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Abstract. As in a previous paper we consider j-mers A_j reacting irreversibly according to the scheme

$$A_j + A_k \xrightarrow[R_{jk}]{} A_{j+k}.$$

The kinetic equations for the concentration of A_j are examined, and particularly their behaviour near gelation. Only the case

$$R_{jk} = j^\alpha k^\alpha \qquad (0 \leqslant \alpha \leqslant 1)$$

is considered; this is a variation of the usual Flory–Stockmayer model to take excluded volume and cyclisation effects roughly into account. The effect on certain critical exponents is estimated.

1. Introduction

In a previous paper (Leyvraz and Tschudi 1981, hereinafter referred to as I) we discussed the mathematical theory of the following model for polymerisation, and in particular gelation: consider the substances A_j ($j = 1, 2, \ldots$) to be j-mers and take them to react in the manner

$$A_j + A_k \xrightarrow[R_{jk}]{} A_{j+k}$$

where R_{jk} is the reaction rate and satisfies $R_{jk} = R_{kj} \geqslant 0$. Dissociation of the polymers into smaller constituents is therefore disregarded. The system of kinetic equations for the concentration c_j of A_j is given in this model by

$$\frac{dc_j}{dt} = \frac{1}{2} \sum_{k=1}^{j-1} R_{k,j-k} c_k c_{j-k} - c_j \sum_{k=1}^{\infty} R_{jk} c_k.$$

Particular cases of this system have been discussed in the literature: the case $R_{jk} = R$ was solved exactly by von Smoluchowsky (1916); the case $R_{jk} = (Aj + B)(Ak + B)$ was first discussed by Stockmayer (1943), who does not, however, give an explicit time-dependent solution. Such a solution was given by McLeod (1962) in the case $R_{jk} = jk$ for times less than 1. He further showed that, if

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

is assumed, the solution cannot be continued beyond $t = 1$.

Dropping this requirement we were able to show (I) that a reasonable solution does exist for all times. This is given by

$$c_j(t)=\begin{cases}\dfrac{j^{j-3}}{(j-1)!}t^{j-1}\,e^{-jt} & (t\leqslant 1)\\[2ex] \dfrac{j^{j-3}\,e^{-j}}{(j-1)!}\dfrac{1}{t} & (t\geqslant 1).\end{cases}$$

The quantity $\Sigma_{j=1}^{\infty} jc(t)$ becomes time-dependent after $t=1$. The significance of this phenomenon and its association with the formation of infinite clusters was discussed in I. We further showed the existence of such global solutions wherever a sequence of numbers r_j could be found, such that

$$\text{(i)}\ R_{jk}\leqslant r_j r_k \qquad \text{(ii)}\ \lim_{j\to\infty}\frac{r_j}{j}=0.$$

A more complete review of the literature concerning these systems can be found in Tompa (1976), Peebles (1971) and Drake (1972). Interesting experiments on the cluster size distribution for high-functionality antigens cross-linked by antibodies have been performed by Cohen *et al* (1980, see also references therein). These are very related systems. The asymptotic cluster size distribution is well-known in the case

$$R_{jk}=(Aj+B)(Ak+B) \qquad A>0 \quad B>-A$$

and has also been investigated for the closely related percolation models (see e.g. Stauffer 1979). The former describes polymers having a number of reactive sites proportional to their size. This would be valid if polyfunctional units were to grow without cycles, each site being equally reactive, independently of where it is situated. This is not the case because of excluded volume and cyclisation effects. We will therefore assume that the number of reactive sites grows as some unspecified power of the size. The aim of this paper is to analyse the critical behaviour near gelation for the case

$$R_{jk}=j^{\alpha}k^{\alpha} \qquad (0\leqslant\alpha\leqslant 1).$$

It is our hope that some kind of 'universality' holds so that reaction constants behaving asymptotically as $(jk)^{\alpha}$ will show the same critical behaviour. In contradistinction to our previous results we shall not attempt to prove much in this paper, and all our reasonings will be of a rather tentative nature.

Let us now define

$$p_j=j^{\alpha}c_j \tag{1}$$

giving rise to the equations

$$\dot{c}_j=j^{-\alpha}\dot{p}_j=\tfrac{1}{2}\sum_{k=1}^{j-1}p_k p_{j-k}-p_j\sum_{k=1}^{\infty}pk. \tag{2}$$

We now formulate conjectures and a theorem.

Conjecture 1. If gelation occurs, then for a fixed time t after gelation we have for large j

$$\left.\begin{aligned}p_j(t)&\sim j^{-\tau+\alpha}=j^{-\lambda}\\ c_j(t)&\sim j^{-\tau}\end{aligned}\right\}\ \text{for some } \lambda,\ \tau.$$

The symbol $\sim$ will be used loosely in the following to indicate the nature of some asymptotic behaviour. In this case we might define it as

$$\lim_{j\to\infty} \frac{p_j}{j^{-\lambda'}} = \begin{cases} 0 & (\lambda' < \lambda) \\ \infty & (\lambda' > \lambda) \end{cases}.$$

Under these circumstances we can show that $\lambda = \frac{3}{2}$, $\tau = \alpha + \frac{3}{2}$. Moreover, if

$$q(t) = \lim_{j\to\infty} j^{3/2} p_j(t) \tag{3}$$

exists, then we can show that

$$q(t) = \left(-\frac{1}{2\pi} \lim_{N\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{N} j c_j(t) \right)^{1/2}. \tag{4}$$

The hypothesis (3) can be verified explicitly in the case $\alpha = 1$. It is unclear, however, whether an extension to the general case is possible.

Conjecture 2. If $\alpha > \frac{1}{2}$ and gelation takes place at a finite time t_g, then for t near t_g but below it we have

$$p_j(t) \sim j^{-3/2} \exp(-G(jF(t))).$$

The inverse 'coherence length' $F(t)$ behaves as

$$F(t) \sim (t_g - t)^{\nu}$$

with

$$\nu = 2/(2\alpha - 1)$$

and therefore, for $\rho - \alpha > \frac{1}{2}$,

$$\sum_{j=1}^{\infty} j^{\rho} c_j(t) = \sum_{j=1}^{\infty} j^{\rho-\alpha} p_j(t) \sim (t_g - t)^{-\delta_\rho}$$

where

$$\delta_\rho = [2(\rho - \alpha) - 1]/(2\alpha - 1).$$

We further conjecture that

$$G(x) \sim x^{\alpha}$$

for $x \ll 1$. The asymptotic form of $G(x)$ for large x is still not quite clear.

Conjecture 3. For $\alpha > \frac{1}{2}$ the system (2) has solutions of the type

$$p_j(t) \sim a_j/t$$

where

$$a_j \geqslant 0 \qquad \sum_{j=1}^{\infty} j^{1-\alpha} a_j < \infty.$$

These solutions are of the same type as the exact gel solution in the case $\alpha = 1$.

Conjecture 4. Gelation occurs for $\alpha > \frac{1}{2}$. In this context we also prove the following:

Theorem: Let $R_{jk} \leq R(jk)^{\alpha}$ where $\alpha < \frac{1}{2}$. Then gelation does not occur.

We now proceed to justify those conjectures by some remarks.

2. Remarks on the first conjecture

We start from the following simple consequence from equations (2):

$$\frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{N} jc_j = -\sum_{j=1}^{N} jp_j \sum_{k=N-j+1}^{\infty} p_k. \tag{5}$$

From a solution after gelation we require

(i) $$\sum_{j=1}^{\infty} jc_j = \sum_{j=1}^{\infty} j^{1-\alpha} p_j < \infty$$

(ii) $$\frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{\infty} jc_j(t) < 0$$

if the derivative exists, which is our basic assumption.

From (ii) and (5) we immediately get

$$\sum_{j=1}^{\infty} jp_j = \infty. \tag{6}$$

So from (i) and (6) we obtain

$$p_j \sim j^{-\lambda} \tag{7}$$

where $2-\alpha \leq \lambda \leq 2$.

Using (5) and (7) we get

$$\begin{aligned}
\left|\frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{N} jc_j\right| &= \sum_{j=1}^{N} jp_j \sum_{k=N-j+1}^{\infty} p_k. \\
&\sim \sum_{j=1}^{N} j^{1-\lambda} \sum_{k=N-j+1}^{\infty} k^{-\lambda} \\
&\sim \sum_{j=1}^{N} j^{1-\lambda} (N-j+1)^{1-\lambda} \\
&\sim N^{3-2\lambda} \int_0^1 \mathrm{d}x\, x^{1-\lambda} (1-x)^{1-\lambda} \\
&\sim N^{3-2\lambda}
\end{aligned}$$

since the integral converges. However, assuming (ii), we obtain $3-2\lambda=0$ or $\lambda=\frac{3}{2}$, which is what we wanted to show. If $q(t)$ as defined by (3) exists, and if $\sum_{j=1}^{\infty} jc_j(t)$ has a derivative, then proving equation (4) is just the tedious calculation shown in appendix 1.

Note that, if this result is correct, it precludes the possibility of gelation for $\alpha < \frac{1}{2}$, since then $\lambda = \frac{3}{2} < 2-\alpha$.

3. Remarks on the second conjecture

As before, we assume that the system gels at time t_g. For $t > t_g$ we can write the solution of the system in the form

$$p_j(t) = j^{-3/2} q_j(t) \qquad q_j(t) \sim 1.$$

To get the behaviour before t_g we further assume: (a) that the functions $q_j(t)$ can be continued for some time below t_g and that the functions $j^{-3/2} q_j(t)$ are still solutions of equations (2); (b) that the real solutions of (2) differ from $j^{-3/2} q_j(t)$ by a somehow strongly decreasing factor which depends on j only in the units of a time-dependent 'coherence length' $\xi(t)$ which diverges at t_g. More formally

$$p_j(t) \simeq j^{-3/2} q_j(t) \exp(-G(j/\xi(t))) \tag{8}$$

$$\xi(t) \sim (t_g - t)^{-\nu}. \tag{9}$$

The symbol $\simeq$ indicates that we consider the asymptotic behaviour in the limit

$$t \to t_g, \qquad j \to \infty \qquad j/\xi(t) = \text{constant}. \tag{10}$$

If we define

$$F(t) = 1/\xi(t) \qquad F(t_g) = 0 \qquad G(0) = 0$$

and put the ansatz (8) in equations (2), we obtain, after some manipulations,

$$F^{\alpha-3/2}\dot{F} = \frac{(jF)^{\alpha-1}}{G'(jF)}\left[\frac{F}{2}\sum_{k=1}^{j-1}\frac{q_k q_{j-k}}{q_j}(kF)^{-3/2}\right.$$
$$\times\left(1-\frac{kF}{jF}\right)^{-3/2}\{\exp[G(jF)-G(kF)-G((j-k)F)]-1\}$$
$$\left.-F\sum_{k=1}^{\infty} q_k (kF)^{-3/2}[\exp(-G(kF))-1]\right].$$

If we eliminate all the q_k since they are of the order of magnitude 1, then perform the limit (10), we obtain

$$F^{\alpha-3/2}\dot{F} \sim \frac{y^{\alpha-1}}{G'(y)}\left[\frac{1}{2}\int_0^y \mathrm{d}x\, x^{-3/2}\left(1-\frac{x}{y}\right)^{-3/2}\right.$$
$$\times[\exp(G(y)-G(x)-G(y-x))-1]$$
$$\left.-\int_0^\infty \mathrm{d}x\, x^{-3/2}(\mathrm{e}^{-G(x)}-1)\right]. \tag{11}$$

It follows that $F^{\alpha-3/2}\dot{F}$ only depends on $y = jF$. Since, however, it does not depend on j, it clearly must be a constant, i.e.

$$\dot{F} \sim F^{3/2-\alpha} \tag{12}$$

leading to

$$F(t) \sim (t_g - t)^{\nu} \qquad \nu = 2/(2\alpha - 1).$$

We now want to know how the moments

$$M_p(t) = \sum_{j=1}^{\infty} j^p c_j(t)$$

diverge when t near t_g and ρ is large enough. We have

$$M_\rho(t) \sim \sum_{j=1}^{\infty} j^{\rho-\alpha-3/2} \exp(-G(jF))$$
$$\sim F^{\alpha+1/2-\rho} \int_0^\infty \mathrm{d}x\, x^{\rho-\alpha-3/2}\, \mathrm{e}^{-G(x)}$$
$$\sim (t_g - t)^{-\nu(\rho-\alpha-1/2)}.$$

This means

$$M_\rho(t) \sim (t_g - t)^{-\delta_\rho} \qquad \delta_\rho = [2(\rho-\alpha)-1]/(2\alpha-1) \tag{13}$$

if $\rho - \alpha > \frac{1}{2}$, otherwise the sum converges. (It can diverge logarithmically if $\rho - \alpha = \frac{1}{2}$.)

To determine the function $G(y)$ we combine (11) and (12) to give

$$G'(y) \sim y^{\alpha-1}\left[\int_0^\infty \mathrm{d}x\, x^{-3/2}[1-\exp(-G(x))] - \int_0^{y/2} \mathrm{d}x\, x^{-3/2}\left(1-\frac{x}{y}\right)^{-3/2}[1-\exp(G(y)-G(x)-G(y-x))]\right]. \tag{14}$$

The integrals in (14) converge if

$$\lim_{y\to 0} \frac{G(y)}{y^{1/2+\varepsilon}} = 0$$

for some $\varepsilon > 0$. We can therefore neglect the second integral on the right-hand side of (13) if $y \ll 1$. This gives

$$G(y) \sim y^\alpha \qquad (y \ll 1).$$

Again, $\alpha = \frac{1}{2}$ is a critical value. The discussion of $G(x)$ for large x is tricky and we will not go into details.

It is fairly easy, however, to get an idea of how the $p_j(t)$ behave for large j at fixed $t < t_g$. Indeed, following McLeod (1962) we note that

$$p_j(t) \leq \pi_j(t) = \frac{j^{j-2}}{(j-1)!} t^{j-1}$$

since these are solutions of the system

$$\dot{\pi}_j = \frac{j}{2} \sum_{k=1}^{j-1} \pi_k \pi_{j-k} \qquad \pi_j(0) = \delta_{j1} \tag{15}$$

and therefore for all times

$$\dot{p}_j \leq \dot{\pi}_j \qquad p_j(0) = \pi_j(0).$$

For $t < 1/\mathrm{e}$ it is easy to see that the $\pi_j(t)$ fall off exponentially in j, and therefore so do the $p_j(t)$. There is, however, no reason to imagine a singularity that would change this state of affairs without causing gelation. We therefore assume that this exponential decay persists up to t_g. This is *not* incompatible with (14) since we are considering large j at a fixed time and therefore not the limit (10).

4. Remarks on the third conjecture

We now consider the following ansatz for a gel solution of the system (2):

$$p_j(t) = a_j/(t+\beta). \tag{16}$$

This ansatz has the remarkable property that it satisfies the system (2) automatically if the a_j satisfy the relations

$$\sum_{j=1}^{\infty} a_j = 1 \tag{17a}$$

$$a_j = \frac{1}{2(1-j^{-\alpha})} \sum_{k=1}^{j-1} a_k a_{j-k}. \tag{17b}$$

The quantities a_j are therefore independent of any specific initial conditions. Indeed we have

$$\sum_{j=1}^{\infty} jc_j(t_g) = \frac{1}{t_g+\beta} \sum_{j=1}^{\infty} j^{1-\alpha} a_j$$

or

$$t_g + \beta = \left(\sum_{j=1}^{\infty} j^{1-\alpha} a_j \right) \Big/ \left(\sum_{j=1}^{\infty} jc_j(t_g) \right).$$

The whole solution therefore depends only on the gelation time t_g and the total mass contained in the system.

We are looking for solutions such that

$$a_j \geq 0 \qquad \sum_{j=1}^{\infty} j^{1-\alpha} a_j < \infty.$$

By a power-counting argument similar to the one used in § 2, we show $a_j \sim j^{-3/2}$ and is therefore only possible for $\alpha > \frac{1}{2}$. To make the existence of such solutions plausible in this case we proceed as follows: define

$$\beta_1(b) = 1 \tag{18a}$$

$$\beta_j(b) = \frac{1}{2b(1-j^{-\alpha})} \sum_{k=1}^{j-1} \beta_k(b)\beta_{j-k}(b). \tag{18b}$$

The quantities $\beta_j(b)/b$ satisfy (17b) for any value of b and (17a) if

$$\sum_{j=1}^{\infty} \beta_j(b) = b.$$

Define further

$$B_N(b) = \sum_{j=1}^{N} \beta_j(b).$$

Since we have

$$\beta_j(b) = b^{1-j} \beta_j(1)$$

$B_N(b)$ is a continuous, monotonically decreasing function of b with a pole at $b=0$.

Therefore the equation

$$B_N(b)=b$$

has exactly one solution: $\mu_N>0$.

In appendix 2 it is shown that for b sufficiently large we have

$$\lim_{N\to\infty} B_N(b)<\infty. \tag{19}$$

Furthermore for all b

$$B_N(b)\leq B_{N+1}(b)$$

and therefore

$$\mu_N\leq\mu_{N+1}.$$

From (19) we obtain that the sequence μ_N is bounded. It must therefore converge to some limit, say μ. We have

$$\begin{aligned}\mu &= \lim_{N\to\infty}\mu_N\\ &=\lim_{N\to\infty}\sum_{j=1}^{N}\beta_j(\mu_N)\\ &=\lim_{N\to\infty}\left(\sum_{j=1}^{M-1}\beta_j(\mu_N)+\sum_{j=M}^{N}\beta_j(\mu_N)\right)\\ &=\sum_{j=1}^{M-1}\beta_j(\mu)+\lim_{N\to\infty}\sum_{j=M}^{N}\beta_j(\mu_N)\\ &=\sum_{j=1}^{\infty}\beta_j(\mu)+\lim_{M\to\infty}\lim_{N\to\infty}\sum_{j=M}^{N}\beta_j(\mu_N).\end{aligned}$$

If we now assume that for all N

$$\sum_{j=1}^{N} j^{1-\alpha}\beta_j(\mu_N)\leq K \tag{20}$$

for some K, then the second term is zero and the sequence

$$a_j=\beta_j(\mu)/\mu$$

satisfies relations (17) as well as the other requirements.

Unfortunately there seems to be no easy way to decide whether (20) holds or not. Table 1 shows numerical results for finite but large N. There is an obvious difference between $\alpha>\frac{1}{2}$ and $\alpha<\frac{1}{2}$. The slow convergence is due to the fact that solutions of (17) have at most a rather slow algebraic decay in j.

From these numerical results we conclude that it is probable that for $\alpha>\frac{1}{2}$ there exist solutions of the type (16) for which of course the total mass $\sum_{j=1}^{\infty} jc_j(t)$ is no longer constant in time. It remains, however, an open question as to whether or not such a solution can be reached in a finite time from an initial condition such as $p_j(0)=\delta_{j1}$.

Table 1.

α	N	μ_N	$\sum_{\alpha=1}^{N} j^{1-\alpha} a_j(\mu_N)$
1.00	50	2.668 601 594 62	2.6686
	100	2.693 833 605 05	2.6938
	200	2.706 218 574 58	2.7062
0.75	50	3.039 689 660 83	4.4736
	100	3.072 070 299 37	4.7312
	200	3.087 806 873 97	4.9416
	400	3.095 465 745 57	5.1165
0.50	50	3.815 439 553 74	10.6174
	100	3.866 968 850 55	12.6017
	200	3.892 068 144 23	14.7030
0.25	50	6.212 010 262 90	47.7926
	100	6.342 163 925 55	70.8638
	200	6.407 089 471 30	103.6175

5. Remarks of the fourth conjecture

The above remarks already indicate strongly that $\alpha = \frac{1}{2}$ is indeed the limit between 'normal' polymerisation and gelation. We now add another independent consideration, which also singles out $\alpha = \frac{1}{2}$. Moreover, it also gives some insight into the mechanism leading to gelation for $\alpha > \frac{1}{2}$.

Consider the systems

$$\dot{c}_j^{(n)} = \tfrac{1}{2} \sum_{k=1}^{j-1} k^\alpha (j-k)^\alpha c_k^{(n)} c_{j-k}^{(n)} - j^\alpha c_j^{(n)} \sum_{k=1}^{\infty} k^\alpha c_k^{(n)} \tag{21}$$

$$c_j^{(n)} = (1/n)\delta_{jn}$$

for $n = 1, 2, 3, \ldots$. They all satisfy

$$\sum_{j=1}^{\infty} j c_j^{(n)}(0) = 1$$

and differ only by the initial condition. Clearly

$$c_j^{(n)}(t) = 0$$

if j is not a multiple of n. We therefore define

$$\mathscr{H}_j^{(n)} = n c_j^{(n)}.$$

These satisfy the equations

$$\mathscr{H}_j^{(n)} = n^{2\alpha-1}\left(\frac{1}{2}\sum_{k=1}^{j-1} k^\alpha (j-k)^\alpha \mathscr{H}_k^{(h)} \mathscr{H}_{j-k}^{(n)} - j^\alpha \mathscr{H}_j^{(n)} \sum_{k=1}^{\infty} k^\alpha \mathscr{H}_k^{(n)}\right)$$

$$\mathscr{H}_j^{(n)}(0) = \delta_{j1}.$$

It follows that

$$c_{nj}^{(n)}(t)=(1/n)c_j^{(1)}(n^{2\alpha-1}t). \tag{22}$$

Now let us consider the original system ($n=1$). After a given time the distribution $(c_j(t))_{j=1}^{\infty}$ may to some extent approximate the initial condition for the system (21) for some $n>1$. From (22) it follows that the polymerisation process then repeats itself on a larger scale and at a different rate—a slower one if $\alpha<\frac{1}{2}$, a faster one if $\alpha>\frac{1}{2}$.

To be more precise, let us consider the moments $M_\rho(t)$: from equation (2) we get

$$\mathrm{d}M_2(t)/\mathrm{d}t=M_{1+\alpha}^2(t)$$

as long as gelation does not occur. In appendix 3 we show that if the c_j are not negative we have

$$M_{1+\alpha}\leqslant M_2^\alpha M_1^{\alpha-1}$$

and since before gelation

$$M_1=1$$

we have

$$\mathrm{d}M_2/\mathrm{d}t\leqslant M_2^{2\alpha}.$$

It follows that

$$M_2^{1-2\alpha}(t)\leqslant t/(1-2\alpha)+M_2(0)^{1-2\alpha}<\infty$$

for $\alpha<\frac{1}{2}$ and for all times. Therefore gelation cannot occur. On the other hand, for $\alpha>\frac{1}{2}$ we have

$$M_2(t)^{2\alpha-1}\geqslant[M_2(0)^{2\kappa-1}-Kt/(2\alpha-1)]^{-1}$$

as long as

$$M_{1+\alpha}(t)\geqslant K\cdot M_2^\alpha(t)$$

is valid, i.e. as long as the distribution is not too spread out. Of course we cannot expect such an inequality to hold near t_g, as inspection of the formula for δ_ρ will show: near t_g we have, according to (13),

$$M_2\sim M_{1+\alpha}^{3-2\alpha}.$$

It follows that for $\frac{1}{2}<\alpha<1$ the distribution spreads out in such a manner that M_2 diverges more strongly than $M_{1+\alpha}^{1/\alpha}$, but not so strongly that it could become infinite while $M_{1+\alpha}$ remained finite.

6. Conclusion

We have generalised the Flory–Stockmayer model of gelation to include, in a very approximate fashion, the effects of excluded volume and cyclisation effects: while still assuming the reaction rate to be roughly proportional to a product of some average number of reactive sites on each reacting molecule, we do not assume this number to grow linearly with the size of the polymer, but rather approximately as some power $\alpha<1$. We have rigorously shown that $\alpha\geqslant\frac{1}{2}$ is necessary for gelation to occur. Further, although this model cannot be solved in closed form, we obtain the following results near the gelation time t_g:

$$c_j(t) \sim \begin{cases} j^{-\tau} \exp(-G(jF(t))) & (t < t_g) \\ j^{-\tau} & (t \geqslant t_g) \end{cases}$$

$$F(t) \sim (t_g - t)^{\nu} \qquad G(x) \sim x^{\alpha} \qquad (x \ll 1)$$

$$\nu = 2/(2\alpha - 1) \qquad \tau = \alpha + \tfrac{3}{2}$$

$$M_\rho(t) = \sum_{j=1}^{\infty} j^{\rho} c_j(t) \sim (t_g - t)^{-\delta_\rho}$$

$$\delta_\rho = [2(\rho - \alpha) - 1]/(2\alpha - 1) \qquad \text{if } \rho - \alpha > \tfrac{1}{2}.$$

In particular we note that for $\frac{1}{2} < \alpha < 1$: (a) τ is smaller than its classical ($\alpha = 1$) value; (b) ν and δ_2 are larger than their classical values. This is in good qualitative agreement with Stauffer's results for percolation on a finite-dimensional lattice as compared with percolation on the Bethe lattice, which has the same exponents as the Flory–Stockmayer model.

Appendix 1

We want to show that if

$$q(t) = \lim_{j\to\infty} j^{3/2} p_j(t)$$

then

$$q(t) = \left(-\frac{1}{2\pi} \lim_{N\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{N} j c_j(t) \right)^{1/2}$$

which can be rewritten as

$$\lim_{N\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{j=1}^{N} j c_j(t) = -2\pi q(t)^2.$$

We first show that for any M we have

$$\lim_{N\to\infty} \sum_{j=M}^{N} j^{-1/2} \sum_{\substack{k=N-j+1 \\ k\geqslant M}}^{\infty} k^{-3/2}$$

$$= \lim_{N\to\infty} \frac{1}{N^2} \sum_{j=M}^{N} \left(\frac{j}{N}\right)^{-1/2} \sum_{\substack{k=N-j+1 \\ k\geqslant M}} \left(\frac{k}{N}\right)^{-3/2}$$

$$= \int_0^1 \mathrm{d}x\, x^{-1/2} \int_{1-x}^{\infty} \mathrm{d}y\, y^{-3/2}$$

$$= 2\pi.$$

Let $\varepsilon > 0$ be arbitrary. Then choose M so that

$$|j^{3/2} p_j - q| \leqslant \varepsilon$$

for all $j \geqslant M$. Since

$$p_j \leqslant C j^{-3/2} \qquad \text{for all } j$$

we have

$$\lim_{N\to\infty}\sum_{j=1}^{M-1} jp_j \sum_{k=N-j+1}^{\infty} p_k=0$$

$$\lim_{N\to\infty}\sum_{j=1}^{N} jp_j \sum_{k=N-j+1}^{M-1} p_k=0$$

and therefore

$$\left|\lim_{N\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\sum_{j=1}^{N} jc_j+2\pi q^2\right|$$

$$=\left|\lim_{N\to\infty}\sum_{j=1}^{N} jp_j\sum_{k=N-j+1}^{\infty} p_k-2\pi q^2\right|$$

$$=\left|\lim_{N\to\infty}\sum_{j=M}^{N} jp_j\sum_{\substack{k=N-j+1\\ k\geqslant M}}^{\infty} p_k-2\pi q^2\right|$$

$$=\left|\lim_{N\to\infty}\sum_{j=M}^{N}\sum_{\substack{k=N-j+1\\ k\geqslant M}}(jp_jp_k-j^{-1/2}k^{-3/2}q^2)\right|$$

$$\leqslant\lim_{N\to\infty}\sum_{j=M}^{N}\sum_{\substack{k=N-j+1\\ k\geqslant M}}^{\infty} j^{-1/2}k^{-3/2}|j^{3/2}p_jk^{3/2}p_k-q^2|$$

$$\leqslant 2\pi(q+C)\varepsilon$$

thus proving the assertion.

Appendix 2

We want to prove that if

$$\beta_1(b)=1$$

$$\beta_j(b)=\frac{1}{2b(1-j^{-\alpha})}\sum_{k=1}^{j-1}\beta_k(b)\beta_{j-k}(b)$$

then for b sufficiently large

$$\sum_{j=1}^{\infty}\beta_j(b)<\infty.$$

Define $\gamma_j(b)$ as

$$\gamma_1(b)=1$$

$$\gamma_j(b)=\frac{1}{2b(1-2^{-\alpha})}\sum_{k=1}^{j-1}\gamma_k(b)\gamma_{j-k}(b).$$

Then we have

$$\beta_j(b)\leqslant\gamma_j(b)$$

for all b and j. Define

$$F(z;b)=\sum_{j=1}^{\infty}\gamma_j(b)z^j.$$

We have

$$F(z;b)=b(1-2^{-\alpha})\left[1-\left(1-\frac{2z}{b(1-2^{-\alpha})}\right)^{1/2}\right]$$

so if $b>2/(1-2^{-\alpha})$ the convergence radius of $F(z,b)$ will be larger than one. It follows that

$$\sum_{j=1}^{\infty}\beta_j(b)\leqslant\sum_{j=1}^{\infty}\gamma_j(b)=F(1;b)<\infty$$

thus proving the assertion.

Appendix 3

If we define

$$M_\rho=\sum_{j=1}^{\infty}j^\rho c_j$$

and we assume $c_j\geqslant 0$, then we show that

$$M_2\geqslant M_{1+\alpha}^{1/\alpha}M_1^{1-1/\alpha}$$

for all $0<\alpha<1$. Define

$$f(x)=x-x^\alpha/\alpha+1/\alpha-1.$$

Then we have for all $x>0$

$$f(x)=\int_1^x(1-y^{\alpha-1})\,\mathrm{d}y\geqslant 0.$$

Now define

$$\psi((c_j)_{j=1}^{\infty})=M_2-M_{1+\alpha}^{1/\alpha}M_1^{1-1/\alpha}.$$

We have

$$\frac{\partial\psi}{\partial c_j}=j^2-\frac{1}{\alpha}M_{1+\alpha}^{1/\alpha-1}M_1^{1-1/\alpha}j^{1+\alpha}-\left(1-\frac{1}{\alpha}\right)M_{1+\alpha}^{1/\alpha}M_1^{+1/\alpha}$$
$$=j\left(\frac{M_{1+\alpha}}{M_1}\right)^{1/\alpha}f\left(j\left(\frac{M_1}{M_{1+\alpha}}\right)^{1/\alpha}\right)\geqslant 0.$$

Since, however, if all the c_j are zero, $\psi((c_j)_{j=1}^{\infty})=0$, then clearly we have

$$\psi((c_j)_{j=1}^{\infty})\geqslant 0$$

if all the c_j are larger than zero.

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