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The asymptotic distributions of the size of the largest length of a reversible Markov process of polymerization

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Abstract
In this paper, the subcritical, near-critical and supercritical asymptotic behaviour of a reversible Markov process as a chemical model for polymerization was studied. We establish the existence of three distinct stages (subcritical, near-critical and supercritical stages) of polymerization (in the thermodynamic limit as $N \to +\infty$), depending on the value of strength of the fragmentation reaction. These three stages correspond to the size of the largest length of polymers of size N to be itself of order $\log N$, N^a $(1/2 < a < 1)$ and N, respectively. Especially, $a = \frac{2}{2\sigma+1}$ when the coagulation (reaction) rate constant R_{ij} of the polymers satisfies $R_{ij} = i^\sigma j^\sigma$ with $1/2 < \sigma < 3/2$.

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1. Introduction

A necessary and sufficient condition for the occurrence of a gelation in a reversible Markov process as a chemical model of reversible polymerization has been given in [12]. In this paper we continue to study the asymptotic behaviour of the reversible Markov process.

The process considered in the paper is a continuous-time reversible Markov chain $\{M_N(t) : t \geqslant 0\}$ with the state space

$$\Omega_N = \left\{ \underline{n} \in N^N : \sum_{k=1}^{N} k n_k = N \right\}. \tag{1}$$

The kth component of the state vector $\underline{n}$ represents the number of k-mers. The only allowed transitions from $\underline{n}$ are to states of the form

$$\underline{n}_{ik}^{+} = \begin{cases} (n_1, n_2, \ldots, n_i - 1, \ldots, n_k - 1, \ldots, n_{i+k} + 1, \ldots, n_N) & \text{if} \quad i \neq k \\ (n_1, n_2, \ldots, n_i - 2, \ldots, n_{2i} + 1, \ldots, \ldots, \ldots, n_N) & \text{if} \quad i = k \end{cases}$$

$$\underline{n}_{ik}^{-} = \begin{cases} (n_1, n_2, \ldots, n_i + 1, \ldots, n_k + 1, \ldots, n_{i+k} - 1, \ldots, n_N) & \text{if} \quad i \neq k \\ (n_1, n_2, \ldots, n_i + 2, \ldots, n_{2i} - 1, \ldots, \ldots, \ldots, n_N) & \text{if} \quad i = k \end{cases}$$

and they occur with rate

$$Q_{\underline{n}\,\underline{n}'} = \begin{cases} \frac{1}{N^2} R_{ij} n_i n_j & \text{if} \quad \underline{n}' = \underline{n}_{ij}^{+} \quad i \neq j \\ \frac{1}{N^2} R_{jj} n_j (n_j - 1) & \text{if} \quad \underline{n}' = \underline{n}_{ij}^{+} \quad i = j \\ \frac{1}{N} F_{ij} n_{i+j} & \text{if} \quad \underline{n}' = \underline{n}_{ij}^{-} \\ 0 & \text{other} \quad \underline{n}' \neq \underline{n} \end{cases}$$

where the coagulation rate constants R_{ij} and fragmentation rate constants F_{ij} satisfy the following detailed balance condition proposed by Van Dongen and Ernst [25]

$$\lambda F_{ij} f(i+j) = R_{ij} f(i) f(j) \qquad i, j \geqslant 1 \tag{2}$$

where $f(k)$ denotes the number of distinct ways of forming a k-mers from k non-distinguishable units with distinguishable functional groups and $1/\lambda$ $(\lambda > 0)$ represents the fragmentation strength which, as in [25], can be written as $1/\lambda = \exp(E/KT)$, where E is the Gibbs free energy of a single chemical bond, T is the absolute temperature and K is Boltzmann's constant. Note that we use $1/\lambda$ here instead of λ used by Van Dongen and Ernst in [25] since it is used to call $\lambda > \lambda_c$ (λ_c is a critical value for the occurrence of gelation) as the supercritical stage. Formula (2) and its meaning can also be found in [25]. 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 one, so that the volume coincides with the total number of units N.

When $F_{ij} = 0$, the above irreversible random polymerization model was proposed first by Marcus [18] and studied in detail by Lushnikov [17] and Buffet and Pulé [4, 5], which is the stochastic counterpart of Smoluchlovski's coagulation equations, namely the Marcus–Lushnikov coagulation model or process. For readers who are interested in the mathematical aspects of the model, we recommend the survey paper of Aldous [1]. As clusters are growing in size, break-up processes become more important, and the irreversible coagulation reaction should be replaced by coagulation–fragmentation reaction. Van Dongen and Ernst [24, 25] and Spouge [22] were the first ones to extend Smoluchlovski's coagulation equations by including the fragmentation reaction. Motivated by the work done by Van Dongen and Ernst [24, 25], Buffet and Pulé [4, 5] and Pittel *et al* [20, 21], we considered in [13] a reversible random polymerization process (reversible Marcus–Lushnikov process) which is a reversible Markov process with the transition rates $Q_{\underline{n}\,\underline{n}'}$ with $F_{ij} > 0$ satisfying the detailed balance condition (2). In recent years various aspects of Smoluchlovski's equations and its stochastic counterpart containing the combined effects of coagulation and fragmentation have been extensively studied by many authors (see [2, 6–9, 11–13, 15, 16]).

Although there are many studies devoted to the deterministic and stochastic models based on the coagulation–fragmentation reaction of polymerization, the asymptotic probability distributions of the size of the largest length of the models have received minimal attention. The research work with respect to this problem can be found in the papers by Pittel *et al* [20, 21].

The objective of this paper is to further study the thermodynamic limit distribution of the size of polymerization of our model depending on the fragmentation strength. To explain the meaning of the limit distribution we present some notation and results in the following. From lemmas 1 and 2 of [13] it follows that the process $M_N(t)$ has a unique stationary distribution

$$P_N(\underline{n}) = \frac{1}{\pi_N} \prod_{k=1}^{N} \left[\left(\frac{N}{\lambda} \right) f(k) \right]^{n_k} \Big/ n_k! \qquad \underline{n} \in \Omega_N \tag{3}$$

where

$$\pi_N = \pi_N\left(\frac{N}{\lambda}\right) = \sum_{\underline{n}\in\Omega_N}\prod_{k\geqslant 1}\frac{\left[\frac{N}{\lambda}f(k)\right]^{n_k}}{n_k!} \tag{4}$$

is usually called the partition function of the process. The generating function of the partition functions $\{\pi_N(y)\}$ is given by

$$\sum_{N=0}^{\infty}\pi_N(y)x^N = \exp\{yF(x)\} \qquad |x| \leqslant \bar{r} \tag{5}$$

for any fixed y, where $\pi_0(y) = 1$ and

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

has a positive radius, $\bar{r}$, of convergence. Furthermore, the partition function has an integral formula

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

where Γ denotes a contour surrounding the origin $x = 0$. In particular,

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

Technically, the present paper studies the asymptotic behaviour of the stationary distribution $P_N(\underline{n})$ in the thermodynamic limit as $N \to \infty$. We shall prove that there exists a critical value λ_c of the fragmentation strength λ such that the size of the largest length of polymers is of order $\log N$, N^a $\left(\frac{1}{2} < a < 1\right)$, or N, respectively, depending upon whether λ is below λ_c, nearly (or equal to) λ_c, or above λ_c as $N \to \infty$, where $a = 1/(\beta - 1)$ and β $(2 < \beta < 3)$ is an exponent of $f(k)$ in (6).

In section 2 we present the main results on the limit distribution of the kth largest length of polymers in the subcritical, near-critical and supercritical stages and explain the relation of our results to the works done by Pittel *et al* in [20, 21]. The proofs of two theorems are given in section 3. An application of the theorems is shown in section 4.

It should be noted that though the process considered in the paper is different from that studied by Pittel *et al* in [20, 21] and some more general results are obtained in our model, Pittel, Woyczyniski and Mann's work provides us with some good ideas and techniques.

2. The main theorems

By theorem 2 of [12] we know that if the positive number $f(k)$ in (2) is of the form $f(k) = (1 + o(1))c\bar{r}^{-k}k^{-\beta}$, where $\bar{r}$ is the positive radius of convergence, c and β are two positive constants, then a necessary and sufficient condition for the occurrence of a gelation in the process is that the number β satisfies $2 < \beta < 3$. So, we shall assume in the following that the positive number $f(k)$ in (2) satisfies

$$f(k) = (1 + o(1))c\bar{r}^{-k}k^{-\beta} \tag{6}$$

where $2 < \beta < 3$. The number β is usually called an exponent of $f(k)$.

It follows from (6) that

$$F'(\bar{r}) = \lim_{x\to\bar{r}-0} F'(x) < +\infty \qquad F''(\bar{r}) = \lim_{x\to\bar{r}-0} F''(x) = +\infty.$$

According to theorem 2 of [12] a critical value of the fragmentation strength λ for the occurrence of a gelation can be determined as follows:

$$\lambda_c = \overline{r}F'(\overline{r}).$$

It can be checked that the number $f(k)$ for many models, such as RA_a ($a \geqslant 3$), RA_∞, A_aRB_b ($\min(a,b) \geqslant 2$), A_aRB_∞ ($a \geqslant 2$), etc, satisfies (6), where a and b are two natural numbers (see [13, 26]).

In order to compare the different results corresponding to different domains of λ, let us first recall the main subcritical result, then mention the near-critical and supercritical results.

Let $L_N^{(k)}$ denote the size of kth largest length of polymers and assume that the positive numbers $f(k)$ satisfy (2) and (6) in the following three theorems. We recall first the subcritical result which has been proved in [13]:

Theorem 1. *If $\lambda < \lambda_c$, then the size of the largest length of polymers in $\underline{n}$ (keeping in mind that $\underline{n} = \underline{n}(N)$) is asymptotically (in probability) a logarithmic function of N, i.e.,*

$$L_N^{(1)} = R^{-1}[\log N - \beta \log\log N + O_p(1)]$$

where $R = \log(\overline{r}/r)$, r is the positive root of $\lambda = xF'(x)$, $x \in (0, \overline{r})$, i.e., $\lambda = rF'(r)$, and $O_p(1)$ denotes random variables bounded in probability.

Now we mention the main results of this paper.

Theorem 2. *Suppose that $\lambda = \lambda_c$ or more general, $\lambda = \lambda_N$ satisfies*

$$\lambda_c/\lambda_N = 1 - a(d_\lambda)^{\frac{1}{\beta-1}} N^{-\frac{(\beta-2)}{(\beta-1)}}$$

where $a \in (-\infty, +\infty)$ is fixed and

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

Then, for every $x > 0$ and $k \geqslant 1$,

$$\lim_{N\to\infty} P\big(L_N^{(k)} \leqslant x(d_\lambda N)^{\frac{1}{\beta-1}}\big) = \mathrm{e}^{-I(x)} \sum_{0\leqslant j\leqslant k-1} [I(x)]^j/j!$$

where

$$I(x) = \frac{(\beta-1)(\beta-2)(3-\beta)}{p(a)} \int_x^{+\infty} y^{-\beta} p(a-y)\,\mathrm{d}y$$

and $p(a) = p(a; \beta-1, \delta)$ is the density of a $(\beta-1)$-stable distribution.

Theorem 3. *Suppose that $\lambda > \lambda_c$. Then*

(i) The distribution of $L_N^{(1)}$ satisfies a local limit-type relation

$$P\big(L_N^{(1)} = j\big) = (1 + o(1))p(x_j)\triangle x_j$$

where

$$x_j := [N(1-\lambda_c/\lambda) - j](d_\lambda N)^{-\frac{1}{\beta-1}} \qquad \triangle x_j := B(d_\lambda N)^{-\frac{1}{\beta-1}}$$

and

$$B = (3-\beta)\Gamma(3-\beta)$$

and $\Gamma(.)$ is the Gamma function. That is, in the distribution,

$$\big[N(1-\lambda_c/\lambda) - L_N^{(1)}\big](d_\lambda N)^{-\frac{1}{\beta-1}} \Longrightarrow X \qquad (N \to +\infty)$$

where the random variable X has the characteristic function

$$E(\exp(\mathrm{i}tX)) = \exp\big\{-|t|^{\beta-1}\mathrm{e}^{-\mathrm{i}\frac{(\beta-3)\pi}{2}\,\mathrm{sign}(t)}\big\}.$$

(ii) For every fixed $x > 0$ and $k \geqslant 2$,

$$\lim_{N\to\infty} P\left(L_N^{(k)} \leqslant xN^{\frac{1}{\beta-1}}\right) = \mathrm{e}^{-J(x)} \sum_{0\leqslant j\leqslant k-2} [J(x)]^j/j!$$

where $J(x) = \frac{c}{\lambda(\beta-1)} x^{-(\beta-1)}$.

Remark 1. By theorems 1–3 we see that the size of the largest length of polymers is of order $\log N - \beta \log\log N$, $N^{\frac{1}{\beta-1}}$, or N, respectively, depending upon whether λ is below λ_c, nearly (or equal to) λ_c, or above λ_c as $N \to \infty$.

Note that there is no other restrictive condition on the coagulation rate constants R_{ij} and fragmentation rate constants F_{ij} in the three theorems except for the detailed balance condition. In order to show the relation between the exponent β and R_{ij} and F_{ij}, a form of R_{ij} and F_{ij} will be given in the following.

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

$$R_{ij} = i^\sigma j^\sigma \tag{7}$$

and

$$\sum_{i+j=k} F_{ij} = \frac{2}{\lambda}(k-1)^\sigma \tag{8}$$

where $\sigma \geqslant 0$. Note that the number $k^\sigma - 1$ proposed by van Dongen and Ernst in [25] is replaced by $(k-1)^\sigma$ here. It follows from proposition 1 in [12] that a necessary and sufficient condition for the occurrence of a gelation is

$$\tfrac{1}{2} < \sigma < \tfrac{3}{2} \tag{9}$$

and

$$\sum_{k=1}^{\infty} k^{1+\sigma} f(k)\bar{r}^k = \infty. \tag{10}$$

Moreover, the positive number $f(k)$ has the following form

$$f(k) = (1 + o(1))c\bar{r}^{-k}k^{-(3/2+\sigma)}$$

if (7), (8), (9) and (10) are given. In this case, $2 < \beta = (3/2 + \sigma) < 3$ and $1/(\beta - 1) = 2/(2\sigma + 1)$. Thus, we have the following corollary.

Corollary 1. *Let R_{ij}, F_{ij} and $f(k)$ satisfy (7), (8), (9) and (10) respectively. Then there exists a critical value λ_c such that $\lambda_c = \bar{r}F'(\bar{r}) < \infty$ and the size of the largest length of polymers is of order* $\log N - (3/2 + \sigma)\log\log N$, $N^{\frac{2}{2\sigma+1}}$, *or N, respectively, depending upon whether λ is below λ_c, nearly (or equal to) λ_c, or above λ_c as $N \to \infty$.*

The model studied by Pittel, Woyczyniski and Mann is a Whittle-type random graph process of polymerization [20, 21] which is rather different from the reversible Marcus–Lushnikov process. They have proved in [21] that the size of the largest component is of the order $\log N - \frac{5}{2}\log\log N$, $N^{2/3}$ and N, respectively, in the subcritical, near-critical and supercritical stages. This result is just the special case of corollary 1 for $\sigma = 1$, i.e. $R_{ij} = ij$. In fact, the gelation in the case $R_{ij} = ij$ 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 [10] and extensively studied by Bollobás [3], Pittel [19] and Janson *et al* [14]. Thus, it is the reversible Marcus–Lushnikov process including the surface interactions ($R_{ij} = i^\sigma j^\sigma$, $1/2 < \sigma < 3/2$) of the polymers that we can obtain more general results.

3. Proofs of the theorems

The key to proving theorems 2 and 3 is to obtain the asymptotic formulae of the partition function π_N in (4).

Let $\lambda_N > 0$, $F_{ij}^{(N)} > 0$ depend on N such that

$$\lambda_N F_{ij}^{(N)} f(i+j) = R_{ij} f(i) f(j) \qquad 2 \leqslant i+j \leqslant N. \tag{11}$$

If $\lambda_N = \lambda$ is independent of N, then $F_{ij}^{(N)}$ is also, and (11) becomes (2).

Lemma 1. *Let N_k be the random number of k-mers and $E(.)$ denote the expectation corresponding to the stationary distribution $P_N(.)$ in (3). Then*

(i) For every fixed $k > 0$ and $\lambda = \lambda_c$ or more general, $\lambda = \lambda_N$ satisfying

$$\lambda_c/\lambda_N = 1 - a_N (d_\lambda)^{\frac{1}{\beta-1}} N^{-\frac{(\beta-2)}{(\beta-1)}}$$

we have

$$E(N_k) = (1+o(1)) c \lambda^{-1} k^{-\beta} N p\big(a_N - k(d_\lambda N)^{-\frac{1}{\beta-1}}\big)\big/ p(a_N)$$

where a_N is uniformly bounded to N.

(ii) For $k < l_N$ and $\lambda > \lambda_c$,

$$E(N_k) = (1+o(1)) c \lambda^{-1} b^{\beta} [k(b - k/N)]^{-\beta} N.$$

(iii) For $l_N < k < L_N$ and $\lambda > \lambda_c$,

$$E(N_k) = (1+o(1)) B b^{\beta} (k/N)^{-\beta} (d_\lambda N)^{-\frac{1}{\beta-1}} p(x_{N,k}).$$

(iv) For $k > L_N$ and $\lambda > \lambda_c$,

$$E(N_k) = (1+o(1)) c \lambda^{-1} b^{\beta} [k(k/N - b)]^{-\beta} N$$

where $x_{N,k} = (b - k/N)(d_\lambda)^{-\frac{1}{\beta-1}} N^{\frac{(\beta-2)}{(\beta-1)}}$, $b = 1 - \frac{\lambda_c}{\lambda}$, $l_N = bN - \omega(N) N^{1/(\beta-1)}$, $L_N = bN + \omega(N) N^{1/(\beta-1)}$ and $\omega(N) \to +\infty$ however slowly.

Proof of lemma 1. It follows from (3), (4) and (6) that

$$\begin{aligned} E(N_k) &= \sum_{\underline{n} \in \Omega_N} n_k P_N(\underline{n}) \\ &= \frac{N f(k)]}{\lambda \pi_N} \sum_{\underline{n} \in \Omega_N} \frac{\left[\frac{N}{\lambda} f(k)\right]^{n_k - 1}}{(n_k - 1)!} \prod_{j \neq k}^{N} \frac{\left[\frac{N}{\lambda} f(j)\right]^{n_j}}{n_j!} \\ &= \frac{N f(k)}{\lambda \pi_N} \sum_{\underline{n} \in \Omega_{N-k}} \prod_{j=1}^{N-k} \frac{\left[\frac{N}{\lambda} f(j)\right]^{n_j}}{n_j!} \\ &= \frac{N f(k)}{\lambda} \frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} = (1+o(1)) c \frac{N}{\lambda} \overline{r}^{-k} k^{-\beta} \frac{\pi_{N-k}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)}. \end{aligned} \tag{12}$$

Note that the numbers, $\pi_N\left(\frac{N}{\lambda}\right)$ and $\pi_{N-k}\left(\frac{N}{\lambda}\right)$, have been estimated in the proof of theorem 2 of [12]. That is

(I) If $\lambda = \lambda_c$, or more generally, $\lambda = \lambda_N$ satisfies $\lambda_c/\lambda_N = 1 - a_N(d_\lambda)^{\frac{1}{\beta-1}} N^{-\frac{(\beta-2)}{(\beta-1)}}$, where a_N is uniformly bounded to *N*, then

$$\pi_N\left(\frac{N}{\lambda}\right) = (1+o(1))D_N(\overline{r})p(a_N)(d_\lambda N)^{-\frac{1}{\beta-1}}$$

and, for every $k > 0$,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))(\overline{r})^k D_N(\overline{r})p\big(a_N - k(d_\lambda N)^{-\frac{1}{\beta-1}}\big)(d_\lambda N)^{-\frac{1}{\beta-1}}$$

where $D_N(\overline{r}) = \exp\left\{\frac{N}{\lambda}F(\overline{r}) - N\log\overline{r}\right\}$.

(II) If $\lambda > \lambda_c$, then

$$\pi_N\left(\frac{N}{\lambda}\right) = (1+o(1))d_\lambda\left(1-\frac{\lambda_c}{\lambda}\right)^{-\beta} D_N(\overline{r})p\left(0; \frac{1}{\beta-1}, 2-\frac{3}{\beta-1}\right)N^{-(\beta-1)} \tag{13}$$

and

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))d_\lambda(\overline{r})^k(b-k/N)^{-\beta}D_N(\overline{r})p\left(0; \frac{1}{\beta-1}, 2-\frac{3}{\beta-1}\right)N^{-(\beta-1)}$$

for $k < l_N$,

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))(\overline{r})^k D_N(\overline{r})p(x_{N,k})(d_\lambda N)^{-\frac{1}{\beta-1}}$$

for $l_N < k < L_N$, and

$$\pi_{N-k}\left(\frac{N}{\lambda}\right) = (1+o(1))d_\lambda(\overline{r})^k(k/N-b)^{-\beta}D_N(\overline{r}) \times p\left(0; \frac{1}{\beta-1}, -\left(2-\frac{3}{\beta-1}\right)\right)N^{-(\beta-1)}$$

for $k > L_N$. Note that $\Gamma(s+1) = s\Gamma(s)$, $\Gamma(s)\Gamma(1-s) = \pi/\sin(s\pi)$ for $0 < s < 1$, $p(x;\beta-1,\delta) = p(-x;\beta-1,-\delta)$ and

$$p\left(0; \frac{1}{\beta-1}, 2-\frac{3}{\beta-1}\right) = \pi^{-1}\Gamma(\beta)\sin[(\beta-2)\pi]$$

(see [23]). Thus, by (6), (12), (I) and (II), we can immediately obtain (i), (ii), (iii) and (iv) of lemma 1. □

Proof of theorem 2. We first prove that $L_N^{(1)}/N^{\frac{1}{\beta-1}}$ is bounded in probability. That is we will prove that there is no polymer of size $k \geqslant k_N = \omega(N)(d_\lambda N)^{\frac{1}{\beta-1}}$, where $\omega(N) \to +\infty$ however slowly. By (i) of lemma 1 we have

$$\begin{aligned}
E\left(\sum_{k\geqslant k_N} N_k\right) &= \sum_{k\geqslant k_N} E(N_k) \\
&= O\left(\sum_{k\geqslant k_N}\left(\frac{k}{N^{\frac{1}{\beta-1}}}\right)^{-\beta} p\big(a_N - k(d_\lambda N)^{-\frac{1}{\beta-1}}\big)\frac{1}{N^{\frac{1}{\beta-1}}}\right) \\
&= O\left(\int_{\omega(N)}^{(d_\lambda)^{-\frac{1}{\beta-1}}N^{\frac{\beta-2}{\beta-1}}} x^{-\beta}p(a_N - x)\,\mathrm{d}x\right) \\
&= O\left((\omega(N))^{-(\beta-1)}\right) = o(1).
\end{aligned}$$

For $y > x$ we set $k_1 = x(d_\lambda N)^{\frac{1}{\beta-1}}$, $k_2 = y(d_\lambda N)^{\frac{1}{\beta-1}}$, $C_N(x, y) = \sum_{k=k_1}^{k_2} N_k$ and

$$I(x, y) = \frac{(\beta-1)(\beta-2)(3-\beta)}{p(a)} \int_x^y u^{-\beta} p(a-u)\,\mathrm{d}u.$$

Let $a_N \to a$ as $N \to \infty$. It follows from (i) of lemma 1 that

$$\begin{aligned} E(C_N(x, y)) &= (1+o(1)) \frac{(\beta-1)(\beta-2)(3-\beta)}{p(a_N)} \sum_{k_1 \leqslant k \leqslant k_2} \left(\frac{k}{(d_\lambda N)^{\frac{1}{\beta-1}}} \right)^{-\beta} \\ &\quad \times p\left(a_N - k(d_\lambda N)^{-\frac{1}{\beta-1}}\right) \frac{1}{(d_\lambda N)^{\frac{1}{\beta-1}}} \\ &= (1+o(1)) \frac{(\beta-1)(\beta-2)(3-\beta)}{p(a_N)} \int_x^y u^{-\beta} p(a_N - u)\,\mathrm{d}u \\ &\quad \to I(x, y) \end{aligned}$$

as $N \to \infty$. Furthermore,

$$\begin{aligned} E(C_N(x, y)(C_N(x, y)-1)) &= \sum_{k_1 \leqslant k \leqslant k_2} \sum_{k_1 \leqslant l \leqslant k_2} \frac{N^2 f(k) f(l)}{\lambda^2} \frac{\pi_{N-k-l}\left(\frac{N}{\lambda}\right)}{\pi_N\left(\frac{N}{\lambda}\right)} \\ &= (1+o(1)) \sum_{k_1 \leqslant k \leqslant k_2} \sum_{k_1 \leqslant l \leqslant k_2} \left(\frac{cN}{\lambda}\right)^2 (kl)^{-\beta} p\left(a_N - (k+l)(d_\lambda N)^{-\frac{1}{\beta-1}}\right) \Big/ p(a_N) \\ &= (1+o(1)) \frac{[(\beta-1)(\beta-2)(3-\beta)]^2}{p(a_N)^2} \\ &\quad \times \int_x^y \int_x^y u^{-\beta} v^{-\beta} p(a_N) p(a_N - u - v)\,\mathrm{d}u\,\mathrm{d}v \\ &\quad \to [I(x, y)]^2 \end{aligned}$$

as $N \to \infty$. By the same method we have, for every $k \geqslant 1$,

$$E([C_N(x, y)]_k) \to [I(x, y)]^k$$

as $N \to \infty$, where $[C_N(x, y)]_k = C_N(x, y)(C_N(x, y)-1)(C_N(x, y)-2)\ldots(C_N(x, y) - k + 1)$ is the total number of ordered k-tuples of different polymers of size $j \in [k_1, k_2]$. Hence, $C_N(x, y)$ is, in the limit, a Poisson distribution with parameter $I(x, y)$. Since $L_N^{(1)} \big/ N^{\frac{1}{\beta-1}} = O_p(1)$, it follows that, for every $x > 0$ $k \geqslant 1$ and large x_1,

$$\begin{aligned} &P\left(L_N^{(k)} \geqslant x(d_\lambda N)^{\frac{1}{\beta-1}}\right) \\ &\quad = P\left(x(d_\lambda N)^{\frac{1}{\beta-1}} \leqslant L_N^{(k)} \leqslant L_N^{(1)} \leqslant x_1(d_\lambda N)^{\frac{1}{\beta-1}}\right) + O\left(P\left(L_N^{(1)} > x_1(d_\lambda N)^{\frac{1}{\beta-1}}\right)\right) \\ &\quad = P(C_N(x, y) \geqslant k) + O\left(P(L_N^{(1)} > x_1\left(d_\lambda N\right)^{\frac{1}{\beta-1}})\right) \to \mathrm{e}^{-I(x)} \sum_{j \geqslant k} [I(x)]^j / j! \end{aligned}$$

as $x_1 \to \infty$ and $N \to \infty$, where $I(x) = \lim_{y\to\infty} I(x, y)$. This completes the proof of theorem 2. □

Proof of theorem 3. (i) By (iii) of lemma 1 we have

$$\begin{aligned} E(N_j) &= (1+o(1)) B b^\beta (j/N)^{-\beta} (d_\lambda N)^{-\frac{1}{\beta-1}} p(x_{N,j}) \\ &= (1+o(1)) p(x_j) \triangle x_j \end{aligned} \tag{14}$$

where $j = N(1-\lambda_c/\lambda) - x_j(d_\lambda N)^{\frac{1}{\beta-1}}$ and $\triangle x_j = B(d_\lambda N)^{-\frac{1}{\beta-1}}$. Set $C_N(j) = \sum_{i\geqslant j} N_i$. Then

$$E(N_j) = P(N_j=1) + \sum_{k\geqslant 2} kP(N_j=k) = P(N_j=1) + O[NP(C_N(j)\geqslant 2)]$$

and

$$\begin{aligned} P(N_j=1) &= P\big(N_j=1, L_N^{(1)}=j\big) + P\big(N_j=1, L_N^{(1)}>j\big) \\ &= P\big(L_N^{(1)}=j\big) - P\big(N_j\geqslant 2, L_N^{(1)}=j\big) + P\big(N_j=1, L_N^{(1)}>j\big) \\ &= P\big(L_N^{(1)}=j\big) + O[P(C_N(j)\geqslant 2)]. \end{aligned}$$

Therefore

$$P\big(L_N^{(1)}=j\big) = E(N_j) + O[NP(C_N(j)\geqslant 2)]. \tag{15}$$

Furthermore, for $j_1, j_2 \geqslant j$,

$$N' = N - (j_1+j_2) = N(2\lambda_c/\lambda - 1) + O\big(N^{\frac{1}{\beta-1}}\big).$$

If $\lambda_c/\lambda < 1/2$, then $N' < 0$. This means that $P(C_N(j)\geqslant 2) = 0$. Let $\lambda_c/\lambda \geqslant 1/2$ and $\lambda_{N'} = \lambda N'/N$, we have

$$\lambda_{N'} \leqslant 2\lambda_c - \lambda + o(1) \leqslant \lambda_c - (\lambda-\lambda_c)/2 < \lambda_c.$$

Let $r' \in (0,\overline{r})$ satisfying $\lambda_{N'} = r'F'(r')$. It follows from (5) that

$$\pi_{N'}\left(\frac{N}{\lambda}\right) \leqslant \exp\left\{\frac{N}{\lambda}F(x) - N'\log x\right\}$$

for any $x > 0$. So,

$$\pi_{N'}\left(\frac{N}{\lambda}\right) \leqslant \exp\left\{\frac{N}{\lambda}F(r') - N'\log r'\right\}. \tag{16}$$

Thus, by (6), (13) and (16), we have

$$\begin{aligned} P(C_N(j)\geqslant 2) &\leqslant E([C_N(j)]_2) \\ &= \sum_{j_1,j_2\geqslant j}\left(\frac{N}{\lambda}\right)^2 f(j_1)f(j_2)\frac{\pi_{N-(j_1+j_2)}\left(\frac{N}{\lambda}\right))}{\pi_N\left(\frac{N}{\lambda}\right)} \\ &\leqslant O\left(\sum_{j_1,j_2\geqslant j}(j_1j_2)^{-\beta}N^{\beta+1}\exp\left\{\frac{N}{\lambda}(F(r')-F(\overline{r})) - N'(\log r' - \log\overline{r})\right\}\right) \\ &= O\left(N^{3-\beta}\exp\left\{\frac{N}{\lambda}(F(r')-F(\overline{r})) - N'(\log r' - \log\overline{r})\right\}\right). \end{aligned}$$

Since

$$\begin{aligned} &\frac{N}{\lambda}(F(r')-F(\overline{r})) - N'(\log r' - \log\overline{r}) \\ &\quad = \frac{N}{\lambda}\left[-\int_{r'}^{\overline{r}} xF'(x)x^{-1}\,\mathrm{d}x + r'F'(r')\int_{r'}^{\overline{r}} x^{-1}\,\mathrm{d}x\right] \\ &\quad = -\frac{N}{\lambda}\int_{r'}^{\overline{r}}[xF'(x) - r'F'(r')]x^{-1}\,\mathrm{d}x \\ &\quad = -\frac{N}{\lambda}c' \end{aligned}$$

where $c' > 0$, it follows that

$$NP(C_N(j) \geqslant 2) \leqslant O\left(N^{4-\beta}\exp\left\{-\frac{N}{\lambda}c'\right\}\right) = o\big(N^{-\frac{1}{\beta-1}}\big).$$

Hence, by (14) and (15),

$$\begin{aligned} P\big(L_N^{(1)} = j\big) &= E(N_j) + o\left(N^{-\frac{1}{\beta-1}}\right) \\ &= (1+o(1))p(x_j)\triangle x_j. \end{aligned}$$

This completes the proof of (i).

(ii) We first prove that there is at most one polymer of size $j \geqslant j_N = \omega(N)N^{\frac{1}{\beta-1}}$, where $\omega(N) \to +\infty$ however slowly. For any $0 < \epsilon < b = 1 - \frac{\lambda_c}{\lambda}$ and $\epsilon + b \leqslant 1$, let $l_N(\epsilon) = bN - \epsilon N$. It follows from (ii) of lemma 1 that

$$\begin{aligned} E\left(\sum_{j_N \leqslant j \leqslant l_N(\epsilon)} N_j\right) &= (1+o(1)) \sum_{j_N \leqslant j \leqslant l_N(\epsilon)} c\lambda^{-1}b^{\beta}[j(b-j/N)]^{-\beta}N \\ &= O\left(N^{-(\beta-2)}\int_{j_N/N}^{b-\epsilon} x^{-\beta}(b-x)^{-\beta}\,\mathrm{d}x\right) \\ &= O((\omega(N))^{-(\beta-1)}) \to 0 \end{aligned}$$

as $N \to \infty$. Therefore, there is no polymer in the ranges from j_N to $l_N(\epsilon)$. We now consider the range from $l_N(\epsilon)$ to N. Suppose that there are two polymers j_1 and j_2 of size between $l_N(\epsilon)$ and N. If $\frac{\lambda_c}{\lambda} < 1/2$, then

$$N - (j_1 + j_2) \leqslant N - 2l_N(\epsilon) = N\left(2\frac{\lambda_c}{\lambda} - 1 + 2\epsilon\right) < 0$$

for all small enough $\epsilon > 0$. This means that there is at most one polymer of size between $l_N(\epsilon)$ and N for $\frac{\lambda_c}{\lambda} < 1/2$. Let $\frac{\lambda_c}{\lambda} \geqslant 1/2$. Then, taking $\epsilon < b/2$ we have

$$0 \leqslant N' = N - (j_1 + j_2) \leqslant N - 2l_N(\epsilon) = N\left(2\frac{\lambda_c}{\lambda} - 1 + 2\epsilon\right)$$

and

$$\lambda_{N'} \leqslant \lambda\left(2\frac{\lambda_c}{\lambda} - 1 + 2\epsilon\right) < \lambda_c$$

where $\lambda_{N'} = \lambda N'/N$. So, as in the proof of (i),

$$E\left(\sum_{l_N(\epsilon) \leqslant j_1, j_2 \leqslant N} N_j\right) \leqslant E([C_N(l_N(\epsilon))]_2) \leqslant O\left(N^{3-\beta}\exp\left\{-\frac{N}{\lambda}c''\right\}\right) \to 0$$

as $N \to \infty$, where $c'' > 0$. Thus, we have proved that there is at most one polymer of size $j \geqslant \omega(N)N^{\frac{1}{\beta-1}}$ as $N \to \infty$. Therefore, for each $\epsilon > 0$, there exists $x_1 = x_1(\epsilon) > x$ so large that

$$\limsup P\big(L_N^{(2)} > x_1 N^{\frac{1}{\beta-1}}\big) < \epsilon.$$

Note that, for every $k \geqslant 2$,

$$\begin{aligned} P\big(L_N^{(k)} \geqslant xN^{\frac{1}{\beta-1}}\big) &= P\big(xN^{\frac{1}{\beta-1}} \leqslant L_N^{(k)} \leqslant L_N^{(2)} \leqslant x_1N^{\frac{1}{\beta-1}}\big) + O\big(P\big(L_N^{(2)} > x_1N^{\frac{1}{\beta-1}}\big)\big) \\ &= P(C_N(x, x_1) \geqslant k-1) + O\big(P\big(L_N^{(2)} > x_1N^{\frac{1}{\beta-1}}\big)\big) \end{aligned}$$

where $C_N(x, x_1) = \sum_{j_1 \leqslant j \leqslant j_2} N_j$, $j_1 = xN^{\frac{1}{\beta-1}}$ and $j_2 = x_1 N^{\frac{1}{\beta-1}}$. So, as in the proof of theorem 2, $C_N(x, x_1)$ is, in the limit, a Poisson distribution with parameter

$$J(x, x_1) = \frac{c}{\lambda(\beta - 1)}\left[x^{-(\beta-1)} - x_1^{-(\beta-1)}\right].$$

Thus

$$\lim_{N\to\infty} \sup \left| P\left(L_N^{(k)} > xN^{\frac{1}{\beta-1}}\right) - \mathrm{e}^{-J(x,x_1)} \sum_{j \geqslant k-1} [J(x, x_1)]^j / j! \right| \leqslant \epsilon$$

and, letting $\epsilon \to 0$, i.e. $x_1(\epsilon) \to +\infty$, we have

$$\lim_{N\to\infty} P\left(L_N^{(k)} \leqslant xN^{\frac{1}{\beta-1}}\right) = \mathrm{e}^{-J(x)} \sum_{0 \leqslant j \leqslant k-2} [J(x)]^j / j!$$

for every $x > 0$ and $k \geqslant 2$, where $\lim_{x_1 \to +\infty} J(x, x_1) = J(x) = \frac{c}{\lambda(\beta-1)} x^{-(\beta-1)}$. This completes the proof. □

4. Applications

As an application of theorems 1–3, we show two examples.

Example 1. RA_a model ($a \geqslant 3$).
It is known that the numbers $f(k)$ for the RA_a model are as follows:

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

By using Stirling's formula we have (see [13])

$$f(k) = (1 + o(1))c\overline{r}^{-k} k^{-5/2}$$

where $c = \sqrt{(a-1)/[2\pi(a-2)^5]}$, $\beta = 5/2$

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

and $\lambda_c = \overline{r}F'(\overline{r}) = (a-1)/[a(a-2)^2]$. Taking the fragmentation coefficients $F(i, j)$ such that

$$F_{ij} = \frac{1}{\lambda} \frac{R_{ij} f(i) f(j)}{f(i+j)} \qquad i, j \geqslant 1$$

it follows from theorems 1–3 that the size of the largest length of polymers is of order $\log N - \frac{5}{2} \log\log N$, $N^{2/3}$ or N, respectively, depending upon whether λ is below λ_c, nearly (or equal to) λ_c, or above λ_c as $N \to \infty$.

Example 2. For the model RA_∞ we have

$$f(k) = \frac{k^{k-2}}{k!}.$$

It can be calculated that

$$f(k) = (1 + o(1))c\overline{r}^{-k} k^{-5/2}$$

where $c = (2\pi)^{-1/2}$ and $\overline{r} = e^{-1}$. Therefore, the size of the largest length of polymers is of order $\log N - \frac{5}{2} \log\log N$, $N^{2/3}$ and N, respectively, in the subcritical, near-critical and the supercritical cases.

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