Journal of Statistical Physics, Vol. 64, Nos. 1/2, 1991

Polymers and Random Graphs

E. Buffet[1,2] **and J. V. Pulé**[2,3]

Received October 23, 1990

We establish a precise connection between gelation of polymers in Lushnikov's model and the emergence of the giant component in random graph theory. This is achieved by defining a modified version of the Erdös–Rényi process; when contracting to a polymer state space, this process becomes a discrete-time Markov chain embedded in Lushnikov's process. The asymptotic distribution of the number of transitions in Lushnikov's model is studied. A criterion for a general Markov chain to retain the Markov property under the grouping of states is derived. We obtain a noncombinatorial proof of a theorem of Erdös–Rényi type.

KEY WORDS: Gelation of polymers; giant component of random graph; grouping of states in a Markov chain; Erdös–Rényi theorem.

1. INTRODUCTION

The study of aggregation reactions among polymers has a long history in theoretical physics.[1–3] 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 sizes j and k link themselves together to form a polymer of size $j+k$. The first, and by far the most studied, is Smoluchovski's differential equation which describes the coupled evolution of the densities of j-mers ($j = 1, 2, 3,...$) in an *infinitely extended* system.[1,3,4] The second model, introduced by Marcus[5] and further studied by

[1] School of Mathematical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland.
[2] School of Theoretical Physics, Dublin Institute for Advanced Studies, Dublin 4, Ireland.
[3] Department of Mathematical Physics, University College, Belfield, Dublin 4, Ireland.

0022-4715/91/0700-0087$06.50/0

Lushnikov,[6] is a continuous-time Markov chain where jumps between states of the *finite* system take place at a rate proportional to R_{jk}; see Section 2 and refs. 7, 8, and 10. Whichever model is used, it must account for the possibility that within a finite time, a polymer of macroscopic length has formed, a phenomenon known as *gelation.*[4,9,10]

Motivated by purely combinatorial considerations, Erdös and Rényi introduced in 1960 the following problem[11–13]: consider a *discrete-time* Markov chain with state space consisting of the set of all graphs without multiple edges on N labeled vertices; transitions between states are effected by adding one edge to the present graph-state, any possible additional edge being chosen with equal probability. One then asks for "typical" properties of the graph-state of a large system after n steps, i.e., properties that hold with probability one as N tends to infinity; a number of these properties can be obtained, but the most striking is the size of the largest connected component of the graph-state after n steps: if $n = cN$, this size is of order $\log N$ whenever $c < 1/2$, whereas it becomes of order N when $c > 1/2$. The change in qualitative behavior that takes place around $N/2$ steps is known as the *emergence of the giant component* in random graph theory.

That gelation and emergence of the giant component are related phenomena is intuitively clear. It is the purpose of this article to make the connection rigorous. In Section 2 we give an overview of Lushnikov's model for reacting polymers. Some of the results are taken from ref. 10, while others, such as Theorem 3, are new. In Section 3 we describe the Erdös–Rényi theorem. We discuss the problem of contracting the graph-description of the Erdös–Rényi process into a polymer-description. We show that such a contraction destroys in general the Markov property. At this stage the following question arises naturally: what kind of grouping of states preserves the Markov property for general Markov chains? We supply a sufficient condition in Theorem 5. This leads us to consider a modified Erdös–Rényi process where graphs with cycles are excluded. This process retains the Markov property under the grouping of graph-states into polymer-states. Moreover, the corresponding reduced process is a discrete-time version of Lushnikov's process. The final connection between the two processes is made in Section 4 by studying the asymptotic distribution of the scaled number of transitions occurring during $(0, t]$ in Lushnikov's process. This turns out to be concentrated at a value $j(t)$ which increases continuously to 1 as t tends to infinity. This can be used to translate properties of the modified Erdös–Rényi process into results on Lushnikov's model and vice versa. So whenever one is interested in properties of the graph process that can be formulated in terms of polymers, one can use the simple Lushnikov process to derive these, thus avoiding tedious combinatorial arguments.

2. THE LUSHNIKOV PROCESS

The Lushnikov process is a continuous-time Markov chain with state space

$$\Omega_N = \left\{ \underline{n} \in \mathbf{N}^N: \ \sum_{j=1}^{N} j n_j = N \right\} \tag{2}$$

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

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

and they occur with rate

$$Q_{jk}(\underline{n}) = \begin{cases} \dfrac{1}{N} R_{jk} n_j n_k & \text{if} \quad j < k \\ \dfrac{1}{2N} R_{jj} n_j (n_j - 1) & \text{if} \quad j = k \end{cases} \tag{4}$$

This choice reflects the fact that in a homogeneous system, reaction (1) 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.

The probability of being in state $\underline{n}$ at time t obeys the usual forward equation:

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

where $\underline{n}_{jk}^{-}$ is defined in a similar way to $\underline{n}_{jk}^{+}$. It turns out that for a whole class of reaction rates R_{jk} and initial conditions $p_0(\underline{n})$, Eq. (5) can be solved in terms of a system of ordinary differential equations.[6,10] Here we concentrate on the reaction rate

$$R_{jk} = jk \tag{6}$$

and the pure monomer initial condition

$$p_0(\underline{n}) = \begin{cases} 1 & \text{if} \quad \underline{n} = (1, 0, 0,..., 0) \\ 0 & \text{otherwise} \end{cases} \tag{7}$$

Theorem 1. With reaction rate (6) and initial condition (7), the solution of Eq. (5) is

$$p_t(\underline{n}) = \begin{cases} \prod_{j=1}^{N} \frac{a_{N,j}^{n_j}(t)}{n_j!} & \text{if } \sum_{j=1}^{N} jn_j = N \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

where the functions $a_{N,j}(t)$ obey the differential system

$$\begin{cases} N\dot{a}_{N,1}(t) = -\frac{1}{2}(N-1)\, a_{N,1}(t) \\ N\dot{a}_{N,j}(t) = \frac{1}{2}\sum_{r=1}^{j-1} r(j-r)\, a_{N,r}(t)\, a_{N,j-r}(t) - \frac{1}{2}(N-j)\, ja_{N,j}(t), j \geqslant 2 \end{cases} \tag{9}$$

and the initial condition

$$a_{N,j}(0) = \begin{cases} (N!)^{1/N} & \text{if } j=1 \\ 0 & \text{if } j \geqslant 1 \end{cases} \tag{10}$$

We refer to ref. 10 for a proof of this result and its extensions. The mean and factorial moments of the random variables $N_j(t)$ that give the number of j-mers of time t are related to the functions $a_{N,j}(t)$ in a simple way:

Proposition 1. We have

$$\mathbf{E}[N_j(t)] = \frac{(N!)^{(N-j)/N}}{(N-j)!}\, e^{-j(N-j)t/2N} a_{N,j}(t) \tag{11}$$

$$\mathbf{E}[N_j(t)(N_j(t)-1)] = \frac{(N!)^{(N-2j)/N}}{(N-2j)!}\, e^{-2j(N-2j)t/2N} a_{N,j}^2(t) \tag{12}$$

Formula (11) is proven in ref. 10, and (12) can be obtained in a similar way. Although an explicit formula for $a_{N,j}(t)$ can be derived,[6,10] we find it more convenient to work with the following bounds:

Proposition 2. We have

$$e^{-jt/2} C_j(t) \leqslant \frac{a_{N,j}(t)}{N} \leqslant e^{j^2t/2N} e^{-jt/2} C_j(t) \tag{13}$$

where

$$C_j(t) = \frac{1}{N^j}(N!)^{j/N} \frac{j^{j-2}}{j!}\, t^{j-1} \tag{14}$$

Proof. The upper bound is proven in Lemma 1 of ref. 10. To get the lower bound, define the functions $\tilde{a}_{N,j}(t)$ as the solutions of the equations

$$\begin{cases} \dot{\tilde{a}}_{N,1}(t) = -\frac{1}{2}\tilde{a}_{N,1}(t) \\ \dot{\tilde{a}}_{N,j}(t) = \frac{1}{2N}\sum_{r=1}^{j-1} r(j-r)\,\tilde{a}_{N,r}(t)\,\tilde{a}_{N,j-r}(t) - \frac{j}{2}\tilde{a}_{N,j}(t), \qquad j \geqslant 2 \end{cases} \tag{15}$$

with initial condition (10). Obviously

$$a_{N,j}(t) \geqslant \tilde{a}_{N,j}(t) \tag{16}$$

[note that the positivity of $\tilde{a}_{N,j}(t)$ can be proven as in Theorem 1 of ref. 10]. Define now

$$C_j(t) = e^{jt/2}\tilde{a}_{N,j}(t)/N \tag{17}$$

and use (15) to obtain

$$\begin{cases} \dot{C}_1(t) = 0 \\ \dot{C}_j(t) = \frac{1}{2}\sum_{r=1}^{j-1} r(j-r)\,C_r(t)\,C_{j-r}(t), \qquad j \geqslant 2 \end{cases} \tag{18}$$

which is well known to have (14) as its solution under the initial condition (10).[9,10] ∎

The double bound of Proposition 2 gives us the limit of $a_{N,j}(t)/N$ as N tends to infinity with j fixed, and thus the limit of $\mathbf{E}[N_j(t)]/N$.

Corollary 1. (i)

$$\lim_{N\to\infty} \frac{a_{N,j}(t)}{N} = e^{-j}e^{-jt/2}\frac{j^{j-2}t^{j-1}}{j!} \tag{19}$$

(ii)

$$\lim_{N\to\infty} \frac{\mathbf{E}[N_j(t)]}{N} = e^{-jt}\frac{j^{j-2}t^{j-1}}{j!} \tag{20}$$

Proof. Formula (19) follows from (13), (14), and the standard Stirling estimate:

$$e^{7/8}N^N e^{-N}\sqrt{N} \leqslant N! \leqslant eN^N e^{-N}\sqrt{N} \tag{21}$$

In order to prove (20), we use (11), (13), and (14) to obtain

$$\frac{N!}{N^j(N-j)!}\, e^{-j(1-j/2N)t}\, \frac{j^{j-2}t^{j-1}}{j!} \leqslant \frac{\mathbf{E}[N_j(t)]}{N} \leqslant \frac{N!}{N^j(N-j)!}\, e^{-j(1-j/N)t}\, \frac{j^{j-2}t^{j-1}}{j!} \tag{22}$$

The result follows since the combinatorial factor

$$N!/N^j(N-j)! = (1-1/N)(1-2/N)\cdots[1-(j-1)/N] \tag{23}$$

tends to 1 as N tends to infinity. ▮

The single most important phenomenon associated with systems of reacting polymers is that of *gelation*, that is, the formation of a polymer of macroscopic size within a finite time. In order to study this effect, we compute the density contributed by polymers of size at least αN:

$$\lim_{N\to\infty} \frac{1}{N} \sum_{\alpha N \leqslant j \leqslant N} j\mathbf{E}[N_j(t)] \tag{24}$$

If, for some $\alpha > 0$, $t \geqslant 0$, the above quantity is strictly positive, we say that *gelation has occurred at time t*. We proved in ref. 10 that for any Borel subset A of $[0, 1]$

$$\limsup_{N\to\infty} \frac{1}{N} \log\left(\frac{1}{N} \sum_{j: j/N \in \bar{A}} j\mathbf{E}[N_j(t)]\right) \leqslant -\inf_{x\in\bar{A}} I_t(x) \tag{25}$$

where

$$I_t(x) = (1-x)\log(1-x) - x\log t + x(1-x)t \tag{26}$$

This implies that if $[\alpha, \beta]$ is an interval where $I_t(x)$ is strictly positive, the density contributed by polymers of size between αN and βN tends to zero exponentially fast as $N\to\infty$. It remains to determine the intervals of positivity of $I_t(x)$. In the following lemma we sharpen the results of ref. 10.

Lemma 1. (i) Let $t_0 < 1$ be the smallest positive root of the function

$$f(t) = [1-u(t)]\{1 + t[1-u(t)]\} + \log u(t) \tag{27}$$

where

$$u(t) = \frac{1}{2t}\,[1-(1+4t\log t)^{1/2}] \tag{28}$$

Then for $t < t_0$, $I_t(x)$ is strictly positive on $(0, 1]$ and vanishes at $x = 0$.

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

Remarks. (i) Formula (27) is obtained from $I'_{t_0}(x_0) = I_{t_0}(x_0) = 0$ by eliminating x_0; see Fig. 1.

(ii) The functions f and u of Lemma 1 are defined on the interval $[t_1, 1)$, where t_1 is the larger of the two roots of $1 + 4t \log t$.

Formula (25) and Lemma 1 can be used to characterize gelation in Lushnikov's model. We quote the following result from ref. 10.

Theorem 2. (i) Let t_0 be as in Lemma 1. Then for any $t < t_0$, $0 < \alpha \leqslant 1$

$$\lim_{N \to \infty} \frac{1}{N} \sum_{\alpha N \leqslant j \leqslant N} j\mathbf{E}[N_j(t)] = 0 \tag{29}$$

(ii) Let $t_\varepsilon > 1$ be the largest solution of

$$te^{-(1-\varepsilon)t} = e^{-1} \tag{30}$$

Then for any $\varepsilon > 0$, $\delta > 0$, and $t > t_\varepsilon$

$$\liminf_{N \to \infty} \frac{1}{N} \sum_{(\beta(t) - \delta)N \leqslant j \leqslant N} j\mathbf{E}[N_j(t)] \geqslant 1 - \frac{x_\varepsilon(t)}{t} > 0 \tag{31}$$

where $\beta(t)$ is as in Lemma 1 and $x_\varepsilon(t)$ is the smallest nonnegative solution of

$$xe^{-x} = te^{-(1-\varepsilon)t} \tag{32}$$

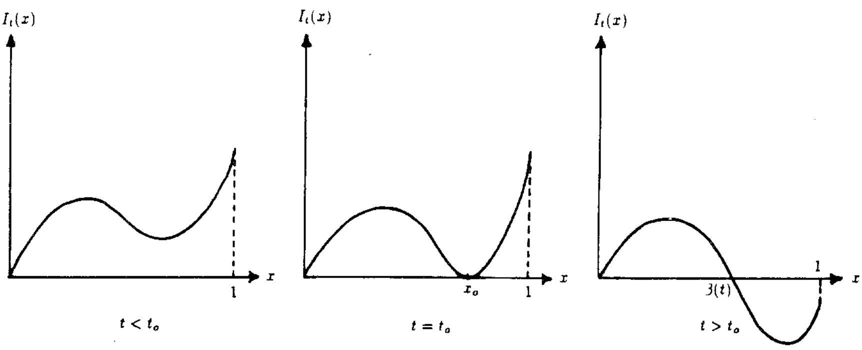


Fig. 1. The function $I_t(x)$ in the three different regimes.

Theorem 2(i) shows that there is no gelation up to time t_0; Theorem 2(ii) shows that at any time $t>1$ the system is in a gelled state, with a polymer of size at least $N\beta(t)$.

To conclude this section, we give a more detailed description of the system for $t<t_0$. Not only is there no polymer of macroscopic length in this regime, but in fact the largest polymer is of size at most $(t-1-\log t)^{-1}\log N$.

Theorem 3. Let $t<t_0$, with t_0 as in Lemma 1, and define

$$\alpha(t)=(t-1-\log t)^{-1} \tag{33}$$

Then for any $\varepsilon>0$

$$\lim_{N\to\infty}\frac{1}{N}\sum_{(\alpha(t)+\varepsilon)\log N\leqslant j\leqslant N} j\mathbf{E}[N_j(t)]=0 \tag{34}$$

Proof. Use Propositions 1 and 2 to obtain

$$\begin{aligned} m_{N,t}(A)&\equiv\frac{1}{N}\sum_{j:\,j/N\in A} j\mathbf{E}[N_j(t)]\\ &\leqslant\frac{1}{N}\sum_{j:\,j/N\in A}\binom{N}{j}\left(\frac{tj}{N}\right)^{j-1}e^{-j(1-j/N)t} \end{aligned}\tag{35}$$

where A is any Borel subset of $[0,1]$. The Stirling estimate (21) yields

$$\begin{aligned}\binom{N}{j}\leqslant\exp\bigg\{&-j\log\left(\frac{j}{N}\right)-(N-j)\log\left(1-\frac{j}{N}\right)\\ &-\frac{1}{2}\log\left[\frac{j(1-j/N)}{N}\right]-\frac{1}{2}\log N-\frac{3}{4}\bigg\}\end{aligned}\tag{36}$$

which combines with (35) to give a bound that we write in the form

$$m_{N,t}(A)\leqslant\int_A e^{-NI_N(t,x)}\mu_N(dx) \tag{37}$$

where

$$\mu_N(dx)=\frac{1}{N}\sum_{j=1}^{N}\delta_{j/N}(dx) \tag{38}$$

is the normalized counting measure and

$$\begin{aligned} I_N(t,x)={}&(1-x)\log(1-x)-x\log t+x(1-x)t+(\log N)/2N\\ &+(\log\{xt[x(1-x)]^{1/2}\})/N+3/4N \end{aligned}\tag{39}$$

Writing

$$I_N(t, x) = I_t(x) + J_N(t, x) \tag{40}$$

with $I_t(x)$ as in (26), we note that the remainder term $J_N(t, x)$ is increasing in x on (0, 3/4). On the other hand,

$$\begin{aligned} m_{N,t}&\left[(\alpha(t)+\varepsilon)\frac{\log N}{N}, 1\right] \\ &= m_{N,t}\left[(\alpha(t)+\varepsilon)\frac{\log N}{N}, \frac{3}{4}\right] + m_{N,t}\left(\frac{3}{4}, 1\right] \end{aligned} \tag{41}$$

and the last term tends to zero as $N \to \infty$ by Theorem 2(i). For the first term we use (37) with

$$A_{N,t} = \left[(\alpha(t)+\varepsilon)\frac{\log N}{N}, \frac{3}{4}\right] \tag{42}$$

to get, for N large enough,

$$\begin{aligned} m_{N,t}(A_{N,t}) &\leqslant \{\exp[-N \inf_{x \in A_{N,t}} I_N(t, x)]\}\, \mu_N(A_{N,t}) \\ &\leqslant \exp\{-N I_N(t, [\alpha(t)+\varepsilon] \log N/N)\} \end{aligned} \tag{43}$$

In obtaining (43) we used the fact that $J_N(t, x)$ is increasing on $A_{N,t}$ and Lemma 1(i).

Finally, we get from (39)

$$\begin{aligned} I_N\left(t, [\alpha(t)+\varepsilon]\frac{\log N}{N}\right) &= [\alpha(t)+\varepsilon]\frac{\log N}{N}(-1-\log t + t) \\ &\quad + \frac{\log N}{N}\left[\frac{1}{2} - \frac{3}{2}\right] + O\left(\frac{\log\log N}{N}\right) \\ &= \varepsilon(t-1-\log t)\frac{\log N}{N} + O\left(\frac{\log\log N}{N}\right) \end{aligned} \tag{44}$$

We get from (43) and (44), noting that $\alpha(t) > 0$ when $t \neq 1$,

$$\limsup_{N \to \infty} m_{N,t}(A_{N,t}) = 0 \tag{45}$$

and since $m_{N,t}(A_{N,t}) \geqslant 0$, (34) follows. ∎

3. THE ERDÖS–RÉNYI PROCESS

Denote by $\mathscr{G}_N$ the set of all graphs (without multiple edges) on N labeled vertices. Define a Markov chain $\{G_n^{(N)},\ n=0,1,2,...\}$ on $\mathscr{G}_N$ by the following transition probabilities:

$$\mathbf{P}[G_{n+1}^{(N)}=\beta \mid G_n^{(N)}=\alpha]$$
$$=\begin{cases} \left(\binom{N}{2}-|\alpha|\right)^{-1} & \text{if the graph } \beta \text{ can be obtained from } \alpha \text{ by adding one edge} \\ 0 & \text{otherwise} \end{cases} \tag{46}$$

where $|\alpha|$ denotes the number of edges of the graph α; note that $\binom{N}{2}$ is the total number of edges that can be supported by N vertices. In words, each step of the process consists in adding one edge, any of the $\binom{N}{2}-|\alpha|$ remaining edges being equally likely to be chosen. Obviously, after $\binom{N}{2}$ steps at most the complete graph is reached, and the definition of the process is supplemented by making this a trap state.

In a series of papers that founded the theory of random graphs Erdös and Rényi[11,12] studied extensively the asymptotic properties of the Markov chain $G_n^{(N)}$ in the limit

$$N\to\infty,\quad n\to\infty,\quad \frac{n}{N}\to c>0 \tag{47}$$

when the initial state is the empty graph. One of their most striking result is the following.[12-14]

Theorem 4. Let $L(\gamma)$ denote the size (i.e., the number of vertices) of the largest connected component of the graph γ. Then, with probability tending to one in the limit (47): (i) if $c<1/2$,

$$L(G_n^{(N)})/\log N \to (2c-1-\log 2c)^{-1} \tag{48}$$

(ii) If $c>1/2$,

$$\frac{L(G_n^{(N)})}{N}\to 1-\frac{1}{2c}\sum_{j=1}^{\infty}\frac{j^{j-1}}{j!}(2ce^{-2c})^j \tag{49}$$

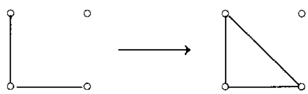
The striking change of regime that takes place at $c=1/2$ is known in random graph theory as the *emergence of the giant component.* The similarity between this phenomenon and gelation of polymers is obvious. However, if one tries to relate the two, one has to face the difficulty that the Lushnikov and Erdös–Rényi processes have different state spaces; moreover, one is in continuous time and the other is discrete time. The second point will be addressed in the next section; as for the first point, each polymer-state $\underline{n}$ in Ω_N corresponds to a set of graph states in $\mathscr{G}_N$. Hence the process $\{G_n^{(N)},\ n=0, 1, 2,...\}$ induces naturally a process with states in Ω_N: this is obtained by lumping together all the graph-states that have the same polymer-description. However, such a procedure does not preserve the Markov character of the original process; indeed, it is easy to see that unless special initial conditions are chosen,

$$\mathbf{P}[G_{n+1}^{(4)} \in (0, 0, 0, 1) \mid G_n^{(4)} \in (1, 0, 1, 0),\ G_{n-1}^{(4)} \in (1, 0, 1, 0)] = 1 \tag{50}$$

whereas

$$\mathbf{P}[G_{n+1}^{(4)} \in (0, 0, 0, 1) \mid G_n^{(4)} \in (1, 0, 1, 0)] < 1 \tag{51}$$

This is because in the second case the $(n+1)$th transition can be of the form



i.e., $(1, 0, 1, 0) \to (1, 0, 1, 0)$, whereas such events are precluded by the further conditioning of the first case.

In fact, the question of the preservation of the Markov property under grouping of states is of much wider interest than the particular example under consideration, and we give a sufficient condition in a general setting:

Theorem 5. Let $\{X_n,\ n=0, 1, 2,...\}$ be a discrete-time Markov chain with states $x_1, x_2,..., x_j,...$. Group states into sets $A_1, A_2,..., A_\alpha,...$. A sufficient condition for the resulting process to retain the Markov property is that either of the functions

$$f_\alpha(x) = \mathbf{P}[X_{n-1} \in A_\alpha \mid X_n = x] \tag{52}$$

$$g_\alpha(x) = \mathbf{P}[X_{n+1} \in A_\alpha \mid X_n = x] \tag{53}$$

is constant on each set A_β for all α, i.e., $f_\alpha(x) = f_{\alpha,\beta}$ or $g_\alpha(x) = g_{\alpha,\beta}$ whenever $x \in A_\beta$.

Proof.

$$\mathbf{P}[X_{n+1} \in A_{n+1} \mid X_1 \in A_1,..., X_n \in A_n]$$

$$= \frac{\sum_{j=1}^n \sum_{x_j \in A_j} \mathbf{P}[X_{n+1} \in A_{n+1}, X_1 = x_1,..., X_n = x_n]}{\sum_{j=1}^n \sum_{y_j \in A_j} \mathbf{P}[X_1 = y_1,..., X_n = y_n]} \tag{54}$$

$$= \frac{\sum_{j=1}^n \sum_{x_j \in A_j} \mathbf{P}[X_{n+1} \in A_{n+1} \mid X_n = x_n]\ \mathbf{P}[X_1 = x_1,..., X_n = x_n]}{\sum_{j=1}^n \sum_{y_j \in A_j} \mathbf{P}[X_1 = y_1,..., X_n = y_n]} \tag{55}$$

where the Markov property of the original process has been used. At this stage, it is clear that if $g_{n+1}(x_n)$ is independent of x_n for x_n in A_n, expression (55) reduces to $g_{n+1,n}$, which is itself equal to $\mathbf{P}[X_{n+1} \in A_{n+1} \mid X_n \in A_n]$, establishing the Markov property in a trivial way.

In order to check the other version of the condition, we write (55) as

$$\frac{\sum_{j=1}^{n} \sum_{x_j \in A_j} g_{n+1}(x_n)\{\prod_{l=1}^{n-1} \mathbf{P}[X_l = x_l \mid X_j = x_j, l+1 \leqslant j \leqslant n]\}\, \mathbf{P}[X_n = x_n]}{\sum_{j=1}^{n} \sum_{y_j \in A_j}\{\prod_{l=1}^{n-1} \mathbf{P}[X_l = y_l \mid X_j = y_j, l+1 \leqslant j \leqslant n]\}\, \mathbf{P}[X_n = y_n]} \tag{56}$$

which, using the Markov property and notation (52), reads

$$\begin{aligned}&\left\{\sum_{j=2}^{n} \sum_{x_j \in A_j} g_{n+1}(x_n) f_1(x_2)\, \mathbf{P}[X_2 = x_2 \mid X_3 = x_3]\right.\\ &\qquad \left. \cdots \mathbf{P}[X_{n-1} = x_{n-1} \mid X_n = x_n]\, \mathbf{P}[X_n = x_n]\right\}\\ &\times\left\{\sum_{j=2}^{n} \sum_{y_j \in A_j} f_1(y_2)\, \mathbf{P}[X_2 = y_2 \mid X_3 = y_3]\right.\\ &\qquad \left. \cdots \mathbf{P}[X_{n-1} = y_{n-1} \mid X_n = y_n]\, \mathbf{P}[X_n = y_n]\right\}^{-1}\end{aligned} \tag{57}$$

If $f_\alpha(x)$ is independent of x for x in A_β, this becomes

$$\begin{aligned}&\left\{\sum_{j=3}^{n} \sum_{x_j \in A_j} g_{n+1}(x_n) f_2(x_3)\, \mathbf{P}[X_3 = x_3 \mid X_4 = x_4]\right.\\ &\qquad \left. \cdots \mathbf{P}[X_{n-1} = x_{n-1} \mid X_n = x_n]\, \mathbf{P}[X_n = x_n]\right\}\\ &\times\left\{\sum_{j=3}^{n} \sum_{y_j \in A_j} f_2(y_3)\, \mathbf{P}[X_3 = y_3 \mid X_4 = y_4]\right.\\ &\qquad \left. \cdots \mathbf{P}[X_{n-1} = y_{n-1} \mid X_n = y_n]\, \mathbf{P}[X_n = y_n]\right\}^{-1}\end{aligned} \tag{58}$$

$$= \cdots = \frac{\sum_{x_n \in A_n} g_{n+1}(x_n)\, \mathbf{P}[X_n = x_n]}{\sum_{y_n \in A_n} \mathbf{P}[X_n = y_n]} = \mathbf{P}[X_{n+1} \in A_{n+1} \mid X_n \in A_n] \tag{59}$$

proving the Markov property. ∎

Remark. In the above proof, we made repeated use of the formula

$$\mathbf{P}[X_1 = x_1 \mid X_2 = x_2, \ldots, X_n = x_n] = \mathbf{P}[X_1 = x_1 \mid X_2 = x_2] \tag{60}$$

which is an easy consequence of the usual form of the Markov property.

As we have already noticed, the Erdös–Rényi process fails in general to retain its Markov character when contracted to a polymer description. This leads us to define a *modified Erdös–Rényi process* $\{\tilde{G}_n^{(N)}, n = 0, 1, 2, \ldots\}$ with state space $\tilde{\mathscr{G}}_N$ the set of all graphs *without cycle* on N labeled vertices.

The transition rule for $\tilde{G}_n^{(N)}$ is as for $G_n^{(N)}$:

$$\mathbf{P}[\tilde{G}_{n+1}^{(N)} = \beta \mid \tilde{G}_n^{(N)} = \alpha] = \begin{cases} P_\alpha & \text{if the graph } \beta \text{ can be obtained from } \alpha \text{ by adding one edge} \\ 0 & \text{otherwise} \end{cases} \tag{61}$$

where the number P_α (independent of β) will be computed shortly. We check now that $\tilde{G}_n^{(N)}$ satisfies the second criterion in Theorem 5:

Proposition 3. Take any graph $\alpha \in \underline{n}$. Then

$$\mathbf{P}[\tilde{G}_{n+1}^{(N)} \in \underline{n}_{jk}^{+} \mid \tilde{G}_n^{(N)} = \alpha] = \begin{cases} \dfrac{2jkn_jn_k}{N^2 - \sum_{j=1}^N j^2 n_j} & \text{if } j < k \\ \dfrac{j^2 n_j(n_j - 1)}{N^2 - \sum_{j=1}^N j^2 n_j} & \text{if } j = k \end{cases} \tag{62}$$

Proof. Since all transitions out of α have the same probability P_α, we just have to count the number of transitions from α to $\underline{n}_{jk}^{+}$; if $j \neq k$, such a transition is effected by adding an extra link between a vertex belonging to a j-mer and another one belonging to a k-mer within the graph α, and this can be done in jkn_jn_k ways, giving the total probability $P_\alpha jkn_jn_k$. If $j = k$, one has to choose two distinct j-mers, so that the probability is $P_\alpha j^2 n_j(n_j - 1)/2$. Finally, the number P_α is determined by normalization:

$$\sum_{\substack{j,k=1 \\ j<k}}^{N} P_\alpha jkn_jn_k + \tfrac{1}{2} \sum_{j=1}^{N} P_\alpha j^2 n_j(n_j - 1) = 1 \tag{63}$$

which, using $\sum_{j=1}^N jn_j = N$, yields

$$P_\alpha = 2\left(N^2 - \sum_{j=1}^{N} j^2 n_j\right)^{-1} \quad \blacksquare \tag{64}$$

Since the transition probability (62) depends on the graph α only through its polymer class $\underline{n}$, Theorem 5 applies and the contracted process $\{\underline{X}_m^{(N)}, m=0, 1, 2,...\}$ defined by

$$\underline{X}_m^{(N)} = \underline{n} \Leftrightarrow \tilde{G}_m^{(N)} \in \underline{n} \tag{65}$$

is a Markov process on Ω_N. We will see in the next section that $\{\underline{X}_m^{(N)}, m=0, 1, 2,...\}$ is closely connected to the Lushnikov process $\{\underline{N}_t, t \geqslant 0\}$ of Section 2.

Remark. We showed in the discussion preceding Theorem 5 that in general the original Erdös–Rényi process loses the Markov property when graph-states are lumped into polymer-states. However, the Markov property is retained if one restricts one's attention to initial conditions concentrated on graphs with a fixed number of edges.

4. RELATION BETWEEN THE LUSHNIKOV PROCESS AND THE MODIFIED ERDÖS–RÉNYI PROCESS

It follows from Proposition 3 that the process $\{\underline{X}_m^{(N)}, m=0, 1, 2,...\}$ obtained by contracting the modified Erdös–Rényi process [see (65)] has the transition probabilities

$$\mathbf{P}[\underline{X}_{m+1}^{(N)} = \underline{n}_{jk}^{+} \mid \underline{X}_m^{(N)} = \underline{n}] = \begin{cases} \dfrac{2jkn_j n_k}{N^2 - \sum_{j=1}^{N} j^2 n_j} & \text{if } j<k \\ \dfrac{j^2 n_j(n_j-1)}{N^2 - \sum_{j=1}^{N} j^2 n_j} & \text{if } j=k \end{cases} \tag{66}$$

Comparing this to (4) with $R_{jk} = jk$, we see that $\underline{X}_m^{(N)}$ is the discrete-time Markov chain embedded in the Lushnikov process $\{\underline{N}(t), t \geqslant 0\}$; in other words, if $J_N(t)$ denotes the (random) number of transitions effected by the Lushnikov process during $(0, t]$, we have

$$\mathbf{P}[\underline{X}_m^{(N)} = \underline{n}] = \mathbf{P}[\underline{N}(t) = \underline{n} \mid J_N(t) = m] \tag{67}$$

Hence, if Λ_N is any set of configurations in Ω_N,

$$\mathbf{P}[\underline{N}(t) \in \Lambda_N] = \sum_{m=0}^{N} \mathbf{P}[\underline{N}(t) \in \Lambda_N \mid J_N(t) = m]\, \mathbf{P}[J_N(t) = m] \tag{68}$$

$$= \sum_{m=0}^{N} \mathbf{P}[\underline{X}_m^{(N)} \in \Lambda_N]\, \mathbf{P}[J_N(t) = m] \tag{69}$$

$$= \int_{[0,1]} \mathbf{P}[\underline{X}_{xN}^{(N)} \in \Lambda_N]\, dF_{N,t}(x) \tag{70}$$

where $F_{N,t}$ is the scaled probability distribution function of $J_N(t)$:

$$F_{N,t}(x) = \mathbf{P}[J_N(t)/N \leqslant x] \tag{71}$$

We see from (70) that in order to relate the asymptotic properties of $\underline{N}(t)$ to those of $\underline{X}^{(N)}_{xN}$ as $N \to \infty$, it suffices to know the asymptotic distribution of $J_N(t)/N$. But in Lushnikov's model each transition reduces the total number of polymers by one unit, so that

$$J_N(t) = N - \sum_{j=1}^{N} N_j(t) \tag{72}$$

We will use (72) to prove that $J_N(t)/N$ is asymptotically concentrated at

$$j(t) = 1 - \sum_{k=1}^{\infty} g_k(t) \tag{73}$$

where

$$g_k(t) = \frac{k^{k-2}}{k!} e^{-kt} t^{k-1} \tag{74}$$

First we prove that (73) is a lower bound for the expected value of $J_N(t)/N$.

Proposition 4. We have

$$\liminf_{N \to \infty} \mathbf{E}[J_N(t)]/N \geqslant j(t) \tag{75}$$

Proof. For any $0 < \alpha < 1$, we have

$$\frac{\mathbf{E}[J_N(t)]}{N} = 1 - \frac{1}{N} \sum_{1 \leqslant j \leqslant \alpha N} \mathbf{E}[N_j(t)] - \frac{1}{N} \sum_{\alpha N < j \leqslant N} \mathbf{E}[N_j(t)] \tag{76}$$

The last term in (76) is easily bounded:

$$\frac{1}{N} \sum_{\alpha N < j \leqslant N} \mathbf{E}[N_j(t)] < \frac{1}{\alpha N} \frac{1}{N} \sum_{\alpha N < j \leqslant N} j\mathbf{E}[N_j(t)] \leqslant \frac{1}{\alpha N} \tag{77}$$

On the other hand, (22) implies

$$\frac{1}{N} \sum_{1 \leqslant j \leqslant \alpha N} \mathbf{E}[N_j(t)] \leqslant \sum_{1 \leqslant j \leqslant \alpha N} \frac{j^{j-2}}{j!} e^{-(1-\alpha)jt} t^{j-1} \tag{78}$$

$$\leqslant \sum_{j=1}^{\infty} \frac{j^{j-2}}{j!} e^{-(1-\alpha)jt} t^{j-1} \tag{79}$$

where the infinite series in (79) converges whenever

$$t \notin [t_0(\alpha), t_1(\alpha)] \tag{80}$$

where $t_0(\alpha) \leqslant t_1(\alpha)$ are the two roots of the equation

$$te^{-(1-\alpha)t} = e^{-1} \tag{81}$$

Hence, for any t satisfying (80),

$$\frac{\mathbf{E}[J_N(t)]}{N} \geqslant 1 - \sum_{j=1}^{\infty} \frac{j^{j-2}}{j!} e^{-(1-\alpha)jt} t^{j-1} - \frac{1}{\alpha N} \tag{82}$$

so that

$$\liminf_{N\to\infty} \frac{\mathbf{E}[J_N(t)]}{N} \geqslant 1 - \sum_{j=1}^{\infty} \frac{j^{j-2}}{j!} e^{-(1-\alpha)jt} t^{j-1} \tag{83}$$

This holds for any α. Let α tend to zero and use dominated convergence to get the result (75) for any $t \neq 1$ [note that $\lim_{\alpha\to 0} t_0(\alpha) = \lim_{\alpha\to 0} t_1(\alpha) = 1$]. The inequality (75) holds also at $t=1$ because $\mathbf{E}[J_N(t)]$ is an increasing function of t. ∎

We show now that $J_N(t)/N$ is bounded above by $j(t)$ in probability.

Proposition 5. For any $\varepsilon > 0$,

$$\lim_{N\to\infty} \mathbf{P}[J_N(t)/N \geqslant j(t) + \varepsilon] = 0 \tag{84}$$

Proof. Using (72), we have, for any $l \leqslant N$,

$$\mathbf{P}[J_N(t)/N \geqslant j(t) + \varepsilon]$$

$$= \mathbf{P}\left[\frac{1}{N}\sum_{k=1}^{N} N_k(t) \leqslant 1 - j(t) - \varepsilon\right] \tag{85}$$

$$\leqslant \mathbf{P}\left[\frac{1}{N}\sum_{k=1}^{l} N_k(t) \leqslant 1 - j(t) - \varepsilon\right] \tag{86}$$

$$\leqslant \mathbf{P}\left[\frac{1}{N}\sum_{k=1}^{l} \{N_k(t) - \mathbf{E}[N_k(t)]\} \leqslant 1 - j(t) - \varepsilon - \sum_{k=1}^{l} \frac{N!}{N^k(N-k)!} g_k(t)\, e^{l^2 t/N}\right] \tag{87}$$

with $g_k(t)$ as in (74). We can rewrite (87) as $F_{N,l}(x_{N,l})$, where $F_{N,l}$ is the probability distribution function of the random variable

$$\frac{1}{N}\sum_{k=1}^{l} \{N_k(t) - \mathbf{E}[N_k(t)]\} \tag{88}$$

For fixed l, the random variable (88) is asymptotically concentrated at zero as $N \to \infty$ because by (12) we can compute the variance of any $N_k(t)/N$ to be

$$\mathbf{D}[N_k(t)/N] = O(N^{-1}) \tag{89}$$

Hence

$$\lim_{N \to \infty} F_{N,t}(x) = I^+(x) = \begin{cases} 1 & \text{if} \quad x \geqslant 0 \\ 0 & \text{if} \quad x < 0 \end{cases} \tag{90}$$

On the other hand,

$$\lim_{N \to \infty} x_{N,l} = 1 - j(t) - \varepsilon - \sum_{k=1}^{l} g_k(t) = -\varepsilon + \sum_{k=l}^{\infty} g_k(t) \equiv x_l \tag{91}$$

By choosing l large enough, we can arrange to have $x_l < -\varepsilon/2$; hence, with this choice of l, there exists M such that

$$x_{N,l} < -\varepsilon/4 \qquad \text{whenever} \quad n \geqslant M \tag{92}$$

Thus

$$F_{N,l}(x_{N,l}) \leqslant F_{N,l}(-\varepsilon/4) \tag{93}$$

converges to zero as N tends to infinity. ∎

Since $J_N(t)/N$ is bounded above by $j(t)$ in probability, whereas its expectation is bounded below by $j(t)$, it follows that it is asymptotically concentrated at $j(t)$; the necessary argument to prove this is best stated as a general lemma:

Lemma 2. Let $\{A_n, \ n = 1, 2, 3, \ldots\}$ be a sequence of random variables such that (i)

$$\forall \varepsilon > 0, \quad \lim_{n \to \infty} \mathbf{P}[A_n \geqslant \varepsilon] = 0 \tag{94}$$

(ii)

$$\liminf_{n \to \infty} \mathbf{E}[A_n] \geqslant 0 \tag{95}$$

and (iii)

$$\forall \varepsilon > 0, \quad \exists b_\varepsilon < \infty: \quad \mathbf{E}[A_n \mid A_n \geqslant \varepsilon] \leqslant b_\varepsilon \quad \forall n \tag{96}$$

Then (a)

$$\lim_{n\to\infty} \mathbf{E}[A_n] = \lim_{n\to\infty} \mathbf{E}[|A_n|] = 0 \tag{97}$$

and (b)

$$\forall\varepsilon > 0, \quad \lim_{n\to\infty} \mathbf{P}[|A_n| \geqslant \varepsilon] = 0 \tag{98}$$

Proof. Define

$$A_n^+ = \begin{cases} A_n & \text{when} \quad A_n \geqslant 0 \\ 0 & \text{when} \quad A_n < 0 \end{cases} \tag{99}$$

We have, using the law of total probability and (96),

$$\mathbf{E}[A_n^+] = \mathbf{E}[A_n^+ \mid A_n \geqslant \varepsilon]\, \mathbf{P}[A_n \geqslant \varepsilon] + \mathbf{E}[A_n^+ \mid A_n < \varepsilon]\, \mathbf{P}[A_n < \varepsilon] \tag{100}$$

$$\leqslant b_\varepsilon \mathbf{P}[A_n \geqslant \varepsilon] + \varepsilon \tag{101}$$

Thus, using (94),

$$\limsup_{n\to\infty} \mathbf{E}[A_n^+] \leqslant \varepsilon \tag{102}$$

Since (102) holds for any ε and $A_n^+ \geqslant 0$, we conclude

$$\lim_{n\to\infty} \mathbf{E}[A_n^+] = 0 \tag{103}$$

Formula (97) follows because

$$\limsup_{n\to\infty} \mathbf{E}[|A_n|] = \limsup_{n\to\infty} \mathbf{E}[2A_n^+ - A_n] \tag{104}$$

$$= -\liminf_{n\to\infty} \mathbf{E}[A_n] \leqslant 0 \tag{105}$$

Finally, (98) follows from (97) by Chebyshev's inequality:

$$\mathbf{P}[|A_n| \geqslant \varepsilon] \leqslant \varepsilon^{-1}\mathbf{E}[|A_n|] \quad \blacksquare \tag{106}$$

We can now characterize the asymptotic distribution of $J_N(t)/N$:

Theorem 6. For any $\varepsilon > 0$

$$\lim_{N\to\infty} \mathbf{P}[|J_N(t)/N - j(t)| \geqslant \varepsilon] = 0 \tag{107}$$

Proof. Apply Lemma 2 with

$$A_N = J_N(t)/N - j(t) \tag{108}$$

Conditions (i) and (ii) hold by Propositions 5 and 4, respectively. Condition (iii) holds trivially because $J_N(t)/N \leqslant 1$. ▌

In order to investigate the properties of the function $j(t)$ defined in (73), it is best to relate it to the series

$$F(u) = \sum_{j=1}^{\infty} \frac{j^{j-1}}{j!} u^j \tag{109}$$

which is well known to have radius of convergence e^{-1} and to be equal to the smaller of the two solutions of the equation

$$xe^{-x} = u, \qquad x \geqslant 0 \tag{110}$$

Proposition 6. (i) We have

$$j(t) = 1 - \frac{1}{t} \int_0^{te^{-t}} du \frac{F(u)}{u} \tag{111}$$

(ii)

$$j(t) = \frac{t}{2} \qquad \text{whenever} \quad t \leqslant 1 \tag{112}$$

and (iii)

$$j(t) \geqslant 1 - \frac{1}{2t} \qquad \text{whenever} \quad t > 1 \tag{113}$$

Proof. Formula (111) follows from (73), (74), and (109) by a straightforward calculation. Moreover, by a simple change of variable,

$$\frac{1}{t} \int_0^{te^{-t}} du \frac{F(u)}{u} = \frac{1}{t} \int_0^{t} \frac{1-v}{v} F(ve^{-v})\, dv \tag{114}$$

But if $t \leqslant 1$, we get from (110)

$$F(ve^{-v}) = v, \qquad 0 \leqslant v \leqslant t \tag{115}$$

so that

$$j(t) = 1 - \frac{1}{t} \int_0^{t} (1-v)\, dv = \frac{t}{2} \tag{116}$$

On the other hand, for $t > 1$,

$$j(t) = 1 - \frac{1}{t} \int_0^1 \frac{1-v}{v} F(ve^{-v})\, dv - \frac{1}{t} \int_1^t \frac{1-v}{v} F(ve^{-v})\, dv \tag{117}$$

$$= 1 - \frac{1}{t} \int_0^1 (1-v)\, dv + \frac{1}{t} \int_1^t \frac{v-1}{v} F(ve^{-v})\, dv \tag{118}$$

$$= 1 - \frac{1}{2t} + \frac{1}{t} \int_1^t \frac{v-1}{v} F(ve^{-v})\, dv \geqslant 1 - \frac{1}{2t} \quad \blacksquare \tag{119}$$

Formulas (70) and (107) allow us to translate all the results that we know on $\underline{N}(t)$ into properties of the modified Erdös–Rényi process $\underline{X}_m^{(N)}$ and vice versa. For instance, define the set of configurations containing polymers of size at least yN:

$$\Lambda_N(y) = \{\underline{n} \in \Omega_N \colon n_j > 0 \text{ for some } j \geqslant yN\} \tag{120}$$

Corollary 2. (i) Let t_0 be as in Lemma 1; then for any $x < t_0/2$, $\varepsilon > 0$,

$$\lim_{N \to \infty} \mathbf{P}[\underline{X}_{xN}^{(N)} \in \Lambda_N(\varepsilon)] = 0 \tag{121}$$

(ii) Let $\beta(t)$ be as in Lemma 1; then for any $x > 1/2$, $\varepsilon > 0$,

$$\liminf_{N \to \infty} \mathbf{P}[\underline{X}_{xN}^{(N)} \in \Lambda_N(\beta(j^{-1}(x)) - \varepsilon)] > 0 \tag{122}$$

Proof. (i) We get from (70), for any $0 < \delta < j(t)$,

$$\mathbf{P}[\underline{N}(t) \in \Lambda_N(\varepsilon)] \geqslant \int_{[j(t)-\delta, 1]} \mathbf{P}[\underline{X}_{xN}^{(N)} \in \Lambda_N(\varepsilon)]\, dF_{N,t}(x) \tag{123}$$

But because of the absence of dissociation, the integrand is an increasing function of x, so that

$$\mathbf{P}[\underline{N}(t) \in \Lambda_N(\varepsilon)] \geqslant \mathbf{P}[\underline{X}_{(j(t)-\delta)N}^{(N)} \in \Lambda_N(\varepsilon)] \int_{[j(t)-\delta, 1]} dF_{N,t}(x) \tag{124}$$

The integral in the right-hand side of (124) tends to one as $N \to \infty$ by Theorem 6, so that

$$\limsup_{N \to \infty} \mathbf{P}[\underline{N}(t) \in \Lambda_N(\varepsilon)] \geqslant \limsup_{N \to \infty} \mathbf{P}[\underline{X}_{(j(t)-\delta)N}^{(N)} \in \Lambda_N(\varepsilon)] \tag{125}$$

On the other hand,

$$\mathbf{P}[N(t)\in \Lambda_N(\varepsilon)]=\mathbf{P}\left[\frac{1}{N}\sum_{\varepsilon N\leqslant j\leqslant N} jN_j(t)\geqslant \varepsilon\right] \tag{126}$$

$$\leqslant \frac{1}{\varepsilon}\mathbf{E}\left[\frac{1}{N}\sum_{\varepsilon N\leqslant j\leqslant N} jN_j(t)\right] \tag{127}$$

tends to zero as $N\to\infty$ when $t\leqslant t_0$ by Theorem 2(i). The conclusion follows since $j(t)=t/2$ when $t<1$.

(ii) We get from (70), for any $0<\delta<1-j(t)$,

$$\mathbf{P}[\underline{N}(t)\in \Lambda_N(\beta(t)-\varepsilon)]\leqslant \int_{[0,j(t)+\delta]} \mathbf{P}[\underline{X}^{(N)}_{xN}\in \Lambda_N(\beta(t)-\varepsilon)]\, dF_{N,t}(x)$$

$$+\int_{(j(t)+\delta,1]} dF_{N,t}(x) \tag{128}$$

$$\leqslant \mathbf{P}[\underline{X}^{(N)}_{(j(t)+\delta)N}\in \Lambda_N(\beta(t)-\varepsilon)]\int_{[0,j(t)+\delta]} dF_{N,t}(x)$$

$$+\int_{(j(t)+\delta,1]} dF_{N,t}(x) \tag{129}$$

again using the fact that the integrand is increasing in x. But by Theorem 6 the first integral in (129) tends to one and the second to zero as $N\to\infty$.

Hence

$$\liminf_{N\to\infty}\mathbf{P}[\underline{N}(t)\in \Lambda_N(\beta(t)-\varepsilon)]\leqslant \liminf_{N\to\infty}\mathbf{P}[\underline{X}^{(N)}_{(j(t)+\delta)N}\in \Lambda_N(\beta(t)-\varepsilon)] \tag{130}$$

On the other hand, introducing the random variable

$$Z_N=\frac{1}{N}\sum_{(\beta(t)-\varepsilon)N\leqslant j\leqslant N} jN_j(t) \tag{131}$$

we have, as in (126),

$$\mathbf{P}[\underline{N}(t)\in \Lambda_N(\beta(t)-\varepsilon)]=\mathbf{P}[Z_N>0]=\mathbf{P}[Z_N\geqslant \beta(t)-\varepsilon] \tag{132}$$

Hence

$$\mathbf{E}[Z_N]=\mathbf{E}[Z_N\,|\,Z_N\geqslant \beta(t)-\varepsilon]\,\mathbf{P}[Z_N\geqslant \beta(t)-\varepsilon]\leqslant \mathbf{P}[Z_N\geqslant \beta(t)-\varepsilon] \tag{133}$$

Combining (31), (130), (132), and (133), we get

$$\liminf_{N\to\infty} \mathbf{P}[\underline{X}^{(N)}_{(j(t)+\delta)N} \in \Lambda_N(\beta(t)-\varepsilon)] \geqslant \liminf_{N\to\infty} \mathbf{E}[Z_N] \geqslant 1-\frac{x_{\varepsilon'}(t)}{t} > 0 \tag{134}$$

The conclusion follows by putting $j(t)+\delta = x$ and using the fact that $j(t)$ and $\beta(t)$ are increasing functions of t. ▌

One can deduce from Theorem 3 that when $x < t_0/2$, the mean numerical density of polymers of size $\alpha(2x)\log N$ or more tends to zero for the process $\underline{X}^{(N)}_{xN}$ as $N\to\infty$; however, in order to prove that the *probability* of $\underline{X}^{(N)}_{xN}$ having a polymer of size exceeding $\chi \log N$ tends to zero for a suitable χ, we need a stronger version of Theorem 3.

Proposition 7. Let $t < t_0$, with t_0 as in Lemma 1; then there exists $\gamma > 0$ such that for every $\varepsilon > 0$, $\delta > 0$,

$$\lim_{N\to\infty} N^{(\varepsilon/\tilde{\alpha}-\delta)} \frac{1}{N} \sum_{(\tilde{\alpha}+\varepsilon)\log N \leqslant j \leqslant N} e^{\gamma j}\mathbf{E}[N_j(t)] = 0 \tag{135}$$

where

$$\tilde{\alpha}(t) = (t-1-\log t-\gamma)^{-1} \tag{136}$$

Proof. As in the proof of Theorem 3, we define the measures

$$l_{N,t}(A) \equiv \frac{1}{N} \sum_{j:\, j/N \in A} e^{\gamma j}\mathbf{E}[N_j(t)] \tag{137}$$

It follows from (37) that

$$l_{N,t}(A) \leqslant \int_A e^{-NK_N(t,x)}\mu_N(dx) \tag{138}$$

where

$$K_N(t,x) = I_N(t,x) - \gamma x \tag{139}$$

Now we choose γ (depending on t) sufficiently small to have $I_t(x)-\gamma(x) > 0$, $0 < x \leqslant 1$, and we argue as in (41), (43). The result follows since

$$K_N\left(t, (\tilde{\alpha}+\varepsilon)\frac{\log N}{N}\right) = \frac{\varepsilon}{\tilde{\alpha}}\frac{\log N}{N} + O\left(\frac{\log\log N}{N}\right) \tag{140}$$

so that

$$l_{N,t}[(\tilde{\alpha}+\varepsilon)(\log N)/N,\ \varepsilon/4] = O(N^{-\varepsilon/\tilde{\alpha}}) \tag{141}$$

whereas $l_{N,t}(3/4, 1]$ tends to zero exponentially fast as $N \to \infty$. ∎

We can now state a result on the probability for $\underline{N}(t)$ and $\underline{X}_{xN}^{(N)}$ to be in the set of configurations

$$\Gamma_N(y) = \{\underline{n} \in \Omega_N : n_j > 0 \text{ for some } j \geqslant y \log N\} \tag{142}$$

containing polymers of size $y \log N$ or more:

Corollary 3. Let γ and $\tilde{\alpha}$ be as in Proposition 7. Then:

(i) For $t < t_0$

$$\lim_{N\to\infty} \mathbf{P}[\underline{N}(t) \in \Gamma_N(2\tilde{\alpha})] = 0 \tag{143}$$

(ii) For $x < t_0/2$ and any $\delta > 0$

$$\lim_{N\to\infty} \mathbf{P}[\underline{X}_{xN}^{(N)} \in \Gamma_N(2\tilde{\alpha}(2x+\delta))] = 0 \tag{144}$$

Proof. Let the random variable Y_N be defined by

$$Y_N = \frac{1}{N} \sum_{2\tilde{\alpha}\log N \leqslant j \leqslant N} e^{\gamma j} N_j(t) \tag{145}$$

Then by (135) with $\varepsilon = \tilde{\alpha}$

$$\lim_{N\to\infty} N^{1-\delta}\mathbf{E}[Y_N] = 0, \qquad \forall \delta > 0 \tag{146}$$

But in view of the definitions (142), (145),

$$\mathbf{P}[\underline{N}(t) \in \Gamma_N(2\tilde{\alpha})] = \mathbf{P}[Y_N > 0] = \mathbf{P}[Y_N \geqslant N^{2\tilde{\alpha}\gamma - 1}] \tag{147}$$

so that

$$\begin{aligned} \mathbf{E}[Y_N] &= \mathbf{E}[Y_N \mid Y_N \geqslant N^{2\tilde{\alpha}\gamma-1}]\,\mathbf{P}[Y_N \geqslant N^{2\tilde{\alpha}\gamma-1}] \\ &\geqslant N^{2\tilde{\alpha}\gamma-1}\mathbf{P}[Y_N \geqslant N^{2\tilde{\alpha}\gamma-1}] \end{aligned} \tag{148}$$

Combining (147) and (148), we obtain

$$\mathbf{P}[\underline{N}(t) \in \Gamma_N(2\tilde{\alpha})] \leqslant N^{1-2\tilde{\alpha}\gamma}\mathbf{E}[Y_N] \tag{149}$$

which tends to zero by (146), thus proving (143). Formula (144) follows from (70) and (143) as in Corollary 2(i). ∎

REFERENCES

1. M. V. Smoluchovski, Versuch einer mathematischen Theorie der Koagulationskinetic kolloider Lösunger, *Z. Phys. Chem.* **92**:129–168 (1917).
2. R. L. Drake, A general mathematical survey of the coagulation equation, in *Topics in Current Aerosol Research*, part 2, G. M. Hidy and J. R. Brock, eds. (Pergamon, Oxford, 1972).
3. F. Family and D. P. Landau (eds.), *Kinetics of Aggregation and Gelation* (North-Holland, Amsterdam, 1984).
4. W. H. White, A global existence theorem for Smoluchovski's coagulation equations, *Proc. Am. Math. Soc.* **80**:273–276 (1980).
5. A. H. Marcus, Stochastic coalescence, *Technometrics* **10**:133–143 (1968).
6. A. A. Lushnikov, Certain new aspects of the coagulation theory, *Izv. Atm. Ok. Fiz.* **14**:738–743 (1978).
7. E. M. Hendriks, J. L. Spouge, M. 'Eibl, and M. Schrekenberg, Exact solutions for random coagulation processes, *Z. Phys. B* **58**:219–228 (1985).
8. P. Van Dongen, Fluctuations in coagulating systems, *J. Stat. Phys.* **49**:879–926 (1987).
9. R. M. Ziff, M. H. Ernst, and E. M. Hendriks, Kinetics of gelation and universality, *J. Phys. A* **16**:2293–2320 (1983).
10. E. Buffet and J. V. Pulé, On Lushnikov's model of gelation, *J. Stat. Phys.* **58**:1041–1058 (1990).
11. P. Erdös and A. Rényi, On random graphs I, *Publ. Math. Debrecen.* **6**:290–297 (1959).
12. P. Erdös and A. Rényi, On the evolution of random graphs, *Publ. Math. Inst. Hung. Acad. Sci.* **5**:17–61 (1960).
13. B. Bollobas, *Random Graphs* (Academic Press, London, 1985).
14. E. M. Palmer, *Graphical Evolution* (Wiley, New York, 1985).