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Subcritical Asymptotic Behavior in the Thermodynamic Limit of Reversible Random Polymerization Processes

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We consider a reversible Markov process as a chemical polymerization model and study the asymptotic behavior (in the thermodynamic limit as $N \to +\infty$) of a particular probability distribution on the set of N-dimensional vectors, the kth component of which is the number of k-mers. The study establishes the existence of three stages (subcritical, near-critical, and supercritical stages) of polymerization, depending on the value of the strength of the fragmentation reaction. The present paper concentrates on the analysis of the subcritical stage. In the subcritical stages we show that the size of the largest length of polymers of size N is of the order $\log N$ as $N \to +\infty$.

KEY WORDS: Polymerization; Markov process; limit behavior; stationary distribution.

1. INTRODUCTION

If we limit ourselves to homogeneous systems where diffusion effects are ignored, there are essentially two models describing systems of 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 polymer of length $j+k$ (the number R_{jk} denotes the corresponding reaction rate[1]): one is Smoluchovski's model, the other is Lushinikov's model. The connection between the two models is as follows: let $N_1(t), N_2(t),..., N_N(t)$ be the random valuables denoting the numbers of monomers, dimers,...,

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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. 2. For Smoluchovski's model the kinetic theory of polymerization does not contain the equilibrium theory of Flory[3] and Stockmayer[4] as a limiting case for large values of the time, due to the absence of fragmentation effects. In fact, as clusters are growing in size, bred-up processes become more important, and the irreversible coagulation reactions should be replaced by reversible coagulation–fragmentation reactions. Many studies[5–7] about the kinetic equation containing the combined effects of coagulation and fragmentation have been done. Recently several papers[1,8,9] have been devoted to the Lushnikov model; a detailed asymptotic analysis of the Flory–Stockmayer–Whittle polymerization process was given by Pittel, Woyczynski, and Mann.[10–13] The studies motivate us to consider a reversible random polymerization process which permits the congulation–fragmentation reaction, i.e.,

$$(j) + (k) \underset{F_{jk}}{\overset{R_{jk}}{\rightleftharpoons}} (j+k) \tag{2}$$

The objective of the present paper is to study the limit distribution (in the thermodynamic limit) of the number of polymers for the process in the subcritical stage; the near-critical and supercritical stages are analyzed in ref. 14. In Section 2 we give the formal description of the reversible random polymerization process $M_N(t)$ and its stationary distribution. The conditions under which the critical value λ_c can be determined are presented in Section 3. In Section 4 we give a precise asymptotic formula of the partition function π_N in the subcritical stage and prove that the size of the largest length of polymers of size N is of the order of $\log N$ as $N \to \infty$ in the subcritical stage.

2. THE REVERSIBLE POLYMERIZATION PROCESS AND ITS STATIONARY DISTRIBUTION

The reversible random polymerization process is a continuous-time Markov chain $\{M_N(t) \colon t \geqslant 0\}$ with the state space

$$\Omega_N = \left\{ \mathbf{n} \in N^N \colon \sum_{k=1}^{N} k n_k = N \right\} \tag{3}$$

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

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

$$\mathbf{n}_{jk}^{-} = \begin{cases} (n_1, n_2, \ldots, n_j + 1, \ldots, n_k + 1, \ldots, n_{j+k} - 1, \ldots, n_N) & \text{if } j \neq k \\ (n_1, n_2, \ldots, n_j + 2, \ldots, n_{2j} - 1, \ldots, \ldots, n_N) & \text{if } j = k \end{cases} \tag{5}$$

and they occur with rate

$$Q_{\mathbf{nn}'} = \begin{cases} \dfrac{1}{N^2} R_{jk} n_j n_k & \text{if } \mathbf{n}' = \mathbf{n}_{jk}^{+}, \quad j \neq k \\ \dfrac{1}{N^2} R_{jj} n_j (n_j - 1) & \text{if } \mathbf{n}' = \mathbf{n}_{jk}^{+}, \quad j = k \\ \dfrac{1}{N} F_{jk} n_{j+k} & \text{if } \mathbf{n}' = \mathbf{n}_{jk}^{-} \\ 0 & \text{other } \mathbf{n}' \neq \mathbf{n} \end{cases} \tag{6}$$

$$Q_{\mathbf{nn}} = - \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{nn}'}$$

where $R_{ij} > 0$, $F_{ij} > 0$; they satisfy the following equations:

$$\sum_{i+j=k} F_{ij} = \frac{2}{\lambda} (k-1), \qquad k \geqslant 2 \tag{7}$$

$$\lambda F_{ij} f(i+j) = R_{ij} f(i) \, f(j) \tag{8}$$

where $\lambda > 0$ is constant, and $\{f(k), \ k \geqslant 1\}$ is a sequence of positive numbers. The formulas (7) and (8) and their meaning can been found in ref. 7. The choice of $Q_{\mathbf{nn}'}$ reflects the fact that in the homogeneous system, reaction (2) 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.

From (6)–(8) we see that the process $M_N(t)$ has a unique stationary distribution.

Lemma 1. The process $M_N(t)$ has a unique stationary distribution which is of the form

$$P_N(\mathbf{n}) = \frac{1}{\pi_N} \prod_{k=1}^{N} \left[\left(\frac{N}{\lambda} \right) f(k) \right]^{n_k} \Big/ n_k!, \qquad \mathbf{n} \in \Omega_N \tag{9}$$

where

$$\pi_N = \sum_{\mathbf{n} \in \Omega_N} \prod_{k=1}^{N} \left[\left(\frac{N}{\lambda} \right) f(k) \right]^{n_k} \Big/ n_k! \tag{10}$$

Moreover, we have

$$P_N(\mathbf{n})\, Q_{\mathbf{n}\mathbf{n}'} = P_N(\mathbf{n}')\, Q_{\mathbf{n}'\mathbf{n}} \tag{11}$$

Proof. It follows from (6) that

$$\begin{aligned}
&\sum_{\mathbf{n}' \in \Omega_N} P_N(\mathbf{n}')\, Q_{\mathbf{n}'\mathbf{n}} \\
&\quad = \sum_{\mathbf{n}' \neq \mathbf{n}} P_N(\mathbf{n}')\, Q_{\mathbf{n}'\mathbf{n}} - P_N(\mathbf{n}) \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} \\
&\quad = \sum_{j,k} P_N(\mathbf{n}_{jk}^-)\, Q_{\mathbf{n}_{jk}^-\mathbf{n}} + \sum_{j,k} P_N(\mathbf{n}_{jk}^+)\, Q_{\mathbf{n}_{jk}^+\mathbf{n}} - P_N(\mathbf{n}) \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} \\
&\quad = \sum_{j \neq k} P_N(\mathbf{n}_{jk}^-) \frac{1}{N^2} R_{jk}(n_j + 1)(n_k + 1) \\
&\qquad + \sum_{j = k} P_N(\mathbf{n}_{jj}^-) \frac{1}{N^2} R_{jj}(n_j + 2)(n_j + 1) \\
&\qquad + \sum_{j \neq k} P_N(\mathbf{n}_{jk}^+) \frac{1}{N} F_{jk}(n_{j+k} + 1) + \sum_{j = k} P_N(\mathbf{n}_{jj}^+) \frac{1}{N} F_{jj}(n_{2j} + 1) \\
&\qquad - P_N(\mathbf{n}) \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} \\
&\quad = P_N(\mathbf{n}) \left[\sum_{j \neq k} \frac{N}{\lambda} \frac{f(j)\, f(k)}{f(j+k)} \frac{n_{j+k}}{(n_j + 1)(n_k + 1)} \frac{1}{N^2} R_{jk}(n_j + 1)(n_k + 1) \right. \\
&\qquad + \sum_{j = k} \frac{N}{\lambda} \frac{f(j)\, f(j)}{f(2j)} \frac{n_{2j}}{(n_j + 2)(n_j + 1)} \frac{1}{N^2} R_{jj}(n_j + 2)(n_j + 1) \\
&\qquad + \sum_{j \neq k} \frac{\lambda}{N} \frac{f(i + j)}{f(i)\, f(j)} \frac{n_j n_k}{(n_{j+k} + 1)} \frac{1}{N} F_{jk}(n_{j+k} + 1) \\
&\qquad \left. + \sum_{j = k} \frac{\lambda}{N} \frac{f(2j)}{f(j)\, f(j)} \frac{n_j(n_j - 1)}{(n_{2j} + 1)} \frac{1}{N} F_{jj}(n_{2j} + 1) - \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} \right] \\
&\quad = P_N(\mathbf{n}) \left(\sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} - \sum_{\mathbf{n}' \neq \mathbf{n}} Q_{\mathbf{n}\mathbf{n}'} \right) = 0
\end{aligned}$$

From this and Theorem 4.37 of ref. 15, we see that $P_N(\mathbf{n})$, $\mathbf{n} \in \Omega_N$, is the unique stationary distribution of $\{M_N(t): t \geqslant 0\}$.

It is easy to show (11). By (11) we know that $M_N(t)$ is a reversible Markov chain. ▮

Next we obtain the generating function of $\{\pi_N\}$.

Lemma 2. Let

$$\pi_N(y) = \sum_{\mathbf{n} \in \Omega_N} \prod_{k=1}^{N} \frac{[yf(k)]^{n_k}}{n_k!}, \qquad N \geqslant 1, \quad y \geqslant 0$$

Then the generating function of the partition function $\{\pi_N(y)\}$ is given by

$$1 + \sum_{N=1}^{\infty} \pi_N(y)\, x^N = \exp[yF(x)], \qquad |x| < r \tag{12}$$

where

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

and r is the radius of convergence for the series $F(x)$.

Proof. Let $\pi_0(y) = 1$. It follows that

$$\begin{aligned} \pi'_N(y) &= \sum_{\mathbf{n} \in \Omega_N} (n_1 + n_2 + \cdots + n_N)\, y^{(n_1 + n_2 + \cdots + n_N) - 1} \prod_{k=1}^{N} \frac{[f(k)]^{n_k}}{n_k!} \\ &= \sum_{j=1}^{N} \sum_{\mathbf{n} \in \Omega_N} n_j \frac{y^{n_j - 1} f(j)^{n_j}}{n_j!} \prod_{k \neq j} \frac{[yf(k)]^{n_k}}{n_k!} \\ &= \sum_{j=1}^{N} \sum_{\mathbf{n}: \sum_{k=1}^{N} k n_k = N-j} f(j) \prod_{k=1}^{N-j} \frac{[yf(k)]^{n_k}}{n_k!} \\ &= \sum_{j=1}^{N} f(j)\, \pi_{N-j}(y) \end{aligned}$$

Hence, if we put

$$A(x, y) = 1 + \sum_{N=1}^{\infty} \pi_N(y)\, x^N$$

then

$$A'_y(x \cdot y) = \sum_{N=1}^{\infty} \pi'_N(y)\, x^N = \sum_{N=1}^{\infty} \sum_{j=1}^{N} f(j)\, x^j \pi_{N-j}(y)\, x^{N-j}$$
$$= \sum_{j-1}^{\infty} f(j)\, x^j \sum_{N=j}^{\infty} \pi_{N-j} x^{N-j} = F(x)\, A(x \cdot y)$$

and therefore

$$\log[A(x \cdot y)] = yF(x)$$
$$A(x \cdot y) = \exp[yF(x)]$$

The lemma is true. ▮

3. THE CONDITIONS OF DETERMINING THE CRITICAL VALUE

In the section, we give the conditions under which the critical value of the parameter λ can be determined.

Suppose that there exists a positive radius $\bar{r}$ of convergence for the series $F(x) = \sum_{k=1}^{\infty} f(k)\, x^k$ such that

$$F'(\bar{r}) < +\infty \tag{13}$$

$$F''(\bar{r}) = +\infty \tag{14}$$

and

$$\frac{F'''(\bar{r})}{[F''(\bar{r})]^3} = \lim_{x \to \bar{r}-0} \frac{F'''(x)}{[F''(x)]^3} \neq 0 \tag{15}$$

Then the critical value λ_c is given by

$$\lambda_c = \bar{r} F'(\bar{r}) \tag{16}$$

Remark. It is shown elsewhere[14] that (14) and (15) are needed to determine the critical value λ_c.

Example 1. For the RA_f model the numbers $f(k)$ have been calculated already by Stockmayer:

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

So we can obtain the radius of convergence for $F(x)=\sum_{k=1}^{\infty} f(k)\, x^k$:

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

In the case $f=2$,

$$\bar{r}=\frac{1}{2}$$

$$F(x)=\sum_{k=1}^{\infty} 2^{k-1}x^k=\frac{x}{1-2x}$$

$$F'(x)=\frac{1}{(1-2x)^2}$$

we can check that $F(x)$ does not satisfy (13) and (15), so one may consider the critical value $\lambda_c=+\infty$.

For $f=3$, we have $\bar{r}=1/12$ and

$$F(x)=\tfrac{1}{108}x^{-2}(1-12x)^{3/2}+\tfrac{1}{6}x^{-1}-\tfrac{1}{108}x^{-2}-\tfrac{1}{2}$$

It is easy to check that (13)–(15) hold for $F(x)$, so we obtain

$$\lambda_c=\tfrac{1}{12}F'(\tfrac{1}{12})=\tfrac{8}{12}=\tfrac{2}{3} \tag{17}$$

For $f\geqslant 4$, we need another method to determine the λ_c, since it is difficulty to obtain the analytic expression of the series $F(x)=\sum_{k=1}^{\infty} f(k)\, x^k$. Notice that F, F', and F'' have the same radius of convergence, and $F''(x)\geqslant 0$ as $x\geqslant 0$, so $\lambda(x)=xF'(x)$ is an increasing function as $x\geqslant 0$, and $\lambda(x)$ reaches a maximum (finite value) at $x=\bar{r}$, that is, $\lambda_c=\lambda(\bar{r})$. By combination of (7) and (8), we have the recursion relation

$$(k-1)\, f(k)=\tfrac{1}{2}\sum_{i+j=k} R_{ij} f(i)\, f(j) \tag{18}$$

Multiply both sides of (18) by x^k and sum over $k=2, 3,\ldots$. Taking $R_{ij}=[(f-2)\,i+2][(f-2)\,j+2]$ (see ref. 7) and using the identity

$$\left(\sum_{k=1}^{\infty} a_k x^k\right)\left(\sum_{k=1}^{\infty} b_k x^k\right)=\sum_{k=2}^{\infty}\left(\sum_{i+j=k} a_i b_j\right)x^k$$

to the series $F(x)=\sum_{k=1}^{\infty} f(k)\, x^k$, we see that

$$2[xF'(x)-F(x)]=(f-2)^2\,[xF'(x)]^2+4(f-2)\,xF'(x)\,F(x)+4F(x)^2$$

Put $\lambda(x) = xF'(x)$; then we have

$$(f-2)^2 \lambda(x)^2 + [4(f-2) F(x) - 2] \lambda(x) + 2F(x) + 4F(x)^2 = 0$$

and therefore

$$\lambda(x) = \frac{1}{(f-2)^2} \{1 - 2(f-2) F(x) \pm [1 - 2f(f-2) F(x)]^{1/2}\}$$

Notice that $\lambda'(x) > 0$ and $F'(x) > 0$ as $x > 0$, so

$$\lambda(x) = \frac{1}{(f-2)^2} \{1 - 2(f-2) F(x) - [1 - 2f(f-2) F(x)]^{1/2}\}, \qquad x \geqslant 0 \quad (19)$$

Hence, if and only if $F(x) = 1/[2f(f-2)]$, $\lambda(x)$ reaches a maximum, that is,

$$\lambda_c = \bar{r}F'(\bar{r}) = \lambda(\bar{r}) = \frac{f-1}{f(f-2)^2} \qquad (20)$$

This coincides a well-known result.[7] By (19) we see that for $f \geqslant 4$, (13)–(15) all hold.

4. THE LARGEST LENGTH OF POLYMERS IN THE SUBCRITICAL STAGE

First we give a precise asymptotic formula for the partition function π_N in the subcritical stage.

Theorem 1. Let $0 < \lambda_0 < \lambda_c$; then for any fixed $j \geqslant 0$ and large N,

$$\pi_{N-j}\left(\frac{N}{\lambda_0}\right) = [1 + V(N-j)] \frac{1}{\sqrt{2\pi}} \left(\frac{F'(x_0)}{x_0 F''(x_0) + F'(x_0)}\right)^{1/2} \times x_0^j (N-j)^{-1/2} \exp N\left(\frac{F(x_0)}{\lambda_0} - \log x_0\right)$$

where x_0 is a positive number satisfying $x_0 F'(x_0) = \lambda_0$, $V(N) \to 0$ as $N \to \infty$.

Proof. By (12) and Cauchy's integral formula

$$\pi_{N-j} = \pi_{N-j}\left(\frac{N}{\lambda_0}\right) = (2\pi i)^{-1} \int_{\mathscr{C}} \exp\left[\frac{N}{\lambda_0} F(x) - (N-j) \log x\right] x^{-1}\, dx$$

where $\mathscr{C}$ is a contour of radius less than $\bar{r}$ surrounding the origin $x = 0$.

Put

$$f_N(x) = \frac{N-j}{\lambda_0} F(x) - (N-j) \log x$$

and choose the radius of $\mathscr{C}$ equal to a root x_0 of $f'_N(x) = 0$. From

$$f'_N(x) = \frac{N-j}{\lambda_0} \left[F'(x) - \frac{\lambda_0}{x} \right] = 0$$

we obtain $f'_N(x_0) = 0$, where x_0 satisfies $x_0 F'(x_0) = \lambda_0$, $x_0 < \bar{r}$. This root is unique, because $xF'(x)$ is strictly increasing as $0 \leqslant x < \bar{r}$. Such a root is a saddle point of $\exp[f_N(x)]$. A standard saddle-point-type argument shows then that

$$\begin{aligned} \pi_{N-j} &= [1 + o(1)] \frac{1}{2\pi} \left[\frac{2\pi}{x_0^2 f''_N(x_0)} \right]^{1/2} \exp \left[f_N(x_0) + \frac{j}{\lambda_0} F(x_0) \right] \\ &= [1 + V(N-j)] \frac{1}{\sqrt{2\pi}} \left[\frac{F'(x_0)}{x_0 F''(x_0) + F'(x_0)} \right]^{1/2} \\ &\quad \times x_0^j (N-j)^{-1/2} \exp N \left[\frac{F(x_0)}{\lambda_0} - \log x_0 \right] \end{aligned}$$

This completes the proof. ▮

Next we study the largest length of polymers in the subcritical stage.

Let N_j denote the total number of polymers of length j in $\mathbf{n} \in \Omega_N$ and L_N denote the size of the largest length of polymers in $\mathbf{n} \in \Omega_N$. For an integer $S \geqslant 1$, let

$$Y_{NS} = \sum_{j \geqslant S} N_j \tag{21}$$

Theorem 2. If the number $f(k)$ defined in (8) satisfies

$$\log f(k) = Ak + B \log k + \varepsilon(k) \tag{22}$$

where A and B are constants, and $\varepsilon(x) \to C$, $\varepsilon'(x) \to 0$ as $x \to +\infty$, then for $0 < \lambda_0 < \lambda_c$, the size L_N of the largest length of polymers in $\mathbf{n}$ is asymptotically, in probability, a logarithmic function of N. More precisely,

$$L_N = \frac{1}{K_0} [\log N + B \log \log N + O_p(1)] \tag{23}$$

or equivalently

$$\lim_{N\to\infty} P_N\left(\left|L_N-\frac{1}{K_0}[\log N+B\log\log N]\right|\geqslant\omega(N)\right)=0 \tag{24}$$

where $O_p(1)$ denotes random variables bounded in probability, $\omega(N)\to+\infty$ slowly as $n\to\infty$, $K_0=-\log x_0-A$, and x_0 is determined by $\lambda_0=x_0F'(x_0)$.

Proof. First we show that $K_0>0$. It follows from $F(x_0)=\sum_{k=1}^{\infty} f(k)\,x_0^k<\infty$, $x_0<\bar{r}$, and (22) that

$$\lim_{k\to\infty} e^{[\ln f(k)]/k}x_0=e^A x_0<1$$

so $\log x_0-A<0$, that is, $K_0>0$.

By (9) and (10) it follows that

$$\begin{aligned}
EN_j&=\sum_{\mathbf{n}\in\Omega_N} n_jP_N(\mathbf{n})\\
&=\frac{1}{\pi_N}\sum_{\mathbf{n}:\,\sum_{k=1}^N kn_k=N}\frac{[Nf(j)/\lambda_0]^{n_j}}{(n_j-1)!}\prod_{k\neq j}\frac{[Nf(k)/\lambda_0]^{n_k}}{n_k!}\\
&=\frac{Nf(j)}{\lambda_0\pi_N}\sum_{\mathbf{n}:\,\sum_{k=1}^N kn_k=N-j}\frac{[Nf(k)/\lambda_0]^{n_j}-1}{(n_j-1)!}\prod_{k\neq j}\frac{[Nf(k)/\lambda_0]^{n_k}}{n_k!}\\
&=\frac{Nf(j)}{\lambda_0\pi_N}\sum_{\mathbf{n}:\,\sum_{k=1}^{N-j} kn_k=N-j}\prod_{k=1}^{N-j}\frac{[Nf(k)/\lambda_0]^{n_k}}{n_k!}\\
&=\frac{Nf(j)}{\lambda_0}\frac{\pi_{N-j}(N/\lambda_0)}{\pi_N(N/\lambda_0)}
\end{aligned}$$

From Theorem 1 we have

$$EN_j=\left[1+\frac{V(N-j)-V(N)}{1+V(N)}\right]\frac{Nf(j)}{\lambda_0}\left(1-\frac{j}{N}\right)^{-1/2}e^{j\log x_0}$$

Let

$$\tilde{N}_j=\frac{N}{\lambda_0}f(j)\left(1-\frac{j}{N}\right)^{-1/2}e^{j\log x_0}$$

Using (22), we have for large N

$$\sum_{j \geqslant S}^{N} \tilde{N}_j = \sum_{j \geqslant S}^{[N/2]} \tilde{N}_j + \sum_{j=[N/2]+1}^{N} \tilde{N}_j$$

$$= [1+o(1)] \left[\frac{N^2}{\lambda_0} \int_{S/N}^{1/2} (1-x)^{-1/2} e^{-K_0 N x} e^{B \log xN + \varepsilon(xN)} \, dx \right.$$

$$\left. + \frac{N^2}{\lambda_0} \int_{1/2}^{1} (1-x)^{-1/2} e^{-K_0 N x} e^{B \log xN + \varepsilon(xN)} \, dx \right]$$

Using integration by parts, we have

$$= [1+o(1)] \left(\frac{N}{K_0 \lambda_0} \left(1 - \frac{S}{N}\right)^{-1/2} e^{-K_0 S + B \log S + \varepsilon(S)} \right.$$

$$+ \frac{N}{2K_0 \lambda_0} \int_{S/N}^{1/2} \left\{ (1-x)^{-3/2} e^{-K_0 N x} e^{B \log xN + \varepsilon(xN)} \right.$$

$$\left. + (1-x)^{-1/2} e^{-K_0 N x} e^{B \log xN + \varepsilon(xN)} \left[\frac{B}{x} + N\varepsilon'(xN) \right] \right\} dx$$

$$- \frac{2N^2}{\lambda_0} (1-x)^{1/2} e^{-K_0 N x} e^{B \log xN + \varepsilon(xN)} \Big|_{1/2}^{1}$$

$$\left. + \frac{2N^2}{\lambda_0} \int_{1/2}^{1} \left\{ (1-x)^{1/2} e^{-K_0 N x} e^{B \log N + \varepsilon(xN)} \left[-K_0 N + \frac{B}{x} + N\varepsilon'(xN) \right] \right\} dx \right)$$

It is obvious that the last two terms go to zero as $N \to \infty$. So $\sum_{j \geqslant S}^{N} \tilde{N}_j$ is bounded away from 0 and ∞ as $N \to \infty$ if and only if

$$S = S_0 = \frac{1}{K_0} (\log N + B \log \log N) \tag{25}$$

Since

$$\sum_{j \geqslant S_0}^{[N/2]} \tilde{N}_j \to e^C \lambda_0^{-1} K_0^{-(B+1)} \qquad (\text{as } N \to +\infty)$$

$$\sum_{j=[N/2]+1}^{N} \tilde{N}_j \to 0, \qquad V(N) \to 0 \qquad (\text{as } N \to +\infty)$$

we have for $N \to \infty$

$$V(N) \sum_{j \geqslant S_0}^{N} \tilde{N}_j \to 0$$

$$\sum_{j \geqslant S_0}^{N} V(N-j)\, \tilde{N}_j = \sum_{j \geqslant S_0}^{[N/2]} V(N-j)\, \tilde{N}_j + \sum_{j=[N/2]+1}^{N} V(N-j)\, \tilde{N}_j \to 0$$

So

$$EY_{NS} = \sum_{j \geqslant S}^{N} \tilde{N}_j + \sum_{j \geqslant S}^{N} \frac{V(N-j) - V(N)}{1 + V(N)} \tilde{N}_j$$

is bounded away from 0 and ∞ as $N \to +\infty$ if and only if $S = S_0$. Hence,

$$EY_{NS_0} = \sigma_0 + o(1)$$

where $\sigma_0 = 1/\beta_0 \lambda_0$, $\beta_0 = e^{-C} K_0^{B+1}$.

If we prove that, for every fixed $m \geqslant 0$,

$$E(Y_{NS_0})_m \to \sigma_0^m, \qquad N \to \infty \tag{26}$$

where $(Y_{NS_0})_m$ is the total number of the ordered m-tuples of polymers of length $j \geqslant S_0$, then, asymptotically, Y_{NS_0} has Poisson distribution with mean σ_0,[16] so that

$$P_N(Y_{NS_0} = k) = e^{-\sigma_0} \frac{\sigma_0^k}{k!} + o(1) \tag{27}$$

for every $k \geqslant 0$.

Let $\pi(N) = \pi_N$ and $(N_i)_k = N_i(N_i - 1) \cdots (N_i - k + 1)$; then

$$\begin{aligned}
E(Y_{NS})_m &= \sum_{k_1 + \cdots k_N = m} E[(N_S)_{k_S} (N_{S+1})_{k_{S+1}} \cdots (N_N)_{k_N}] \\
&= \left(\frac{N}{\lambda_0}\right)^m \sum_{\substack{j_1 + j_2 + \cdots + j_m \leqslant N \\ j_i \geqslant S,\, i \geqslant 1}} \prod_{i=1}^{m} f(j_i) \frac{\pi(N - \sum_{i=1}^m j_i)}{\pi(N)} \\
&= \sum_{j'_m \leqslant N} [1 + G(N, j'_m)] \left(\frac{N}{\lambda_0}\right)^m \prod_{i=1}^{m} f(j_i) \left(1 - \frac{j'_m}{N}\right)^{-1/2} e^{j'_m \log x_0}
\end{aligned}$$

where $j'_m = j_1 + \cdots + j_m$, $G(N, j'_m) = [V(N - j'_m) - V(N)]/1 + V(N)$.

Let

$$\tilde{Y}_{NS}(j'_m) = \left(\frac{N}{\lambda_0}\right)^m \prod_{i=1}^{m} f(j_i) \left(1 - \frac{j'_m}{N}\right)^{-1/2} e^{j'_m \log x_0}$$

Taking $S = S_0$ defined in (25) and using integration by parts, we have for large N

$$\begin{aligned}
&\sum_{\substack{j'_m \leqslant [N/2] \\ j_i \geqslant S}} \tilde{Y}_{NS_0}(j'_m) \\
&\quad = [1 + o(1)] \frac{N^{2m}}{\lambda_0^m} \int_{S_0/N}^{1/2 - (m-1) S_0/N} dx_1 \int_{S_0/N}^{1/2 - x_1 - (m-2) S_0/N} dx_2 \\
&\quad \times \cdots \int_{S_0/N}^{1/2 - \sum_{i=1}^{m-1} x_i} \left(1 - \sum_{i=1}^{m} x_i\right)^{-1/2} \exp\left(-K_0 N \sum_{i=1}^{m} x_i\right) \\
&\quad \times \exp\left\{B \sum_{i=1}^{m} [\ln(N x_i) + \varepsilon(N x_i)]\right\} dx_m \\
&\quad = [1 + o(1)] \left[\frac{1}{\beta_0^m \lambda_0^m} + \sum_{i=1}^{m} I_i(N)\right]
\end{aligned}$$

where

$$\begin{aligned}
I_i(N) = &\frac{N^{2m-2i+1}}{2\beta_0^i \lambda_0^m} \underset{\substack{x_1 + \cdots + x_{m-i+1} + (i-1) S_0/N \leqslant 1/2 \\ x_j \geqslant S_0/N}}{\iint \cdots \int} H(i)^{-3/2}\, T(i)\, dx_1 \cdots dx_{m-i+1} \\
&+ \frac{N^{2m-2i+1}}{2\beta_0^i \lambda_0^m} \underset{\substack{x_1 + \cdots + x_{m-i+1} + (i-1) S_0/N \leqslant 1/2 \\ x_j \geqslant S_0/N}}{\iint \cdots \int} H(i)^{-1/2}\, T(i) \\
&\times \left[\frac{B}{x_i} + N\varepsilon'(N x_0)\right] dx_1 \cdots dx_{m-i+1}
\end{aligned}$$

where

$$H(i) = \left[1 - \sum_{j=1}^{m-i+1} x_j - (i-1)\frac{S_0}{N}\right], \qquad 1 \leqslant i \leqslant m$$

$$T(i) = \exp\left\{-K_0 N \sum_{j=1}^{m-i+1} x_j + B \sum_{j=1}^{m-i+1} [\ln(N x_j) + \varepsilon(N x_j)]\right\}, \qquad 1 \leqslant i \leqslant m$$

Using again the interpretation by parts for $I_i(N)$, we can show that $\lim_{N\to\infty} I_i(N)=0$ $(1\leqslant i\leqslant m)$. By the same method, we have

$$\lim_{N\to\infty}\sum_{\substack{j'_m\geqslant[N/2]+1\\ j_i\geqslant S_0}} \tilde{Y}_{NS_0}$$

$$=[1+o(1)]\lim_{N\to+\infty}\frac{N^{2m}}{\lambda_0^m}\iint\cdots\int_{\substack{1\geqslant x_1+\cdots+x_m\geqslant 1/2\\ x_i\geqslant S_0/N}} H(1)\,T(1)\,dx_1\cdots dx_m=0$$

Thus

$$\lim_{N\to\infty} E(Y_{NS_0})_m$$

$$=\lim_{N\to\infty}\sum_{j'_m\leqslant[N/2]}[1+G(N,j'_m)]\,\tilde{Y}_{NS_0}(j'_m)$$

$$+\lim_{N\to\infty}\sum_{j'_m\geqslant[N/3]+1}^{N}[1+G(N,j'_m)]\,\tilde{Y}_{NS_0}(j'_m)=\frac{1}{\beta_0^m\lambda_0^m}=\sigma_0^m$$

since $\lim_{N\to\infty} G(N,j'_m)=0$, as $j'_m\leqslant[N/2]$. This proves (26).

By the same method, we have

$$P_N(Y_{N(S_0+c_N)}=k)=e^{-\sigma_1}\frac{\sigma_1^k}{k!}+o(1)$$

$$P_N(Y_{N(S_0-c_N)}=k)=e^{-\sigma_2}\frac{\sigma_2^k}{k!}+o(1)$$

for any bounded positive number series $\{c_N\}$, where $c_N<S_0$, $\sigma_1=\sigma_0\exp(-K_0c_N)$ and $\sigma_2=\sigma_0\exp(K_0c_N)$.

Hence

$$P_N(|L_N-S_0|\geqslant c_N)$$

$$\leqslant P_N(L_N\geqslant S_0+c_N)+P_N(L_N\leqslant S_0-c_N)$$

$$=P_N(Y_{N(S_0+c_N)}\geqslant 1)+P_N(Y_{N(S_0-c_N)}=0)$$

$$=1-e^{-\sigma_1}+e^{-\sigma_2}+o(1)$$

When $c_N\to\infty$ slowly as $N\to\infty$, we obtain (24) immediately. This completes the proof. ▌

As an application of Theorem 2, we take two examples.

Example 2. For the RA_f model we take

$$f(k)=\frac{f^k[(f-1)k]!}{[(f-2)k+2]!\,k!} \qquad (f\geqslant 3)$$

It is not difficult to calculate by Stirling's formula that

$$\log f(k)=Ak+B\log k+\varepsilon(k)$$

where

$$A=\log\left(\frac{f(f-1)^{f-1}}{(f-2)^{f-2}}\right), \qquad B=-\frac{5}{2}$$

$$\varepsilon(k)\to\frac{1}{2}\log\left(\frac{f-1}{2\pi(f-2)^5}\right)$$

so, for the RA_f model in the subcritical stage

$$L_N=\frac{1}{K_0}\left[\log N-\frac{5}{2}\log\log N+O_p(1)\right]$$

where

$$K_0=-\log x_0-\log\left(\frac{f(f-1)^{f-1}}{(f-2)^{f-2}}\right)$$

Example 3. For the RA_∞ model we take

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

where k^{k-2} is the number of trees with k labeled vertices by Cayley's formula.

It can be calculated that

$$\log f(k)=k-\tfrac{5}{2}\log k+\varepsilon(k)$$

$$\varepsilon(k)\to-\tfrac{1}{2}\log 2\pi$$

so, for the RA_∞ model in the subcritical stage

$$L_N=\frac{1}{K_0}\left[\log N-\frac{5}{2}\log N+O_p(1)\right]$$

where $K_0=-\log x_0-1$. This result is similar to Pittel's; see ref. 13.

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