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1984 J. Phys. A: Math. Gen. 17 2281

(http://iopscience.iop.org/0305-4470/17/11/023)

J. Phys. A: Math. Gen. 17 (1984) 2281–2297. Printed in Great Britain

Size distribution in the polymerisation model A_fRB_g

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Received 22 December 1983

Abstract. The polymer size distribution in Flory's polymerisation model A_fRB_g is in equilibrium and non-equilibrium of the general form $c_k = AN_k\xi^k$ both below and above the gelation transition. Here explicit expressions are derived for $A(\alpha)$ and $\xi(\alpha)$ as a function of the extent of reaction α. The combinatorial factors N_k are calculated from the recursion relation $2(k-1)N_k = \Sigma_{i+j=k} K_{ij}N_iN_j$ with $K_{ij} = s_i(f)s_j(g) + s_i(g)s_j(f)$ and $s_k(f) = (f-1)k+1$. Using a generating function technique we express N_k in terms of Laguerre polynomials ($g \to \infty$) and Jacobi polynomials (g finite), whose large-k behaviour is of the form $N_k \simeq Bk^{-\tau}\xi_c^{-k}$ with $\tau = \frac{3}{2}$ (no gelation occurs) if f or g equals 1, and with $\tau = \frac{5}{2}$ (gelation occurs) if $f > 1$ and $g > 1$.

1. Introduction

In this paper we discuss the equilibrium distribution of polymer sizes for Flory's A_fRB_g model of polymerisation, in which monomers carry f and g equi-reactive functional groups of type A and B respectively ($f, g = 1, 2, \ldots$), and branched non-cyclic polymers are formed through A–B bonding.

The *equilibrium size distribution* c_k, representing the concentration of k-mers, can be obtained from the theory of Flory and Stockmayer for the most probable distribution, and has the general form $c_k = AN_k\xi^k$ (Flory 1953, Stockmayer 1943). The Lagrange multipliers A and ξ are determined from the constraints $\Sigma_k c_k = \mu$ (total concentration of polymers) and $\Sigma_k kc_k = M$ (total concentration of units), and N_k represents the number of ways of assembling a k-mer from its constituent units. As we shall see below, the study of the equilibrium size distribution is also relevant for the time dependence of the size distribution in the kinetic theory of polymerisation. Therefore this paper is devoted to the study of the most probable distribution for the A_fRB_g model.

In the *kinetic theory of polymerisation*, the time evolution of the k-mer concentration $c_k(t)$ may be described by Smoluchowski's equation for rapid coagulation. This equation represents an infinite set of coupled non-linear rate equations describing the irreversible bonding of polymers (Ziff 1980). It may also be extended to include both bonding and break-up of polymers (van Dongen and Ernst 1983). The solution of this equation (Trubnikov 1971, Ziff 1980, Spouge 1983a, b, van Dongen and Ernst 1983) for an initial distribution containing monomers only has the general form $c_k(t) = A(\mu)N_k(\xi(\mu))^k$ where $A(\mu)$ and $\xi(\mu)$ are the same functions of μ as in equilibrium and where the time dependence of the total polymer concentration $\mu(t)$ is determined by the macroscopic rate equation with or without break-up processes. Also the combinatorial factors N_k are the same in both kinetic and equilibrium theory.

0305-4470/84/112281+17$02.25

The factors N_k can be obtained from combinatorial methods (Flory 1953, Stockmayer 1943), from the theory of branching processes (Ziman 1979) and from the following recursion relation (Ziff 1980, Spouge 1983a, van Dongen and Ernst 1983)

$$(k-1)N_k = \tfrac{1}{2} \sum_{i+j=k} K_{ij} N_i N_j \qquad (N_1 = 1). \tag{1.1}$$

In the present model, the coagulation kernel K_{ij} represents the number of possible A–B bonds formed out of free groups on an i-mer and on a j-mer, i.e.

$$K_{ij}(A_f RB_g) = s_i(f)s_j(g) + s_i(g)s_j(f) \tag{1.2}$$

with

$$s_k(f) = (f-1)k + 1 \tag{1.3}$$

where $s_k(f)$ and $s_k(g)$ are respectively the number of unreacted A and B groups on a k-mer. In fact, a simple combinatorial interpretation of (1.1) has been given by Spouge (1983c). The above models include after minor modifications Flory's random polycondensation model RA_f (A–A bonding; monomers with f equi-reactive A groups; no cycles) with coagulation rates:

$$K_{ij}(RA_f) = \sigma_i(f)\sigma_j(f) \tag{1.4}$$

where $\sigma_k(f)$ gives the number of unreacted A groups on a k-mer, i.e.

$$\sigma_k(f) = (f-2)k + 2. \tag{1.5}$$

In the RA_f model, the combinatorial factors are also determined by (1.1).

The large-k behaviour of N_k, which is in general of the form $N_k \simeq Bk^{-\tau}\xi_c^{-k}$ ($k \to \infty$), determines the possibility of occurrence of a *gelation transition*, i.e. for $\tau \leq 2$ no gelation occurs and for $\tau > 2$ gelation may occur (Cohen and Benedek 1982). It appears that a gelation transition occurs in the $A_f RB_g$ model provided $f, g > 1$.

The present models are in the general class of mean field models having the critical exponents of the Flory–Stockmayer theory and of classical percolation theory ($\tau = \vartheta = \frac{5}{2}$, $\sigma = \frac{1}{2}$, $\alpha = -1$, $\beta = 1$, $\gamma = 1$, $\delta = 2$) (Stanley *et al* 1982). In these models it is assumed that cyclic structures are forbidden and that all bonds are equally probable. This is modelled through a coagulation kernel $K \sim ij$ (volume interactions). In more realistic models bonds are formed only between reactive groups at the surface, i.e. $K_{ij} \sim (ij)^{\omega}$ with $\omega = (d-1)/d$ in d dimensions, where the critical exponents are given by $\tau = \omega + \frac{3}{2}$, $\vartheta = 2\omega$, $\sigma = \omega - \frac{1}{2}$ (Leyvraz and Tschudi 1982, Ziff *et al* 1982, Hendriks *et al* 1983, Ernst *et al* 1984). These results are in better agreement with those of lattice percolation theories. The classical result is typical for a Bethe lattice, on which the surface of a cluster is proportional to its volume ($\omega = 1$).

In the kinetic versions (Smoluchowski equation) of the Flory–Stockmayer theory of polymerisation the clusters have infinite mobility. In the lattice theories the clusters are completely static. Recently, several kinetic models with finite mobility have been simulated (Herrmann *et al* 1983, Bansil *et al* 1984) in attempts to construct better models for the kinetics of polymerisation and gelation.

Apart from the unrealistic features of equi-reactivity of all functional groups and infinite mobility of clusters, the classical polymerisation models have the great advantage of complete solubility.

The purpose of this paper is to present a simple method leading to *explicit* expressions for the quantities $A(\mu)$, $\xi(\mu)$ and N_k in the size distribution $c_k = AN_k\xi^k$

in the A_fRB_g model. For the present model Spouge (1983a, c) has already shown that A and ξ are *implicitly* related to macroscopic parameters μ and M through the generating function of the N_k's, and he has determined this generating function—at least in principle. However, his method is too complicated to lead to any explicit results for N_k at general functionalities f and g, whereas our method leads to closed expressions for N_k in terms of Laguerre polynomials ($g \to \infty$) and Jacobi polynomials (g finite).

Along completely different lines, using the theory of branching processes, Spouge (1983c) has recently calculated c_k (including N_k) in explicit form for general f and g, where N_k is represented as a sum of a finite number of terms. However it seems rather difficult to analyse the large-k behaviour of such sums, which is essential for describing the behaviour of the size distribution in the vicinity of the gelation transition.

The plan of this paper is as follows. In § 2 we calculate the combinatorial factors N_k and the complete size distribution c_k for the model A_fRB_∞ with many reactive B groups per monomeric unit ($g \to \infty$), and in § 3 for the general A_fRB_g model (g finite). The asymptotic size distribution as $k \to \infty$, and the scaling form of c_k in the vicinity of the gel point, are discussed in § 4 using the saddle-point method. In an appendix we show that our results for N_k in terms of Jacobi polynomials agree with Spouge's results.

2. Model A_fRB_∞

Certain simplifications occur in case the functionality of one type of reactive group becomes large. We therefore consider first the limit $g \to \infty$, where the coagulation kernel (1.2) (after rescaling by a factor g) takes the form

$$K_{ij} = is_j + js_i = 2(f-1)ij + i + j \tag{2.1}$$

with $s_k = s_k(f) = (f-1)k + 1$.

In order to solve the recursion relation (1.1) and determine the equilibrium size distribution c_k, it appears convenient to use two generating functions:

$$\begin{aligned} G(x) &= \sum_{k=1}^{\infty} N_k \, \mathrm{e}^{kx} = \sum_{k=1}^{\infty} N_k \xi^k \\ F(x) &= \sum_{k=1}^{\infty} s_k N_k \, \mathrm{e}^{kx} = \sum_{k=1}^{\infty} s_k N_k \xi^k \end{aligned} \tag{2.2}$$

related by

$$F = (f-1)G' + G. \tag{2.3}$$

The prime denotes an x derivative.

The size distribution takes the form $c_k = AN_k\xi^k$, and the constraints

$$\mu = \sum_k c_k = AG(x) \tag{2.4}$$

$$M = 1 = \sum_k kc_k = AG'(x) \tag{2.5}$$

determine A and $\xi = \mathrm{e}^x$ as a function of μ. It is convenient to choose the unit of volume such that the total concentration of units equals 1 ($M = 1$). Of course, A and ξ may be expressed in other parameters, equivalent to μ, such as the extent of reaction

α (i.e. the fraction of reacted A groups), which for the present model is given by

$$\alpha = \sum_{k=1}^{\infty} (k-1)c_k \Big/ \sum_{k=1}^{\infty} fkc_k = (1-\mu)/f. \tag{2.6}$$

In this case it is convenient to replace the constraint (2.4) by the following relation for the concentration of unreacted A groups

$$\sum_k s_k c_k = (f-1)+\mu = f(1-\alpha) \tag{2.7a}$$

where the right-hand side can be expressed in the generating function $F(x)$ in (2.2) on account of (2.4) and (2.5):

$$\sum_k s_k c_k = AF(x) = F(x)/G'(x). \tag{2.7b}$$

The constraints (2.5) and (2.7*a*, *b*) determine $A(\alpha)$ and $\xi(\alpha)$ as functions of α.

We start by solving the recursion relation (1.1) in terms of generating functions and obtain $A(\alpha)$ and $\xi(\alpha)$ from (2.5) and (2.7*a*, *b*); next we calculate N_k from the generating function F by inversion of the relation (2.2).

Apart from (2.3) two other relations between F and G may be deduced from the recursion relation. Multiplication of both sides of (1.1) with e^{kx} and summation over k yields

$$G' - G = G'F. \tag{2.8}$$

Alternatively, both sides of (1.1) may be multiplied by $s_k\, e^{kx}$ and summed over k with the result:

$$F' - F = (f-1)F'G' + FF'. \tag{2.9}$$

Elimination of G from (2.3) and (2.8) gives

$$G' = F/(f-F) \tag{2.10}$$

and subsequent substitution into (2.9) yields a differential equation for $F(x)$:

$$F' = F(f-F)(F^2 - 2fF + f)^{-1}. \tag{2.11}$$

On account of the limiting behaviour $F \simeq f\, e^x$ $(x \to -\infty)$ the required solution of (2.11) for $\xi = e^x$ in terms of F is

$$\xi = e^x = (F/f)(1-F/f)^{f-1}\, e^{-F}. \tag{2.12}$$

The radius of convergence ξ_c of $\bar{F}(\xi) = F(x)$ in (2.2) is determined from (2.12) by the condition $d\xi/dF = 0$ (maximum). Calling the solution F_c, it follows that

$$F_c = \bar{F}(\xi_c) = f - (f^2 - f)^{1/2}. \tag{2.13}$$

The solution (2.12), valid for $0 \leqslant F \leqslant F_c$, may be analytically continued to hold for all complex values of F.

To obtain the size distribution $c_k(\alpha) = A(\alpha)N_k\xi(\alpha)^k$ we first express $A(\alpha)$ in terms of $F(x(\alpha))$ by means of (2.5) and (2.10):

$$A(\alpha) = 1/G'(x(\alpha)) = [f - F(x(\alpha))]/F(x(\alpha)). \tag{2.14a}$$

Hence we have from (2.7*a*, *b*) for the extent of reaction, $\alpha = F(x(\alpha))/f$, which yields

upon substitution into (2.14*a*)

$$A(\alpha) = (1-\alpha)/\alpha. \tag{2.14b}$$

Analogously the fugacity $\xi(\alpha)$ may be determined from (2.12). The result is

$$\xi(\alpha) = \alpha(1-\alpha)^{f-1}\,\mathrm{e}^{-f\alpha}. \tag{2.15}$$

Combination of (2.14*b*) and (2.15) yields the following expression for the size distribution in terms of the extent of reaction

$$c_k(\alpha) = N_k\alpha^{k-1}(1-\alpha)^{s_k}\,\mathrm{e}^{-f\alpha k} \tag{2.16}$$

where N_k will be calculated below.

Equation (2.16) has a simple probabilistic interpretation, since α gives the probability that an A group, selected at random, has reacted. Hence the k-mer concentration $c_k(\alpha)$ equals the number of different configurations, N_k, multiplied with the probability for a specific k-mer configuration with $k-1$ bonds (yielding a factor α^{k-1}), with s_k unreacted A groups (yielding $(1-\alpha)^{s_k}$), and with k infinite sets of B groups ($\mathrm{e}^{-f\alpha k}$). Actually it will be seen in the next section that the factor $\mathrm{e}^{-f\alpha k}$ is obtained in the limit of high functionality ($g\to\infty$) from the probability for $s_k(g) = (g-1)k+1$ unreacted B's.

Once the explicit form (2.16) of the size distribution $c_k(\alpha) = AN_k\xi^k$ is known, the higher moments, $\Sigma k^n c_k (n \geqslant 2)$, can be simply calculated by $(n-1)$ times differentiating the relation $M = 1 = A\Sigma kN_k\xi^k$ with respect to α. This yields e.g. for the second moment:

$$\sum_{k=1}^{\infty} k^2 c_k = -A'\xi/A\xi' \tag{2.17a}$$

$$= (f\alpha^2 - 2f\alpha + 1)^{-1} \tag{2.17b}$$

where A' and ξ' denote derivatives with respect to α of A and ξ. They are explicitly given in (2.14) and (2.15).

The derivation of (2.16) for the size distribution is valid only for $\alpha \leqslant \alpha_c$, where the critical extent of reaction is defined by

$$\alpha_c = F_c/f = 1-(1-1/f)^{1/2} \tag{2.18}$$

and (2.13) has been used. At $\alpha = \alpha_c$ (or $\xi = \xi_c$) the generating functions G and F are non-analytic, and one finds that the weight-average cluster size $\Sigma_{k=1}^{\infty} k^2 c_k = (f\alpha^2 - 2f\alpha + 1)^{-1}$ diverges as $(\alpha_c - \alpha)^{-1}$ for $\alpha \uparrow \alpha_c$ (or $x(\alpha) \uparrow x_c$). At α_c an infinite cluster (gel) appears in the system, and a *gelation transition* takes place provided $f > 1$.

In the presence of a gel we assume, following *Flory's method*, that the bonding process is also random. Thus the concentration $c_k(\alpha)$ of finite size clusters (sol) is given by (2.15)–(2.16) for all $\alpha (0 \leqslant \alpha \leqslant 1)$, where α retains the interpretation of the probability that an A group be bonded. For $\alpha > \alpha_c$ a finite fraction of all units is contained in the gel, and the mass fraction $M(\alpha)$ in the sol is given by

$$M(\alpha) = A(\alpha)\sum_{k=1}^{\infty} kN_k\xi(\alpha)^k \tag{2.19a}$$

$$= A(\alpha)/A(\alpha^*) = \alpha^*(1-\alpha)/[\alpha(1-\alpha^*)]. \tag{2.19b}$$

For a given value of α, i.e. for a given $\xi(\alpha)$, equation (2.15) has a solution, called α^*, with $\alpha^* < \alpha_c$ (see figure 1). Since $\alpha^* < \alpha_c < \alpha$, it follows from (2.19) that $M(\alpha) < 1$. The gel fraction $G(\alpha) = 1 - M(\alpha)$ is a monotonically increasing function of α, which

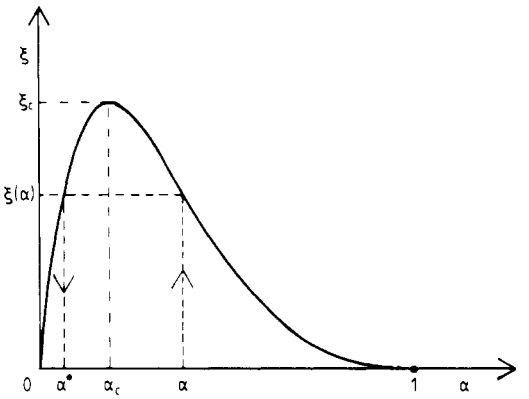

Figure 1. The fugacity $\xi(\alpha)=\alpha(1-\alpha)^{f-1}\exp(-f\alpha)$ in the A_fRB_∞ model (here we have chosen $f=3$) as a function of the extent of reaction α. The broken line shows the graphical construction of the root α^* for α in the interval $\alpha_c<\alpha<1$, as described in the text.

approaches unity as $\alpha \to 1$. Similarly one obtains for the number of clusters, using (2.19),

$$\mu(\alpha)=A(\alpha)\sum_{k=1}^{\infty} N_k\xi(\alpha)^k = M(\alpha)(1-f\alpha^*). \tag{2.20}$$

From its definition we deduce that the extent of reaction of the sol particles is $\alpha_s=\alpha^*$. We also note that Flory's post-gel cluster size distribution (2.16) can be written as $c_k(\alpha)=(A(\alpha)/A(\alpha^*))c_k(\alpha^*)=M(\alpha)c_k(\alpha_s)$, as is well known from the theory of branching processes (Ziman 1979). This formula has a simple probabilistic interpretation. $M(\alpha)$ equals the probability that a unit is in the sol, i.e. is contained in a finite size cluster, and $c_k(\alpha_s)$ is the cluster size distribution for polymer conditioned to be in the sol, in which the extent of reaction has the value $\alpha_s=\alpha^*$. The extent of reaction of the gel, α_g, can be deduced from the relation

$$\alpha = M(\alpha)\alpha_s + G(\alpha)\alpha_g \tag{2.21}$$

and it is found to be

$$\alpha_g = \alpha + \alpha^* - \alpha\alpha^*. \tag{2.22}$$

At the gelpoint $\alpha_g(\alpha_c)=1/f$, which equals the fraction of reacted groups in a large cluster without cycles. However, for $\alpha>\alpha_c$ one has $\alpha_g>1/f$, indicating that in the gel on the average more than one A group per monomeric unit is bonded. This indicates that the gel cannot be acyclic, as already argued by Stockmayer (1943). The total number of clusters is, therefore, different from $(1-f\alpha)$.

Stockmayer's (1943) *model* of a gel is somewhat different. Here the assumption (i) of an acyclic gel is strictly maintained. In addition it is assumed (ii) that the fugacity $\xi(\alpha)=\xi_c$ is fixed at the critical value. The fraction of reacted A groups is in general given by (2.21) with $G(\alpha)+M(\alpha)=1$. Here $\alpha_g=1/f$ on account of assumption (i); the extent of reaction of the sol is a constant, i.e. $\alpha_s=\alpha_c$ on account of assumption (ii) and (2.15). Hence the sol and gel fractions are linear functions of α and the *relative* size distribution has the same value as for α_c, i.e.

$$c_k(\alpha)=M(\alpha)c_k(\alpha_c). \tag{2.23}$$

Consequently,

$$\mu(\alpha) = M(\alpha)(1 - f\alpha_c). \tag{2.24}$$

Since $\mu(\alpha) = 1 - f\alpha$ on account of assumption (i) the mass fraction of the sol in Stockmayer's model of the gel is

$$M(\alpha) = \mu(\alpha)/\mu(\alpha_c) = (1 - f\alpha)/(1 - f\alpha_c). \tag{2.25}$$

The behaviour of these coagulating systems near the critical extent of reaction α_c will be studied in § 4.

We continue with the calculation of the combinatorial factors N_k and use Cauchy's formula to obtain the coefficient of ξ^k in the expansion (2.2) of $F'(x)$, i.e.

$$\begin{aligned} ks_k N_k &= (2\pi i)^{-1} \oint_C d\xi\, \xi^{-k-1} (dF/dx) \\ &= (2\pi i)^{-1} \oint_C dF\, \xi^{-k}. \end{aligned} \tag{2.26}$$

The path of integration C is a closed contour around the origin, such that other zeros of $\xi(F)$ are outside C. Inserting (2.12) and calling $F = fz$ yields then the following explicit expression for the combinatorial factors

$$ks_k N_k = f(2\pi i)^{-1} \oint z^{-k}(1 - z)^{-(f-1)k}\, e^{fkz}\, dz. \tag{2.27}$$

The integral can be evaluated straightforwardly by expanding $\exp(fkz)$ and $(1 - z)^a$ in powers of z and selecting the coefficient of z^{k-1} with the result

$$ks_k N_k = f \sum_{m+n=k-1} (-)^m \binom{-(f-1)k}{m} (fk)^n / n! \tag{2.28}$$

where $\binom{a}{m}$ is a binomial coefficient. A different representation is obtained by rewriting the summand in terms of Pochhammer symbols $(a)_m = \Gamma(a + m)/\Gamma(a)$ and using the series representation of the confluent hypergeometric function given by equation (13.1.2) of Abramowitz and Stegun (1965, henceforward referred to as AS):

$${}_1F_1(a, b, x) = \sum_{m=0}^{\infty} (a)_m x^m / (b)_m m!. \tag{2.29}$$

For $a = -n (n = 0, 1, 2, \ldots)$ this expression reduces to a polynomial of the nth degree. Thus, we obtain

$$\begin{aligned} ks_k N_k &= f \binom{fk-2}{k-1} {}_1F_1(1 - k, 2 - fk, fk) \\ &= f(-)^{k-1} L_{k-1}^{(1-fk)}(fk) \end{aligned} \tag{2.30}$$

where $L_n^{(\alpha)}(x)$ is a Laguerre polynomial, and AS (13.6.9) has been used.

A third representation follows directly from the integral (2.27), i.e.

$$ks_k N_k = f[(k-1)!]^{-1} U(1 - k, 2 - fk, fk) \tag{2.31}$$

since (2.27) corresponds to an integral representation (Erdelyi *et al* (1953) equation 6.12.2(9)) for the confluent hypergeometric function $U(a, b, x)$. The path of integration in the general expression (which is a loop around a cut in the complex z plane,

encircling the origin) reduces here to a closed contour around the origin, since the integrand has no branch points. Equation (2.31) immediately implies the expression (2.30) in terms of $L_n^{(\alpha)}(x)$ on account of AS (equation 13.6.27). The above expressions for N_k in the A_fRB_∞ model are new results.

Next, we consider some special cases, covered by our general result (2.28)–(2.31). For $f=1$ only the term with $m=0$ contributes to (2.28), so that

$$N_k = k^{k-1}/k! \qquad (ARB_\infty). \tag{2.32}$$

This is the well known result of Golovin and Scott (see Drake 1972) for the model ARB_∞ with $K_{ij}=i+j$.

In the limit $f\to\infty$ the binomial coefficient in (2.28) reduces to $(-fk)^m/m!$, and the sum on the right-hand side of (2.28) can be carried out, yielding to dominant order in f

$$N_k \simeq (2f)^{k-1}k^{k-2}/k!. \tag{2.33}$$

If one rescales for large f the kernel K_{ij} in (2.1) and the corresponding combinatorial factors N_k, defined by (1.1), by factors f (resp. $2f$) and f^{k-1} (resp. $(2f)^{k-1}$) respectively, one finds the kernels $K_{ij}=2ij$ (resp. $K_{ij}=ij$) for the model $A_\infty RB_\infty$ (resp. RA_∞) and the corresponding combinatorial factors as obtained by McLeod (1962).

The special case $f=2$, where $K_{ij}=2ij+i+j$ corresponds to the *needle model* of Hendriks and Ernst (1984). In this A_2RB_∞ model monomers may be thought of as needles, where the two needle points carry a reactive A group and where the cylindrical surface of a needle is uniformly covered with reactive B groups, and polymerisation occurs through A–B bonding. In this case the combinatorial factors are still relatively simple. They can be obtained most easily from (2.31) using AS, equations (13.1.29) and (13.6.21). The result is

$$N_k = (2ke)^k[(k+1)!]^{-1}(2/\pi k)^{1/2}K_{k-1/2}(k) \tag{2.34}$$

where $K_{n+1/2}(x)$ is a spherical Bessel function.

3. Model A_fRB_g

Next we consider the size distribution in the general model A_fRB_g. In view of the subsequent calculations, it is convenient to write the kernel (1.2) as

$$K_{ij} = s_i[(g-1)j+1]+s_j[(g-1)i+1] \tag{3.1}$$

where $s_k = s_k(f) = (f-1)k+1$. The derivation of a differential equation for the generating function $F(x)$, defined in (2.2), the construction of the size distribution and the calculation of the combinatorial factors N_k, proceed along the same lines as in the previous section.

First, one has again (2.3), relating F and G. From the recursion relation (1.1) one finds in the present case:

$$G'-G = F[(g-1)G'+G] \tag{3.2a}$$

$$F'-F = F[(g-1)F'+F]+(f-1)F'[(g-1)G'+G]. \tag{3.2b}$$

By taking a suitable linear combination of equations (2.3) and (3.2a) it follows that $(g-1)G'+G = gF/[f-(g-f)F]$. This yields in combination with (3.2b) the following

differential equation for $F(x)$

$$F'[f-2f(g-1)F+(g-1)(g-f)F^2]=F(1+F)[f-(g-f)F]. \tag{3.3}$$

The variables can be separated and splitting in partial fractions yields the solution

$$\xi=e^x=(F/f)(1+F)^{1-f-g}[1+(f-g)F/f]^{f-1} \tag{3.4}$$

satisfying the boundary condition $F(x)\simeq f\,e^x(x\to-\infty)$. It may readily be shown from (3.4) that the radius of convergence ξ_c of $\bar{F}(\xi)=F(x)$ is finite and determined by

$$F_c=\bar{F}(\xi_c)=f(g-f)^{-1}\{1-[g(f-1)/f(g-1)]^{1/2}\}. \tag{3.5}$$

The generating function $\bar{F}(\xi)$ is therefore defined by the branch $0\leqslant F\leqslant F_c$ of $\xi(F)$ given in (3.4).

The next step in obtaining the size distribution for the A_fRB_g model is the calculation of $A(\alpha)$ and $\xi(\alpha)$. Since $A=1/G'(x)$ on account of (2.5), we eliminate G from (2.3) and (3.2*a*) to obtain an expression for G' in terms of F. The result is

$$A(\alpha)=[f+(f-g)F(x(\alpha))]/\{F(x(\alpha))[1+F(x(\alpha))]\}. \tag{3.6}$$

As the extent of reaction of the A groups satisfies $f(1-\alpha)=AF$ by virtue of (2.7*a*, *b*), we eliminate F in favour of α to obtain

$$A(\alpha)=(1-\alpha)(1-\beta)(g/\alpha). \tag{3.7}$$

Here we have introduced the extent of reaction β, representing the fraction of reacted B groups. It is simply related to α by $g\beta=f\alpha$, since in the A_fRB_g model the concentrations of reacted B groups ($g\beta$) and reacted A groups ($f\alpha$) are equal. Analogously $\xi(\alpha)$ may be obtained from (3.4):

$$\xi(\alpha)=(\alpha/g)(1-\alpha)^{f-1}(1-\beta)^{g-1} \tag{3.8}$$

and we have for the size distribution

$$c_k(\alpha)=N_k(\alpha/g)^{k-1}(1-\alpha)^{s_k(f)}(1-\beta)^{s_k(g)}. \tag{3.9}$$

As in the previous section, equation (3.9) has a probabilistic interpretation, where now $\alpha/g(=\beta/f)$ gives the probability that a specific A (resp. B) group is bonded to one particular B (resp. A) group out of g (resp. f) groups on the next unit, and $(1-\beta)^{s_k(g)}$ gives the probability for $s_k(g)=(g-1)k+1$ unreacted B's. It is readily seen that the factor $(1-\beta)^{s_k(g)}$ reduces to $e^{-f\alpha k}$ in the limit of high functionality ($g\to\infty$). A phase transition takes place at $\alpha=\alpha_c$ (or equivalently: $\beta=\beta_c$), where the critical extent of reaction α_c is the solution of the equation $d\xi(\alpha)/d\alpha=0$ with $\xi(\alpha)$ given by (3.8):

$$f\alpha_c=g\beta_c=fg(f+g-1)^{-1}\{1-[(f-1)(g-1)/fg]^{1/2}\}. \tag{3.10}$$

The moments, $\Sigma\, k^n c_k$, can be calculated as in § 2, and we obtain from (2.17*a*), (3.7) and (3.8) for the second moment:

$$\sum_{k=1}^{\infty} k^2 c_k=(1-\alpha\beta)/[1-f\alpha-g\beta+(f+g-1)\alpha\beta]. \tag{3.11}$$

It diverges like $(\alpha_c-\alpha)^{-1}$ as $\alpha\uparrow\alpha_c$.

Using *Flory's model of a gel*, we assume that c_k is given by (3.9) in the post-gel stage ($\alpha>\alpha_c$) as well, where α and β retain the interpretation of bonding probabilities. Since the mass fraction of the sol $M(\alpha)<1$ according to (2.19*a*), a macroscopic gel phase may occur in the system provided $\max\{\alpha_c,\beta_c\}<1$, and it follows from (3.10)

that gelation takes place for f, $g > 1$. The extent of reaction of the sol is given by $\alpha_s = \alpha^*$, where α^* is defined in a similar way as before (see figure 1). The extent of reaction of the gel, α_g, can be calculated from (2.21) and one finds the result

$$\alpha_g = [\alpha + \alpha^* - \alpha^*(\alpha + \beta)]/(1 - \alpha^*\beta) \tag{3.12}$$

with $f\alpha = g\beta$. For $\alpha > \alpha_c$ this quantity is larger than $1/f$, indicating that the gel has a cyclic structure. In *Stockmayer's model of a gel* equations (2.23)–(2.25) should be used again.

To calculate N_k the relation (3.4) for $\xi(F)$ may be continued analytically to hold for all F in the complex plane, and we have from (2.26)

$$ks_k N_k = \oint \frac{dF}{2\pi i} \frac{f^k(1+F)^{(g+f-1)k}}{F^k[1+(f-g)F/f]^{(f-1)k}} \tag{3.13}$$

where the contour is a closed path around the origin that excludes all other singularities of the integrand.

As the integrand in (3.13) is of the form $z^{-k}A(z)$, the right-hand side of (3.13) is equal to the coefficient of z^{k-1} in the Taylor expansion of $A(z)$, yielding the following explicit expression for the combinatorial factors N_k of the model A_fRB_g:

$$ks_k N_k = f^k \sum_{m+n=k-1} (1-g/f)^n \binom{-(f-1)k}{n} \binom{(g+f-1)k}{m} \tag{3.14a}$$

$$= f(-g)^{k-1} P_{k-1}^{(\alpha,\beta)}(1-2f/g) \tag{3.14b}$$

where $\alpha = 1 - fk$ and $\beta = (g+f-2)k + 1$. This is a new result. We have used the Jacobi polynomials in the form (Erdelyi *et al* (1953) equation 10.8(12)):

$$P_k^{(\alpha,\beta)}(x) = [(x-1)/2]^k \sum_{m+n=k} [(x+1)/(x-1)]^n \binom{k+\alpha}{n} \binom{k+\beta}{m} \tag{3.15}$$

which is a special case of the hypergeometric function.

The result (2.30) for large g may be obtained from (3.14b) using AS, equation 22.15.5:

$$\lim_{\beta\to\infty} P_k^{(\alpha,\beta)}(1-2x/\beta) = L_k^{(\alpha)}(x). \tag{3.16}$$

In the explicit form (3.14) the symmetry of N_k upon interchanging f and g is not obvious. As is shown in an appendix, a more symmetric form can be obtained from (3.13) by changing integration variables and performing a partial integration. The resulting expression reduces to the symmetric form of Spouge (1983c):

$$ks_k(f)s_k(g)N_k = \sum_{m+n=k-1} f^m g^n (fgk - fn - gm) \binom{(g-1)k+m}{m} \binom{(f-1)k+n}{n} \tag{3.17}$$

as derived in equation (A6) of the appendix.

The general formula for N_k in the model A_fRB_g covers several well known cases. For $f = 1$ one has the model ARB_g corresponding to the coagulation kernel $K_{ij} = (g-1)(i+j)+2$. In this case only the term with $n = 0$ contributes to (3.14a), yielding

$$kN_k = \binom{gk}{k-1} \qquad (ARB_g). \tag{3.18}$$

In the special case $f=g$, where $K_{ij}=2s_i(f)s_j(f)$, one obtains again a simple expression for N_k, since only the term with $n=0$ contributes to (3.14*a*). Hence, the combinatorial factors for the model A_fRB_f become:

$$ks_k(f)N_k = f^k\binom{(2f-1)k}{k-1} \qquad (A_fRB_f). \tag{3.19}$$

The coagulation kernel of this model is related to that of the RA_{2f} model on account of (1.2)–(1.5), namely

$$K_{ij}(A_fRB_f) = \tfrac{1}{2}K_{ij}(RA_{2f}). \tag{3.20}$$

Consequently, the recursion relation (1.1) implies

$$N_k(RA_{2f}) = 2^{k-1}N_k(A_fRB_f) \tag{3.21}$$

which has an obvious combinatorial interpretation. Since the extent of reaction for $\alpha<\alpha_c$ is given by $\alpha=(1-\mu)/f$ in both the RA_{2f} and the A_fRB_f model, the size distribution for the RA_{2f} model readily follows from (3.9) in combination with (3.21). Hence we have for the size distribution in the RA_f model (cf Flory, Stockmayer)

$$c_k(\alpha) = (\alpha/f)^{k-1}(1-\alpha)^{\sigma_k(f)}f^k[(f-1)k]!/[k!\sigma_k(f)!] \tag{3.22}$$

where $\sigma_k(f)$ is given in (1.5). The interpretation of (3.22) is, that any specific configuration has probability $(\alpha/f)^{k-1}(1-\alpha)^{\sigma_k(f)}$ for having $k-1$ bonds between a specific A on one unit and one out of f possible A's on another, and $\sigma_k(f)$ unreacted groups. Finally the combinatorial factor gives the number of different configurations. In the RA_f model with $f>2$ the phase transition takes place at $\alpha_c=1/(f-1)$. For $\alpha>\alpha_c$ one may use either Flory's or Stockmayer's gel model, where the relevant formulae can be simply deduced from § 2.

4. Asymptotic results

In the previous section we have calculated explicit expressions for the size distribution in the form $c_k(\alpha)=A(\alpha)N_k\xi(\alpha)^k$. Here we obtain asymptotic expressions ($k\to\infty$) for the combinatorial factors N_k, and hence for the size distribution of the A_fRB_∞ and A_fRB_g models. They will be derived from the integral representations (2.27) and (A1) using the saddle-point method. From the asymptotic behaviour of the combinatorial factors we further obtain the scaling properties of the size distribution near the critical point $\alpha=\alpha_c$.

No standard asymptotic expressions seem to be available for (confluent) hypergeometric functions with large parameters *and* large argument. The only exception is a result applicable to the A_2RB_∞ model. In the latter case, AS (equation 9.7.8) may be used to obtain the following large-k approximation

$$N_k = k^{-5/2}[2\pi(2+\sqrt{2})]^{-1/2}[2(1+\sqrt{2})\,e^{2-\sqrt{2}}]^k[1+O(k^{-1})] \tag{4.1}$$

which has also been given by Hendriks and Ernst (1984).

Consider the A_fRB_∞ model first. In this case N_k is given by the integral representation (2.27). We define

$$w = F/f$$

$$V(w) = fw - \log w - (f-1)\log(1-w) \tag{4.2}$$

and rewrite (2.27) in the following form

$$ks_k N_k/f = (2\pi \mathrm{i})^{-1} \oint_C \mathrm{d}w\, \mathrm{e}^{kV(w)}. \tag{4.3}$$

Here the path of integration C may be any closed contour around the origin, provided $w = 1$ is outside C. The (complex) function $V(w)$ has a saddle point where $\mathrm{d}V/\mathrm{d}w = 0$, i.e. at

$$w_c = 1 - (1 - 1/f)^{1/2} \tag{4.4}$$

located in between the two poles $w = 0$ and $w = 1$. We now choose the circle $|w| = w_c$ in the complex plane as our contour, so that we have from (4.3)

$$ks_k N_k/f = (2\pi \mathrm{i})^{-1} \int_{x_c - \mathrm{i}\pi}^{x_c + \mathrm{i}\pi} \mathrm{d}x\, \mathrm{e}^{x + k\bar{V}(x)} \tag{4.5}$$

where by definition $x = \log w$ and $\bar{V}(x) = V(w)$.

For $k \to \infty$ the dominant contribution to the integral (4.5) comes from x values near the saddle point $x_c = \log w_c$, since for large values of k the integrand $\exp[x + k\bar{V}(x)]$ is sharply peaked about its maximum at x_c. The function $\bar{V}(x)$ may be expanded in a Taylor series near $x = x_c$ as follows

$$\bar{V}(x) = \bar{V}(x_c) + (x - x_c)\bar{V}'(x_c) + \tfrac{1}{2}(x - x_c)^2 \bar{V}''(x_c) + \ldots \tag{4.6}$$

and one finds the result

$$\bar{V}(x) = 1 + \tfrac{1}{2}(x - x_c)^2 + \ldots \qquad (f = 1) \tag{4.7a}$$

$$= \bar{V}(x_c) + (x - x_c)^2 f \exp(x_c) + \ldots \qquad (f > 1). \tag{4.7b}$$

Note that the special case (4.7*a*) cannot be recovered from (4.7*b*) as $f \downarrow 1$, and should be treated separately. The reason is that

$$\lim_{f \to 1} \left(\lim_{x \to x_c} \bar{V}''(x) \right) \neq \lim_{x \to x_c} \left(\lim_{f \to 1} \bar{V}(x) \right)''. \tag{4.8}$$

The dominant large-k behaviour of (4.5) then becomes

$$ks_k N_k/f \simeq (2\pi)^{-1} \exp(x_c + k\bar{V}(x_c)) \int_{-\pi}^{\pi} \mathrm{d}y \exp[-\tfrac{1}{2}ky^2 \bar{V}''(x_c)]$$

$$\simeq (2\pi k \bar{V}''(x_c))^{-1/2} \exp(x_c + k\bar{V}(x_c)) \qquad (k \to \infty) \tag{4.9}$$

yielding

$$N_k \simeq B k^{-\tau} \xi_c^{-k} \qquad (k \to \infty). \tag{4.10}$$

In the special case $f = 1$ we have $\tau = \frac{3}{2}$ and

$$B = (2\pi)^{-1/2}, \qquad \xi_c = \mathrm{e}^{-1} \tag{4.11}$$

whereas for $f > 1$ we have $\tau = \frac{5}{2}$ and

$$B = [f w_c / 4\pi (f-1)^2]^{1/2}, \qquad \xi_c = w_c (1 - w_c)^{f-1} \exp(-f w_c) \tag{4.12}$$

where w_c is given by (4.4). In the special case $f = 2$ it may be readily verified that the result (4.12) reduces to the expression (4.1).

Next we consider the large-k behaviour of the N_k in the $A_f RB_g$ model. We start from the integral representation (A1), which is equivalent to (3.13) but has the advantage

of obvious symmetry with respect to f and g. As a result our asymptotic expressions will also show a symmetric dependence on the functionalities. First we assume that $f, g > 1$, and we define the auxiliary functions

$$h(w) = (1 - gfw)[w(1 - gw)(1 - fw)]^{-1} \tag{4.13a}$$

$$V(w) = -\log w - (f-1)\log(1 - gw) - (g-1)\log(1 - fw) \tag{4.13b}$$

in order to write (A1) in the form

$$s_k(f)s_k(g)N_k = (2\pi\mathrm{i})^{-1} \oint_C \mathrm{d}w\, h(w)\, \mathrm{e}^{kV(w)} \tag{4.14}$$

where C is a closed contour around the origin such that $w = 1/f$ and $w = 1/g$ are outside C. The function V has a saddle point at

$$w_c = (g + f - 1)^{-1}(1 - r), \qquad r = [(f-1)(g-1)/fg]^{1/2} \tag{4.15}$$

located in between the pole $w = 0$ and the zero $w = 1/fg$ of the integrand $h(w)\exp(kV(w))$ of (4.14).

In order to determine the dominant large-k behaviour of the integral (4.14) we choose for our contour a circle of radius $|w| = w_c$ and we define $x_c = \log w_c$, $x = \log w$, $x = x_c + \mathrm{i}y$, and $\bar{V}(x) = V(w)$. As before we may expand $\bar{V}(x)$ in a Taylor series about x_c, where

$$\begin{aligned} \bar{V}''(x_c) &= (2f-1)/2(f-1) && (f = g) \\ &= 2fg(f-g)^{-2}[(f+g-2) - (g+f)r] && (f \neq g). \end{aligned} \tag{4.16}$$

Calculation of $\bar{V}''(x_c)$ in the case $f \neq g$ is lengthy but straightforward. Evaluation of $wh(w)$ at the saddle point shows that

$$w_c h(w_c) = \tfrac{1}{2}\bar{V}''(x_c). \tag{4.17}$$

Inserting (4.17) and the Taylor expansion (4.6) combined with (4.16) into (4.14), and replacing the contour C for large k by the line $x = x_c + \mathrm{i}y$, with $-\infty < y < \infty$, yields a dominant asymptotic behaviour of N_k in the form (4.10) with $\tau = \frac{5}{2}$. The case $f = g > 1$ yields the following explicit results for B and ξ_c

$$\begin{aligned} B &= \tfrac{1}{4}(f-1)^{-5/2}[(2f-1)/\pi]^{1/2} \\ \xi_c &= [2(f-1)]^{2(f-1)}/[f(2f-1)^{2f-1}]. \end{aligned} \tag{4.18}$$

The case $f \neq g$, $f, g > 1$ yields

$$\begin{aligned} B &= (\bar{V}''(x_c)/2\pi)^{1/2}/[2(f-1)(g-1)] \\ \xi_c &= w_c(1 - gw_c)^{f-1}(1 - fw_c)^{g-1} \end{aligned} \tag{4.19}$$

where w_c and $\bar{V}''(x_c)$ are given in (4.15) and (4.16) respectively.

The special case where $f = 1$ or $g = 1$ cannot be recovered from (4.18) or (4.19) in the limit $f \downarrow 1$ or $g \downarrow 1$. By symmetry of f and g, we assume that $f = 1$. Here we have instead of (4.13)

$$h(w) = [w(1-w)]^{-1}, \qquad \mathrm{e}^{V(w)} = [w(1-w)^{g-1}]^{-1} \tag{4.20}$$

and it follows that $w_c = 1/g$, and $\bar{V}''(x_c) = g/(g-1) = w_c h(w_c)$. Substitution of these results into the integral representation (4.14) with $s_k(1) = 1$ yields an asymptotic result

for N_k of the form (4.10) with $\tau = \frac{3}{2}$ and

$$B = (g-1)^{-3/2}(g/2\pi)^{1/2}, \qquad \xi_c = w_c(1-w_c)^{g-1} \tag{4.21}$$

provided $g > 1$. For $f = g = 1$ one does not find a saddle point, and clearly the saddle-point method is not applicable to this case. However, the large-k behaviour of N_k in this model is well understood, since we have the explicit form $N_k = 1$.

In the limit $g \to \infty$ our results (4.19) and (4.21) reduce to the previous result (4.11)–(4.12), provided we rescale w_c and N_k by factors g and g^{k-1} respectively. Similarly asymptotic expressions for the combinatorial factors of the $A_\infty RB_\infty$ and RA_∞ models are obtained (which read $B = [2(2\pi)^{1/2}]^{-1}$, $\xi_c = (2e)^{-1}$ and $B = 1/(2\pi)^{1/2}$, $\xi_c = e^{-1}$ respectively) from (4.12) with $f \to \infty$ or alternatively from (4.18) with $f = g \to \infty$.

In order to obtain asymptotic expressions for the size distribution $c_k(\alpha)$, we first note that the parameter $\xi_c = \exp[-V(w_c)]$, which determines the exponential k-dependence of N_k as $k \to \infty$, is clearly identical to the radius of convergence of the generating function $\bar{F}(\xi)$. This quantity has also been denoted by ξ_c and is given by (2.12)–(2.13) for the model A_fRB_∞, and by (3.4)–(3.5) for the model A_fRB_g. The equivalence of (3.4)–(3.5) and (4.19) is not immediately obvious but may be shown straightforwardly. Thus we have on account of (4.10) for the large-k behaviour of the size distribution

$$\begin{aligned} c_k(\alpha) &= A(\alpha)N_k\xi(\alpha)^k \\ &\simeq k^{-\tau}A(\alpha)B(\xi(\alpha)/\xi_c)^k \qquad (k \to \infty) \end{aligned} \tag{4.22}$$

where the values of B, ξ_c and τ in the various models have been calculated above.

To study the properties of the size distribution near the phase transition, we assume that f, $g > 1$ in order to ensure that gelation takes place, i.e. that $\max\{\alpha_c, \beta_c\} < 1$, and we expand $\log(\xi(\alpha)/\xi_c)$ in powers of $\varepsilon \equiv (\alpha - \alpha_c)/\alpha_c$. In the case of the A_fRB_∞ model we have from comparison of (2.15) and (4.2)

$$\begin{aligned} \xi(\alpha)/\xi_c &= \exp[V(\alpha_c) - V(\alpha)] \\ &\simeq \exp[-\tfrac{1}{2}\alpha_c^2 V''(\alpha_c)\varepsilon^2] \end{aligned} \tag{4.23}$$

where we have used the fact that $V'(\alpha_c) = V'(w_c) = 0$. It is readily demonstrated that $\alpha_c^2 V''(\alpha_c) = \bar{V}''(x_c)$ (the primes denote differentiation with respect to α and x respectively), and one finds that

$$\xi(\alpha)/\xi_c \simeq \exp[-\tfrac{1}{2}\bar{V}''(x_c)\varepsilon^2] \tag{4.24}$$

where $\bar{V}''(x_c) = 2f\alpha_c$ on account of (4.7b).

In the case of the A_fRB_g model we have $\xi(\alpha) = \exp[-V(\alpha/g)]$ where $V(w)$ is defined in (4.13b). Expanding $V(\alpha/g)$ in powers of ε shows that equation (4.24) holds for the A_fRB_g model as well, with $\bar{V}''(x_c)$ now given by (4.16). Combining (4.22) and (4.24) finally shows that for $\alpha \to \alpha_c$ the size distribution takes the following scaling form

$$c_k(\alpha) \simeq k^{-\tau}A(\alpha)B \exp[-\tfrac{1}{2}k\bar{V}''(x_c)|\varepsilon|^{1/\sigma}] \qquad (k \to \infty) \tag{4.25}$$

where the critical exponent $\tau = \frac{5}{2}$ and $\sigma = \frac{1}{2}$ are universal within the class of A_fRB_g type models, provided we take f, $g > 1$. The result (4.25) applies to Flory's model of gelation both below ($\alpha \uparrow \alpha_c$) and above ($\alpha \downarrow \alpha_c$) the critical point. In Stockmayer's model of a gel the fugacity $\xi(\alpha)$ remains constant for $\alpha \geqslant \alpha_c$, and the corresponding form

$$c_k(\alpha) \simeq k^{-\tau}M(\alpha)A(\alpha_c)B \qquad (k \to \infty) \tag{4.26}$$

holds for all $\alpha \geqslant \alpha_c$.

Finally, we compare the behaviour of $M(\alpha)=1-G(\alpha)$ for $\alpha \downarrow \alpha_c$ in Flory's and Stockmayer's gel model. By expanding equations (2.19) and (2.25) in powers of $\varepsilon=(\alpha-\alpha_c)/\alpha_c$ one obtains for all three polymerisation models RA_f, A_fRB_∞ and A_fRB_g:

$$\begin{aligned} M(\alpha) &\simeq 1-2\varepsilon/r \qquad \text{(Flory, } \varepsilon \downarrow 0\text{)} \\ &\simeq 1-\varepsilon/r \qquad \text{(Stockmayer, } \varepsilon \downarrow 0\text{)} \end{aligned} \tag{4.27}$$

where the coefficient r is given by

$$\begin{aligned} r &= (f-2)/f && (RA_f) \\ r &= [(f-1)/f]^{1/2} && (A_fRB_\infty) \\ r &= [(f-1)(g-1)/fg]^{1/2} && (A_fRB_g). \end{aligned} \tag{4.28}$$

We remark in concluding this paper, that our results hold for real values of f and g as well, provided $f \geq 1$ and $g \geq 1$, and for complex conjugate f and $g=f^*$ with $\mathrm{Re}(f) \geq 1$ and $\mathrm{Re}(g) \geq 1$. Thus we have in fact obtained the equilibrium size distribution and its asymptotic behaviour ($k \to \infty$) for the general bilinear kernel $K_{ij}=A+B(i+j)+Cij$ with real A, B and $C \geq 0$, since (1.2)–(1.3) may always be written in this form by transforming f and g according to

$$f, g = (A+B \pm D)/A \tag{4.29}$$

with $D^2=B^2-AC$ being positive or negative, and subsequent rescaling of K_{ij} (resp. N_k) by a factor $A/2$ (resp. $(A/2)^{k-1}$). The special case $A=0$ corresponds to the limit $g \to \infty$.

Acknowledgment

The work of one of us (PvD) is part of a research programme of the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', which is financially supported by the 'Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO)'.

Appendix

In order to put (3.6) into a more symmetric form, we change integration variables, i.e. $F=fw/(1-fw)$, and subsequently perform a partial integration using $f(1-fw)^{-a-1}=a^{-1}(\mathrm{d}/\mathrm{d}w)(1-fw)^{-a}$. The resulting expression for N_k is

$$s_k(f)s_k(g)N_k=(2\pi\mathrm{i})^{-1}\oint_C \mathrm{d}w\, w^{-k-1}(1-fgw)(1-fw)^{-s_k(g)}(1-gw)^{-s_k(f)} \tag{A1}$$

where $s_k(f)$ is defined in (1.3). The representation (A1) is obviously symmetric upon interchanging f and g.

The integral can be evaluated as in (3.6) with the result

$$\begin{aligned} s_k(f)s_k(g)N_k = {} & (-)^k f^k g \sum_{m+n=k-1} (g/f)^n \binom{-s_k(g)}{m}\binom{-s_k(f)}{n} \\ & +(-)^k f^k \sum_{m+n=k} (g/f)^n \binom{-s_k(g)}{m}\binom{-s_k(f)}{n} \end{aligned} \tag{A2}$$

which may, if desired, be expressed in Jacobi polynomials by virtue of (3.8). Here we want to combine both sums in (A2) into a single sum. In order to do so, we multiply (A2) by k and write the second sum on the RHS as $k\Sigma S_{mn} = \Sigma(m+n)S_{mn}$. First we consider

$$\sum_{m=0}^{k} mS_{m,k-m} = \sum_{m=0}^{k-1} (m+1)S_{m+1,k-m-1}$$
$$= -f \sum_{m+n=k-1} [(g-1)k+m+1]S_{mn}. \tag{A3}$$

As the term with $m=0$ does not contribute to LHS (A3), we replace m by $m+1$, yielding the first equality. In the second equality we have used the relation

$$(m+1)\binom{a}{m+1} = (a-m)\binom{a}{m}. \tag{A4}$$

In a similar way we find

$$\sum_{n=0}^{k} nS_{k-n,n} = -g \sum_{m+n=k-1} [(f-1)k+n+1]S_{mn}. \tag{A5}$$

Combination of (A2), (A3) and (A5) then yields Spouge's result (1.7), namely

$$ks_k(f)s_k(g)N_k = (-)^{k-1} \sum_{m+n=k-1} f^m g^n (fgk-fn-gm)\binom{-s_k(g)}{m}\binom{-s_k(f)}{n}$$
$$= \sum_{m+n=k-1} f^m g^n (fgk-fn-gm)\binom{(g-1)k+m}{m}\binom{(f-1)k+n}{n} \tag{A6}$$

where we have used the relation

$$\binom{-a}{n} = (-)^n \binom{a+n-1}{n}. \tag{A7}$$

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