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# Smoluchowki's equation and the $\theta$ -exponent for branched polymers

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**Abstract.** Bonding of large clusters by surface reactions can be modelled by Smoluchowski's coagulation equation with coagulation rates  $K_{ij} = (ij)^\omega$  with  $\omega = (d-1)/d$  in  $d$ -dimensional systems. It is shown that the cluster size distribution for large clusters well below the gelation transition has the form  $c_k \sim k^{-\theta} \xi^k$  ( $k \rightarrow \infty$ ) where  $\theta = 2\omega$ . Results are compared with those from lattice theories and from the Flory–Stockmayer theory.

For the models  $K_{ij} = \frac{1}{2}(i^\mu j^\nu + i^\nu j^\mu)$  with  $\mu, \nu < 1$  one finds  $\theta = \mu + \nu$ ; for  $K_{ij} = ij^\omega + ji^\omega$  with  $-1 \leq \omega < 1$  one finds  $\theta = \frac{1}{2}(1 + \omega)$  and for  $K_{ij} = ij$  one has  $\theta = \frac{5}{2}$ .

## 1. Introduction

Smoluchowski's coagulation equation describes cluster growth due to coagulation processes through the following equation (Drake 1972):

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \quad (1)$$

which usually has to be solved with monodisperse initial conditions,  $c_k(0) = \delta_{k1}$ . The size distribution  $c_k(t)$  denotes the time dependent concentration of clusters of size  $k$  ( $k$ -mers), and  $K_{ij}$  the rate constant for a coagulation reaction between an  $i$ -mer and a  $j$ -mer.

Equation (1) can be used to model the kinetics of polymerisation (Stockmayer 1943, Ziff 1980). If the reactivity of a cluster is assumed to be independent of or proportional to the size of the reacting clusters (e.g.  $K_{ij} = 1$ ,  $i+j$  or  $ij$ ) then the coagulation equation yields the same results as the classical theories of Flory and Stockmayer. In recent years Leyvraz and Tschudi (1982) and Ziff *et al* (1982) have tried to improve upon the classical kinetic theories by considering the reactivity of a  $k$ -mer to be proportional to its effective surface area  $s_k$ , such that  $K_{ij} \sim s_i s_j$ . For large clusters one assumes  $s_k \sim k^\omega$ , where  $\omega$  is an exponent characterising the surface area, leading to  $K_{ij} \approx (ij)^\omega$ .

One of the most interesting results of these models has been the prediction that the cluster size distribution in the vicinity of the gel point  $t_c$  behaves as  $c_k(t) \approx k^{-\tau} \Phi(k^\sigma | t - t_c|)$  for  $k \rightarrow \infty$  and  $t \rightarrow t_c$ , where  $\Phi(x)$  is some scaling function and where the exponents are  $\tau = \omega + \frac{3}{2}$  and  $\sigma = \tau - 2$ . If one assumes that the dimensionality of

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the effective surface of a large cluster is one lower than the dimension  $d$  of the system, namely  $\omega = (d - 1)/d$ , then the above value for the exponent  $\tau$  is both in two and three dimensions very close to the values obtained for percolating clusters in lattice theories. For the second exponent  $\sigma$  the relation  $\sigma = \tau - 2$  holds universally in our model. The same exponent relation was recently found by Rácz and Vicsek (1983) in diffusion controlled deposition. It is, however, in sharp contrast with the results obtained from percolation theory.

The purpose of the present paper is to apply these kinetic models with surface reactions to determine the cluster size distribution  $c_k(t)$  of branched polymers in the sol phase, well below the gel point ( $t < t_c$ ). It is customary to represent the asymptotic decay of  $c_k$  as (Stauffer *et al* 1982)

$$c_k \approx Ak^{-\theta} \exp(-Ck^\zeta) \quad (k \rightarrow \infty), \quad (2)$$

where  $A$  and  $C$  are some constants, and  $\theta$  and  $\zeta$  are two geometric exponents, characterising the size distribution. An expression similar to (2) is being used for the cluster size distribution of lattice animals in percolation theories.

To the present state of knowledge (Stauffer *et al* 1982, p 113) these exponents, referring to the sol phase, are not related to the critical exponents at the gelation transition, and are independent of the extent of reaction, measured here by the parameter  $t$ . One may therefore calculate these exponents from a solution of Smoluchowski's equation at short times with conveniently chosen initial conditions, here taken to be monodisperse. The results for  $\theta$  and  $\zeta$ , obtained in this manner for a large class of coagulation kernels  $K_{ij}$ , are expected to be independent of these special initial conditions, as they agree with special cases already known in the literature. Here we are referring first to the exponents for the coagulation kernels  $K_{ij} = 1$ ,  $i + j$  and  $ij$ , determined from the general solution  $c_k(t)$  at arbitrary initial conditions (see e.g. Ziff *et al* 1983), and secondly to the exponents determined by Lushnikov and Piskunov (1976) for the kernel  $K_{ij} \sim i^\mu j^\nu$  from a similarity solution, that does not correspond to monodisperse initial conditions. We start by considering the initial growth ( $t \rightarrow 0$ ) for the model  $K_{ij} = (ij)^\omega$  with monodisperse initial conditions. Here

$$c_k(t) \approx a_{k0} t^{k-1} (1 + O(t)), \quad (3)$$

where  $a_{10} = 1$  and  $a_{k0}$  ( $k = 2, 3, \dots$ ) are determined from the recursion relation

$$(k-1)a_{k0} = \frac{1}{2} \sum_{i+j=k} K_{ij} a_{i0} a_{j0}. \quad (4)$$

At large values of  $k$  the coefficients decay asymptotically as

$$a_{k0} \approx Ak^{-\theta} R^{-k} \quad (k \rightarrow \infty), \quad (5)$$

as will be shown below. Combination of (3) and (5) then yields an expression for the initial behaviour of  $c_k$  of the general form (2), from which  $\theta$  and  $\zeta = 1$  can be determined.

More generally, we consider the Taylor series expansion

$$c_k(t) = \sum_{l=0}^{\infty} a_{kl} t^{k+l-1} \quad (6)$$

where the coefficients  $a_{kl}$  can be obtained from the recursion relations (Hendriks *et al* 1983)

$$(k+l-1)a_{kl} = \frac{1}{2} \sum_{i+j=k} K_{ij} \sum_{m=0}^l a_{im} a_{j,l-m} - \sum_{j=1}^l \sum_{m=0}^{l-j} K_{kj} a_{km} a_{j,l-j-m}. \quad (7)$$

In § 2 we consider the somewhat more general coagulation rates

$$K_{ij} = \frac{1}{2}(i^\mu j^\nu + i^\nu j^\mu) \quad (8)$$

for different ranges of  $(\mu, \nu)$ -values. In § 3 we apply the results to branched polymers with  $K_{ij} \sim (ij)^\omega$  and compare the results with those known in the literature.

## 2. Asymptotics of solution of the recursion relation

### 2.1. Case $K_{ij} = \frac{1}{2}(i^\mu j^\nu + j^\mu i^\nu)$ ( $\mu, \nu < 1$ )

In order to determine the asymptotic solution of equation (4) we may try to substitute the ansatz (5), and determine  $A$  and  $\theta$  self-consistently. The value of  $R$  is found to be proportional to  $a_{10}$  with an unknown factor of proportionality. We find it slightly more convenient to follow the method used by Hendriks *et al* (1983), and define the generating functions  $f_\lambda(x)$  for  $\lambda = \mu, \nu, 0$ :

$$f_\lambda(x) = \sum_{k=1}^{\infty} a_{k0} k^\lambda e^{kx}. \quad (9)$$

The large- $k$  behaviour of the  $a_{k0}$  follows from the nature of the leftmost singularity in the complex  $x$ -plane of any of the  $f_\lambda(x)$ . We suppose that the leftmost singularity of  $f_\lambda(x)$  is located at  $x = x_0 = \log R$ , and that this singularity in  $f_0(x)$  is of the form  $(x_0 - x)^\alpha$ ; then the dominant behaviour of  $f_\lambda(x)$  ( $\lambda = \mu, \nu, 0$ ) as  $x \uparrow x_0$  is given by

$$f_\lambda(x) \approx a_\lambda + \dots + b_\lambda (x_0 - x)^{\alpha - \lambda} + \dots \quad (10)$$

The coefficients  $b_\lambda$  and  $b_0$  are according to Hendriks *et al* (1983) related as

$$b_\lambda = b_0 \Gamma(\lambda - \alpha) / \Gamma(-\alpha), \quad (11)$$

where the exponent  $\alpha$  may be positive or negative, and (10) corresponds to an asymptotic decay of the coefficients in (9):

$$a_{k0} \approx (b_0 / \Gamma(-\alpha)) k^{-\alpha - 1} e^{-kx_0} \quad (k \rightarrow \infty). \quad (12)$$

The three generating functions  $f_\lambda(x)$  ( $\lambda = \mu, \nu, 0$ ) are related as

$$f'_0 - f_0 = \frac{1}{2} f_\mu f_\nu \quad (13)$$

as a consequence of (4) and (8).

Next we insert the ansatz (10) into (13) and equate the most dominant terms for  $x \uparrow x_0$  on both sides of the equation. For  $\mu$  or  $\nu$  larger than unity no consistent solution of the form (10) can be found. For  $\mu, \nu < 1$  the exponent  $\alpha$  in (10) is found to be  $\alpha = \mu + \nu - 1$ , and  $b_0 = \frac{1}{2} \Gamma(1 - \mu - \nu) / B(1 - \nu, 1 - \mu)$ . Comparison of (12) and (5) yields then for  $\mu, \nu < 1$

$$\theta = \mu + \nu, \quad A^{-1} = \frac{1}{2} B(1 - \mu, 1 - \nu), \quad (14)$$

with  $x_0 = \log R$  left undetermined. Equation (14) also contains the exactly solved model  $K_{ij} = 1$  (Drake 1972) and the models  $K_{ij} = \frac{1}{2}(i^\omega + j^\omega)$ , for which the size distribution  $c_k(t)$  can be determined sequentially as a function of a transformed time variable (Hendriks *et al* 1983). We also note that the constant  $A$  in (14) vanishes when  $\mu$  and  $\nu$  approach unity from below.

These analytical calculations have been confirmed for  $\mu = \nu = \omega$  by numerically solving the recursion relations. These calculations also yield the radius of convergence  $R$  in (5). The results are listed in table 1.

**Table 1.** Theoretical and numerical values for  $\theta$ ,  $A$  and  $R$  for the model  $K_{ij} = (ij)^\omega$ ,  $\omega = 0(0.2)1$ . For  $\omega \rightarrow 1$  the numerical accuracy is lowered because of the relative importance of the correction term to equation (2).

$\omega$	$\theta_{num}$	$\theta_{theor}$	$A_{num}$	$A_{theor}$	$R$	$R_{theor}$
0.0	0.0000	0.0	2.0000	2.0000	2.0000	2
0.2	0.4003	0.4	1.3210	1.3184	1.4555	?
0.4	0.8010	0.8	0.8336	0.8281	1.0529	?
0.6	1.2033	1.2	0.4842	0.4732	0.7554	?
0.8	1.6165	1.6	0.2370	0.2105	0.5348	?
1.0	2.4998	2.5	0.3985	0.3989	0.3679	0.3679

An independent confirmation of (14) comes from the work of Lushnikov and Piskunov (1976), who have obtained similarity solutions of Smoluchowski's equation for the kernel (8) in the triangular region  $\{\mu + \nu < 1; \mu, \nu > 0\}$ , where no gelation occurs (see § 3). These authors have shown that  $c_k$  behaves at fixed  $t$  and for  $k \rightarrow \infty$  as  $c_k(t) \approx Ak^{-\mu-\nu} \exp(-Ck)$ . However, these similarity solutions correspond to some polydisperse initial distribution, and not to  $c_k(0) = \delta_{k1}$ .

Our conclusions for the case  $\mu, \nu > 1$  are consistent with McLeod's result for the special case  $\mu = \nu = \omega > 1$ , showing that the generating function (9) with  $\lambda = \omega$  does not exist, as it has a zero radius of convergence  $R = \exp(x_0)$ .

2.2. Case  $K_{ij} = ij^\omega + ji^\omega$  ( $|\omega| \leq 1$ )

When  $\max(\mu, \nu) = 1$ , the derivation of (14) is no longer valid, and the case  $K_{ij} = ij^\omega + ji^\omega$  ( $\omega \leq 1$ ) remains to be investigated. This class of models contains the exactly solved cases  $\omega = 0, 1$  (Drake 1972) and  $\omega = -1$  (Lushnikov and Piskunov 1975). In the range  $-1 \leq \omega < 0$ , Lushnikov and Piskunov have already determined the large- $k$  behaviour of  $a_{k0}$ , using a method similar to ours. Here we discuss the whole range of  $\omega$ -values.

For the present class of models equation (4) reduces to

$$f'_0 - f_0 = f'_0 f_\omega \tag{15}$$

Again we try to solve this equation consistently in the vicinity of  $x_0$  with  $f_0$  and  $f_\omega$  of the form (10). Under the restrictions  $0 < \alpha < 1$  and  $0 < \alpha - \omega < 1$  consistency requires  $a_\omega = 1$  and  $\alpha = \frac{1}{2}(1 + \omega)$  with  $|\omega| < 1$ , whereas the coefficients  $b_\omega$  and  $b_0$  are left undetermined. Thus we have on account of (5) and (12)

$$\theta = \frac{1}{2}(\omega + 3) \quad (|\omega| < 1), \tag{16}$$

but the amplitude  $A$  and radius of convergence  $R = \exp x_0$  in (5) cannot be determined.

Comparison of (14) and (16) shows that the present case,  $(\mu, \nu) = (1, \nu)$  with  $\nu < 1$ , cannot be obtained as a limiting case from  $(\mu, \nu)$  with  $\mu \uparrow 1$ . The exponent is discontinuous on the border lines  $\mu = 1$  and  $\nu = 1$ .

The above class of models with  $|\omega| < 1$  contains the case  $K_{ij} = i + j$  (with  $\omega = 0$ ), that has been exactly solved by Golovin and Scott (see Drake 1972). Here (15) becomes a differential equation for  $f_0(x)$ . Its solution, that satisfies the boundary condition  $f_0(x) \approx e^x$  as  $x \rightarrow -\infty$ , is implicitly given by the relation  $x = \ln f_0 - f_0$ . Then the coefficient  $a_{k0}$  of  $\xi^k \equiv \exp(kx)$  in (9) is determined by

$$a_{k0} = (2\pi i)^{-1} \oint d\xi \xi^{-k-1} f_0(\xi) = k^{k-1}/k! \tag{17}$$

where the contour integral has been evaluated by changing to  $f_0$  as a new integration variable. The large- $k$  behaviour of (17) gives  $a_{k0} \approx (2\pi)^{-1/2} k^{-3/2} e^k$  ( $k \rightarrow \infty$ ), so that the coefficients in (5) are given by  $A = (2\pi)^{-1/2}$ ,  $R = 1/e$  and  $\theta = \frac{3}{2}$  in agreement with (16) for  $\omega = 0$ .

The derivation of (16) is not valid for  $\omega = +1$  or  $\omega = -1$ , corresponding to the model  $K_{ij} = ij$ , solved by McLeod (1962) and  $K_{ij} = i/j + j/i$ , solved by Lushnikov and Piskunov (1975). In the case  $\omega = 1$ , equation (15) reduces to a simple differential equation for  $f_1(x)$  with solution  $x = \ln f_1 - f_1$ , and we obtain for the coefficient

$$ka_{k0} = (2\pi i)^{-1} \oint d\xi \xi^{-k-1} f_1(\xi) = k^{k-1}/k! \tag{18}$$

This yields for large  $k$

$$a_{k0} \approx (2\pi)^{1/2} k^{-5/2} e^k \tag{19}$$

leading to  $A = (2\pi)^{-1/2}$ ,  $R = (1/e)$  and  $\theta = \frac{5}{2}$ . Note that this result is not contained in (16) for  $\omega = 1$ . Thus,  $\theta$  is also discontinuous in  $(\mu, \nu) = (1, 1)$  along the lines  $\mu = 1$  and  $\nu = 1$ .

For  $\omega = -1$  equation (15) reduces to a differential equation for  $f_1(x)$ , where  $f'_{-1} = f_0$ . The solution, satisfying  $f_{-1}(x) \approx e^x$  as  $x \rightarrow -\infty$ , is

$$x = -\gamma - E_1(f_0) \tag{20}$$

where  $\gamma$  is Euler's constant and  $E_1(z) = \int_z^\infty y^{-1} e^{-y} dy$ . The RHS of (20) is a monotonically increasing function of  $f_0$ , approaching  $x_0 = -\gamma$  as  $f_0 \rightarrow \infty$ . Thus, the radius of convergence  $R$  in (5) equals  $\exp(x_0) = \exp(-\gamma)$ . At the singular point  $x = -\gamma$  the function  $f_0(x)$  approaches  $\infty$ . We determine the behaviour of  $f_0(x)$  in the vicinity of this singularity from the large- $f_0$  behaviour of  $E_1(f_0)$ , namely

$$-x - \gamma = E_1(f_0) \approx f_0^{-1} \exp(-f_0) [1 + O(f_0^{-1})] \tag{21a}$$

or inversely for  $x \uparrow -\gamma$ :

$$f_0(x) \approx \ln[-(x + \gamma)]^{-1} - \ln \ln[-(x + \gamma)]^{-1} + \dots \tag{21b}$$

This leads to the following large- $k$  behaviour:

$$a_{k0} \approx k^{-1} e^{k\gamma} \{1 + O[(\ln k)^{-1}]\} \tag{22}$$

so that the parameters in (5) become  $A = 1$ ,  $R = \exp(-\gamma)$  and  $\theta = 1$ . For the present case the exponent  $\theta$  in (16) is continuous along the lines  $(\mu, 1)$  and  $(1, \nu)$  as  $\mu \downarrow -1$  and  $\nu \downarrow -1$  respectively. One can of course write an exact expression for  $a_{k0}$  from (20) in the form of a contour integral, namely

$$a_{k0} = (2\pi i)^{-1} \oint dz z^{-k} \exp[-z + kb(z)] \tag{23a}$$

where  $b(z)$  is an analytic function at the origin and defined as

$$b(z) = \gamma + \ln z + E_1(z) = \sum_{n=1}^{\infty} (-)^{n+1} z^n / (nn!). \tag{23b}$$

However, this expression cannot be evaluated any further.

For the case  $\omega < -1$ , we have not been able to find any consistent solution of the form (10) or its modifications including powers of  $\ln x$ .

The results of this section for the exponent  $\theta$  are summarised in the diagram of figure 1. It should be noted that  $\theta$  is discontinuous on the lines  $\mu = 1$  and  $\nu = 1$ , when approached from  $\mu, \nu < 1$ ; and moreover discontinuous in the point (1, 1) when approached from  $(\mu, 1)$  with  $\mu < 1$  or from  $(1, \nu)$  with  $\nu < 1$ . For instance, for the well studied coagulation kernel  $K_{ij} = (ij)^\omega$  ( $\omega < 1$ ) we have  $\theta = 2\omega$ , but  $\theta = \frac{5}{2}$  for  $K_{ij} = ij$ . Therefore, the model  $K_{ij} = ij$  and, more generally, the models  $K_{ij} = A + B(i + j) + Cij$  with  $C \neq 0$  (which contain Flory's polymerisation models  $A_gRB_f$ , showing a gelation transition (Cohen and Benedek 1982)) seem to be rather isolated soluble cases, the results of which cannot be generalised directly to more general kernels, such as in (8).

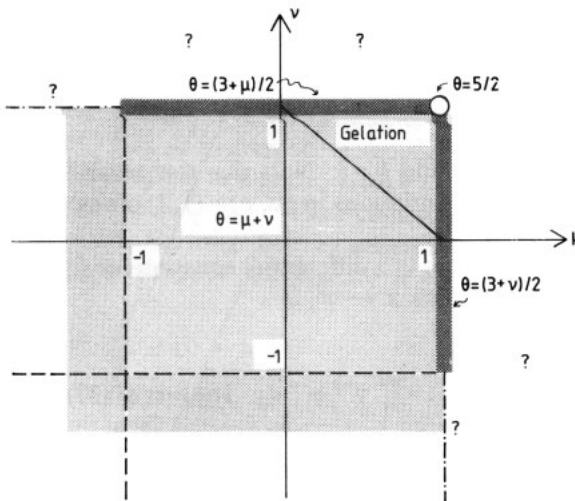


Figure 1. The exponent  $\theta(\mu, \nu)$  for the model  $K_{ij} = i^\mu j^\nu + i^\nu j^\mu$  in the  $(\mu, \nu)$  plane. Question marks on the lines (---) and in the regions  $\mu > 1$  or  $\nu > 1$  indicate that no consistent solution of the form (5) can be found. For  $(\mu, \nu)$  inside the region  $\{\mu + \nu > 1; \mu, \nu \leq 1\}$  the model yields a gelation transition.

In figure 1 we have also indicated the triangular region  $\{\mu + \nu > 1; \mu, \nu \leq 1\}$  of the  $(\mu, \nu)$  plane which contains coagulation kernels (8) leading to a gelation transition, as has been discussed by Hendriks *et al* (1983).

Before closing this section we note that the dominant large- $k$  behaviour of  $a_{kl}$  ( $l = 1, 2, \dots$ ) can be determined from the recursion relations (7), and one easily verifies by direct substitution that for fixed  $l$  and  $k \rightarrow \infty$

$$a_{kl} \approx a_{k0} \frac{(-)^l}{l!} (bk)^l \{1 + O(k^{-1})\} \tag{24}$$

where  $a_{k0}$  for  $k \rightarrow \infty$  has been evaluated in the preceding part of this section and  $b$  is

left undetermined. Note that only the first term in (7) contributes to the dominant large- $k$  behaviour.

It is tempting to insert (24) into (6), and interchange the small- $t$  and large- $k$  limits, to find

$$c_k(t) \approx a_{k0} t^{k-1} \exp(-bkt). \quad (25)$$

However, the large- $k$  behaviour in (24) is non-uniform in  $l$ . We may not conclude that (25) represents the large- $k$  behaviour of  $c_k(t)$  at a fixed point in time.

### 3. Application and discussion

As argued in § 1, the kernel  $K_{ij} = (ij)^\omega$  can be used to model the bonding processes in branched polymers, where the surface exponent  $\omega$  is a fixed model parameter with the same value in the sol and gel phase. For this model we have found in § 2 that the cluster size distribution takes the form (2) well below the gel point, where the exponents are given by  $\zeta = 1$  and  $\theta = 2\omega$ , on account of (14) and (8).

If we assume that the dimensionality of the effective surface of a large cluster is one lower than the dimension of the system, then  $\omega = (d-1)/d$ , leading to  $\theta(d) = 2(d-1)/d$ .

Another possible choice for  $\omega$  is based on the radius of gyration  $R_k$  of a branched polymer. This quantity describes the linear dimensions of a cluster and behaves asymptotically as  $R_k \sim k^\rho$  ( $k \rightarrow \infty$ ). It leads to a surface exponent  $\omega = (d-1)\rho$ .

This alternative is somewhat inconsistent, because  $\omega$  is a fixed model parameter, whereas  $\rho$  has one value  $\rho_<$  in the sol phase (which is very accurately given by Flory's formula  $\rho_F = 5/(2d+4)$ ), a different value  $\rho_c$  at the gel point, and still another value,  $\rho_> = 1/d$ , in the gel phase (Stanley *et al* 1982).

We have listed the  $\theta$ -values in table 2 for  $d = 2, 3$  and for two choices of  $\omega$ , and compared the results with the supposedly exact values, found by Parisi and Sourlas (1981), and with the classical value  $\theta = \frac{5}{2}$ . The results, obtained with the choice  $\omega = (d-1)/d$  based on physical grounds, show a considerable improvement when compared with the classical value. Note that Parisi and Sourlas' exact results lead to the exponent relation  $\theta = (d-2)\rho_< + 1$ .

**Table 2.**  $\theta$ -values according to the various approaches.

$d$	$\theta(\omega = 1 - 1/d)$	$\theta(\omega = (d-1)\rho_F)$	$\theta_{\text{exact}}$	$\theta_{\text{classical}}$
2	1	0.625	1.0	2.5
3	1.33	1	1.5	2.5

**Table 3.**  $\tau$ -values according to the various approaches.

$d$	$\tau(\omega = 1 - 1/d)$	$\tau(\omega = (d-1)\rho_c)$	$\tau_{\text{exact}}$	$\tau_{\text{classical}}$
2	2.00	2.03	2.06	2.5
3	2.17	2.30	2.20	2.5



To complement the survey of results obtained from the kinetic model  $K_{ij} = (ij)^\omega$ , we recall that the analogue of  $\theta$  at the gel point, called  $\tau$ , is given by  $\tau = \omega + \frac{3}{2}$  for  $\omega > \frac{1}{2}$ , and we have listed in table 3 (Ziff *et al* 1982) the  $\tau$ -values based on the same choices of  $\omega$  as above, together with their classical value and their exact value, numerically obtained from lattice theories. Gelation occurs only for  $\frac{1}{2} < \omega \leq 1$ .

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