *is the critical value of the gelation and*

(i) For $\lambda < \lambda_c$,

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-(1+1/2+\sigma)} \exp\{-\text{const} \times k\} \qquad (N > k \to \infty).$$

(ii) For $\lambda = \lambda_c$,

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-(1+1/2+\sigma)} \qquad (N > k \to \infty).$$

(iii) For $\lambda > \lambda_c$ *and* $k < l_N = bN - N^{1/(\sigma+1/2)} \log N$ *or* $k > L_N = bN + N^{1/(\sigma+1/2)} \log N$,

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-(1+1/2+\sigma)} \qquad (N > k \to \infty)$$

where $b = 1 - \lambda/\lambda_c$.

(iv) For $\lambda > \lambda_c$ *and* $M_N(-C) \leqslant k \leqslant M_N(C)$,

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-\frac{1+1/2+\sigma}{1/2+\sigma}} \qquad (N > k \to \infty)$$

where $M_N(C) = bN + CN^{1/(\sigma+1/2)}$ *and* C *is an arbitrary positive constant.*

Proof. From proposition 1 we know that $\lambda_c = rF'(r)$ is the critical value of the gelation and $f(k) = c_k r^{-k} k^{-(1+\sigma+1/2)}$. Since $\pi_N\left(\frac{N}{\lambda}\right)$ and $\pi_{N-k}\left(\frac{N}{\lambda}\right)$ have been estimated in theorems 1 and 2 for $\lambda < \lambda_c$, $\lambda = \lambda_c$ or $\lambda > \lambda_c$, by (14), i.e.

$$E(N_k) = \frac{Nf(k)}{\lambda} \frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)}$$

we can obtain proposition 2. □

Remark 3. Without the fragmentation effects, i.e. $F(k, l) = 0$, the critical value of gelation is the critical time, t_c. The concentration of k-mers, $c_k(t_c)$, at the gel point, has been given by Ziff [48] as follows:

$$c_k(t_c) \sim \text{const} \times k^{-\tau}$$

asymptotically as $k \to \infty$, where $5/2 - 1/d < \tau < 5/2$ and d denotes the dimensions. Obviously, gelation cannot occur for $d = 1$. Let $d \geqslant 2$, then $2 < \tau < 5/2$. This is different from the result (iv) in proposition 2

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-(1+1/2+\sigma)} \qquad (N > k \to \infty)$$

since $2 < 1 + 1/2 + \sigma < 3$. That is, $1 + 1/2 + \sigma$ can be greater than $5/2$.

Remark 4. It should be noted that, if $\lambda > \lambda_c, k$ and j satisfy respectively $|(k - bN)N^{-1/(\sigma+1/2)}| = O(1)$ and $|(j - bN)N^{-1/(\sigma+1/2)}| \to \infty$ as $N \to \infty$, then

$$\frac{1}{N} E(N_k) \sim \text{const} \times k^{-\frac{1+1/2+\sigma}{1/2+\sigma}} > \frac{1}{N} E(N_j) \sim \text{const} \times j^{-(1+1/2+\sigma)}$$

since $(1 + 1/2 + \sigma) > (1 + 1/2 + \sigma)/(1/2 + \sigma)$. That is, the concentration of j-mers is less than the concentration of k-mers for the above case.

5. Summary and discussion

As can be seen, the necessary and sufficient condition for gelation in this paper is mainly based on the assumption that $f(k)$ is of the form $c_k r^{-k} k^{-\beta}$ or $r^k f(k) = O(1/k^{\beta})$. It is known that many polymer models such as RA_a, RA_∞ and $A_a RB_b$ are of this form. When $2 < \beta < 3$, $r^k f(k) = O(1/k^{\alpha+1})$ corresponds to Lévy stable densities $p_\alpha(x)$, where $\alpha = \beta - 1$, since Lévy stable densities are asymptotically of the form $1/x^{\alpha+1}$. If one extends the condition, for example, $\beta \geqslant 3$, then the definition of a gelation in (9) and (10) must be modified.

For the coagulation rate kernels $R(j,k) = j^\sigma k^\sigma$, there exists a gelation when $1/2 < \sigma \leqslant 1$ and instantaneous gelation when $\sigma > 1$ in irreversible polymer model (Jeon [24]). Comparing this with proposition 1 we see that the property of gelation in an irreversible polymer model is different from that in the reversible polymer model especially when $1 < \sigma < 1 + 1/2$.

From the results of this paper we can draw the conclusion that the reversible Markov process of polymerization is more complete than the deterministic counterpart (the kinetic model of reversible polymerization proposed by Van Dongen and Ernst [41]), in the sense that it allows the investigation of finite-size effects and fluctuations.

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