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A two-parameter perturbation series for the reciprocal length of polymer chains and subchains

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Abstract. Generating functions are defined which permit the computation of moments of the end-to-end length of random walks. These functions are applied, within the framework of the Domb–Joyce model, to the development of a two-parameter perturbation series for the contraction factor α_{ij}^{-1} of the mean reciprocal distance $\langle R_{ij}^{-1}\rangle$ between the segments i and j of self-avoiding walks. The case where i or j denotes a chain end is shown to be fundamentally different from the case where neither denotes a chain end.

1. Introduction

The quantity $\langle R_{ij}^{-1}\rangle$ first attracted attention during the study of viscous and frictional properties of polymer solutions. It appears, for instance, in the familiar Kirkwood–Riseman formula (1948) for the intrinsic viscosity $[\eta]$. The average of $\langle R_{ij}^{-1}\rangle$ taken over the entire chain serves as a definition of the reciprocal of the 'hydrodynamic radius' or 'Stokes radius' of the chain (Stockmayer and Albrecht 1958) and appears in the Kirkwood expressions for the diffusion and sedimentation coefficients (Kirkwood 1954). It has not been as extensively studied as other moments of the chain length because of the formidable nature of the inverse moment—it depends not only on $|j-i|$ but also on i and on the total chain length. (One should, however, mention the perturbation series for the hydrodynamic radius developed by Stockmayer and Albrecht in 1958.) Consequently, those wishing to extend the Kirkwood theories to include the effects of excluded volume have had to make assumptions of uncertain accuracy (e.g. Ullman 1981, Akcasu *et al* 1981). It would, therefore, be useful if more precise results concerning $\langle R_{ij}^{-1}\rangle$ were available, so that these assumptions could be tested.

The Domb–Joyce (1972) model of a polymer chain has recently been applied with some success (Domb and Barrett 1976, Barrett and Domb 1979, 1981) to furnish accurate closed-form expressions for chain moments, against which other approximate expressions may be tested. The same procedure may be applied, with profit, to moments of intra-chain distances. Since, however, the envisaged formula is an interpolation between known results on self-avoiding walks and the two-parameter expansion, a necessary prerequisite is the establishment of the perturbation series which is the object of this work.

In addition to the difficulties mentioned above, the calculation of the inverse moment is further complicated by the fact that the moment is *odd*. Odd moments of

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chain length are, strictly speaking, zero. One is interested really in moments of $R=(R_x^2+R_y^2+R_z^2)^{1/2}$, which are somewhat more difficult to compute. It is easy to imagine earlier investigators renouncing the computation on the grounds that the result would, in any case, be too complicated to be useful. Such an argument is, however, no longer valid given the present availability of automatic computing devices.

2. Some fundamentals

We consider a random walk, on a lattice or in the continuum, which is characterised by the function

$$P(\boldsymbol{R}, x)=\sum_n p_n(\boldsymbol{R})x^n$$

where $p_n(\boldsymbol{R})$ is the fraction of n-step random walks whose nth step is located at a distance $\boldsymbol{R}$ from the walk origin. (For continuum walks, $p_n(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R}$ is the probability that the walk terminates in the volume element $\mathrm{d}\boldsymbol{R}$ at $\boldsymbol{R}$ after n steps.) We may further define the generating function:

$$P(x)=\sum_{\boldsymbol{R}} P(\boldsymbol{R}, x)=(1-x)^{-1}\equiv u^{-1}.$$

The sum is to be replaced by an integral for continuum walks.

The universal nature of the Domb–Joyce model derives from the fact that $P(\boldsymbol{R}, x)$ has the same form for a large class of random walks. Chandrasekhar (1943) showed that for a random flight with a Gaussian distribution of step lengths

$$P(\boldsymbol{R}, x)=a^{-1}2(\pi)^{1/2}h_0R^{-1}\exp[-(6u)^{1/2}R] \tag{1}$$

and Joyce (1971) has shown that this expression holds asymptotically for cubic lattices if the constant h_0 is appropriately defined. This is, to be sure, an expression of the central limit theorem and leads to results which are universally applicable to random walks regardless of the specific nature of those walks.

The constant h_0 is defined by

$$h_0=(3/2\pi)^{3/2}g/a^3.$$

Here a is the step length (or a^2 the mean square step length as appropriate), and g the volume per lattice site. For Gaussian continuum walks $g=1$.

It is possible to think of such a random walk, with a total contour length of n segments, as consisting of a central subchain of N segments, a 'short' endchain of ζN segments, and a 'long' endchain of λN segments. Then

$$n=(1+\zeta+\lambda)N.$$

Without loss of generality, we may take $\zeta\leqslant\lambda$. We are interested in the moments of the distribution for the central subchain and denote its end-to-end length by $R_N(\zeta,\lambda)$. This length is more commonly represented by $(R_{ij})_n$, which is the distance between the ith and jth segments of a chain of total contour length n. The indices i and j are related to ζ and λ by

$$i=\zeta N \qquad j=(1+\zeta)N \qquad i\leqslant j.$$

A similar relation exists for $j<i$.

In the Domb–Joyce model, the excluded volume interaction is introduced by assigning a statistical weight $1-w$ to each self-intersection of the complete chain. If $w=1$, then all self-intersecting configurations have a weight of 0, and the statistics are those of self-avoiding walks. Random walk statistics result when $w=0$. It can be seen that w corresponds to the binary cluster integral and is related to the usual two-parameter variable z by

$$z = h_0 n^{1/2} w.$$

For a more complete exposition see Domb and Joyce (1972) and Barrett and Domb (1979).

It is now possible to define formally a generating function (or partition function) for interacting chains which is analogous to $P(x)$. We write

$$P(x, w) = \sum_n p_n(w) x^n$$

which defines $p_n(w)$ (see Barrett and Domb 1979). It is a simple matter to extend this formal definition to the case of three contiguous chains. Set $L=\zeta N$, $M=\lambda N$, and write

$$P(x, y, z : w) = \sum_{L,N,M} p_{LNM}(w) x^L y^N z^M$$

where $p_{LNM}(w)$ is an obvious generalisation of $p_n(w)$ For convenience, we shall suppress the arguments x, y, z and write this function as $P(w)$.

If the end-to-end length of the central subchain is the vector $\boldsymbol{R}_N$, then $P(w)$ may be written as

$$P(w) = \sum_{\boldsymbol{R}_N} P(\boldsymbol{R}_N, w)$$

where $P(\boldsymbol{R}_N, w)$ is the generating function for interacting chains whose central subchain has end-to-end length $\boldsymbol{R}_N$. Moments of this distribution function are then defined by

$$\langle R_N^m(w)\rangle = P(w)^{-1} \sum_{\boldsymbol{R}} R_N^m P(\boldsymbol{R}_N, w) = P^{(m)}(w)/P(w)$$

and then the following expansions made:

$$P(w) = T_0 - T_1 w + T_2 w^2 - \cdots$$

$$P^{(m)}(w) = V_0 - V_1 w + V_2 w^2 - \ldots$$

$$\alpha_N^m(w) = \langle R_N^m(w)\rangle / \langle R_N^m(0)\rangle = 1 - K_1^{(m)} w + K_2^{(m)} w^2 - \ldots.$$

The desired coefficients $K_r^{(m)}$ are given by

$$K_1^{(m)} = \nu_1 - \tau_1 \qquad K_2^{(m)} = \nu_2 - \tau_2 - K_1^{(m)} \tau_1$$

etc where τ_r and ν_r are the coefficients of $x^N y^L z^M$ in T_r and V_r respectively. The coefficients τ_r and ν_r, in general, involve statistics of configurations with r or more self-intersections, and may be evaluated by means of the generating functions. In the following section we demonstrate how this may be done.

3. The generating functions $\Phi(s)$

At this point we introduce a function

$$\phi_N(s)=\sum_{\boldsymbol{R}} p_N(\boldsymbol{R})\,\mathrm{e}^{-sR}$$

and also

$$\Phi(s,x)=\sum_N \phi_N(s)x^N.$$

Note that

$$\Phi(0,x)=P(x)=u^{-1}$$

is the generating function for random walks, and that

$$R=-\frac{\mathrm{d}}{\mathrm{d}s}\mathrm{e}^{-sR}\Big|_{s=0} \qquad R^{-1}=\int_0^\infty \mathrm{e}^{-sR}\,\mathrm{d}s$$

so that

$$P^{(1)}=-\frac{\mathrm{d}}{\mathrm{d}s}\Phi(s,x)\Big|_{s=0}\equiv D\Phi$$

and

$$P^{(-1)}=\int_0^\infty \mathrm{d}s\ \Phi(s,x)\equiv I\Phi.$$

Indeed, identifying I with D^{-1}, we may formally write

$$P^{(m)}=D^m\Phi$$

as the generating function for the mth power of the end-to-end length of the walk.

For our purposes, it is not necessary to compute Φ exactly—the dominant singular part of Φ suffices to give the two-parameter result. (The interested reader is referred to appendix A of Barrett and Domb (1979) for a fuller discussion.) Now

$$\Phi(s,x)=\sum_{\boldsymbol{R}} P(\boldsymbol{R},x)\,\mathrm{e}^{-sR}.$$

To obtain the dominant singular part, we apply the Euler–Maclaurin formula, replacing the summation by an integral

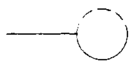
$$\sum_{\boldsymbol{R}}\ldots\to g^{-1}\int \mathrm{d}\boldsymbol{R}\ldots.$$

Substitution of (1) yields, upon evaluation of the integral, the very simple function

$$\Phi(s,x)_{\mathrm{sing}}=\frac{6}{a^2}\left(\frac{\sqrt{6}u^{1/2}}{a}+s\right)^{-2}.$$

This is the simplest of the Φ functions. Other such functions may be defined, as necessary, for more complicated configurations. Those required in the computation of $K_1^{(-1)}$ are listed in table 1.

Table 1.

Graph	Φ	$I\Phi$
	$6a^{-2}(\beta - r)^{-2}$	$6a^{-2}\beta^{-1}$
R: 	$12a^{-3}\sqrt{6\pi}h_0(\gamma+\delta)^{-1}(r+\beta+\delta)^{-1} \times (r+\beta+\gamma)^{-1}$	$12a^{-3}\sqrt{6\pi}h_0(\gamma^2-\delta^2)^{-1} \times \ln[(\beta+\gamma)/(\beta+\delta)]$
T: 	$12a^{-3}\sqrt{6\pi}h_0[2r(r^2-\beta^2)^{-2} \times \ln[(r+\beta+\gamma)/(2\beta+\gamma)] - (r^2-\beta^2)^{-1}(r+\beta+\gamma)^{-1}]$	$12a^{-3}\sqrt{6\pi}h_0\beta^{-2}\ln[(2\beta+\gamma)/(\beta+\gamma)]$

$\beta = a^{-1}\sqrt{6}\,u^{1/2} = a^{-1}\sqrt{6}\,(1-x)^{1/2}$; $\gamma = a^{-1}\sqrt{6}\,t^{1/2} = a^{-1}\sqrt{6}\,(1-y)^{1/2}$; $\delta = a^{-1}\sqrt{6}\,v^{1/2} = a^{-1}\sqrt{6}(1-z)^{1/2}$.

4. Application to random walks

The dimensions of an ideal chain are unaffected by endchains, so ζ and λ may be set to 0, leaving a random walk of N steps. Such a walk is represented by an unadorned straight-line graph. The first reciprocal moment is given by the generating function

$$I\Phi = \sqrt{6}u^{-1/2}/a.$$

Now the coefficient of x^N in u^ν is (see e.g. Domb and Joyce 1972)

$$\frac{N^{-\nu-1}}{\Gamma(-\nu)}[1+O(1/N)] \tag{2}$$

so that

$$\langle R_N^{-1}(0)\rangle = (6/\pi a^2)^{1/2}N^{-1/2}.$$

If it is desired to compute the average of this quantity taken over the entire chain (all possible values of ζ and λ), it is necessary to attach the endchains to the simple chain, and then sum over all possible endchain lengths. Since $P(x)$ is the generating function for chains of all lengths, the graph is represented by the generating function $P\Phi P = P^2\Phi$. The total number of such configurations is the coefficient of x^N in $P^2\Phi(0)$, and the average moment, or inverse hydrodynamic radius R_H^{-1} where

$$R_H^{-1}(0) = 2N^{-2}\sum_{i<j}\langle R_{ij}^{-1}(0)\rangle$$

is twice the coefficient of x^N in

$$P^2 I\Phi = \sqrt{6}u^{-5/2}/a$$

from which it follows that

$$R_H^{-1}(0) = \tfrac{4}{3}(6/\pi a^2)^{1/2}N^{-1/2}.$$

These results are not new (see Yamakawa 1971): they are re-derived here for the purposes of illustration.

5. Application to interacting walks

The calculation of $K_1^{(-1)}$ follows essentially the rules given in Barrett and Domb (1979) generalised according to the principles outlined in the previous section. The details are very tedious, and not particularly illuminating, and for this reason we simply quote the result here, outlining the contributions from the various diagrams in tables 1, 2 and 3. The contribution from graphs 5 and 6 is calculated in an appendix for the interested reader.

The principal result of this paper is the formula

$$K_1^{(-1)} = 4h_0N^{1/2}[(1+\zeta+\lambda)^{1/2} - \tfrac{1}{2}(\zeta+\lambda)^{1/2} + \mathrm{Ti}_2((4\zeta)^{-1/2}) - \mathrm{Ti}_2(\zeta^{1/2}) + \tfrac{1}{4}\pi\ln(4\zeta) - \tfrac{1}{2}\zeta^{1/2} + \mathrm{Ti}_2((4\lambda)^{-1/2}) - \mathrm{Ti}_2(\lambda^{1/2}) + \tfrac{1}{4}\pi\ln(4\lambda) - \tfrac{1}{2}\lambda^{1/2} - \tfrac{1}{2}(1+\zeta)\tan^{-1}\zeta^{1/2} - \tfrac{1}{2}(1+\lambda)\tan^{-1}\lambda^{1/2} + \tfrac{1}{2}(1+\zeta+\lambda)\tan^{-1}(\lambda+\zeta)^{1/2} - \tfrac{1}{4}\pi].$$

Table 2.

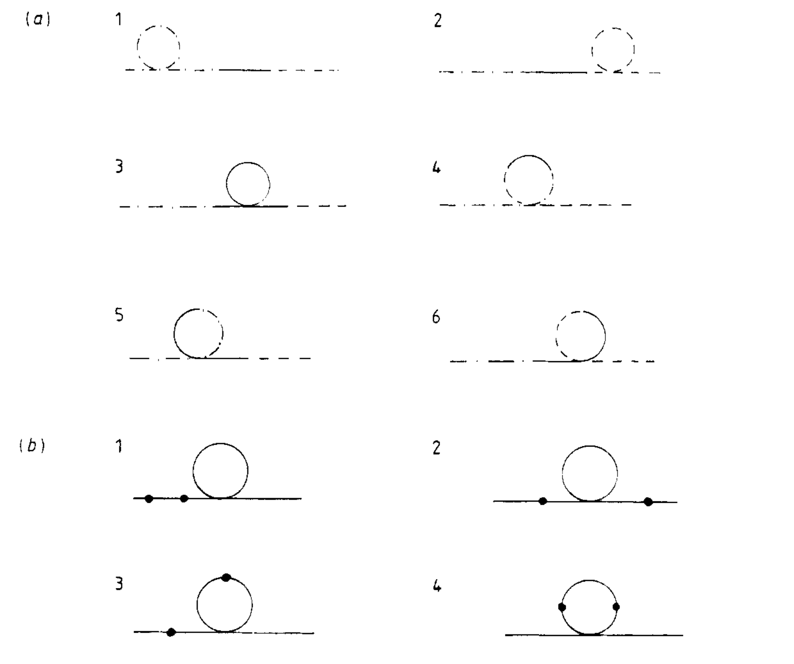


Table 3. Contributions of two-parameter graphs.

Graph	
1 and 2	0
3	$(4-\pi)h_0N^{1/2}$
4	$4h_0N^{1/2}[1+(1+\zeta+\lambda)^{1/2} - \tfrac{1}{2}(\zeta+\lambda)^{1/2} - (1+\zeta)^{1/2} - (1+\lambda)^{1/2} + \tfrac{1}{2}\zeta^{1/2} + \tfrac{1}{2}\lambda^{1/2} - \tfrac{1}{2}(1+\zeta)\tan^{-1}\zeta^{1/2} - \tfrac{1}{2}(1+\lambda)\tan^{-1}\lambda^{1/2} + \tfrac{1}{2}(1+\zeta+\lambda)\tan^{-1}(\zeta+\lambda)^{1/2}]$
5	$4h_0N^{1/2}[\mathrm{Ti}_2((4\zeta)^{-1/2}) - \mathrm{Ti}_2(\zeta^{1/2}) + \tfrac{1}{4}\pi\ln(4\zeta) + (1+\zeta)^{1/2} - \zeta^{1/2} - 1]$
6	$4h_0N^{1/2}[\mathrm{Ti}_2((4\lambda)^{-1/2}) - \mathrm{Ti}_2(\lambda^{1/2}) + \tfrac{1}{4}\pi\ln(4\lambda) + (1+\lambda)^{1/2} - \lambda^{1/2} - 1]$

The function Ti_2 is the 'inverse tangent integral', defined by

$$\mathrm{Ti}_2(x) = \int_0^x y^{-1} \tan^{-1} y \, dy$$

(see Lewin (1958); I am most grateful to the very thorough referee who identified this function).

It is clear that $K_1^{(-1)}$ is not an analytic function of ζ and λ. However if we define ρ as the ratio of ζ to λ:

$$\rho = \zeta/\lambda \leqslant 1$$

then $K_1^{(-1)}$ is seen to be an analytic function of $\lambda^{1/2}$ and $\rho^{1/2}$ and may, therefore, be expanded in MacLaurin series of these two variables. For $\lambda < 1/2$:

$$K_1^{(-1)} = -4h_0 N^{1/2}[(1-\tfrac{1}{4}\pi)+\tfrac{1}{2}\lambda(1+\rho)-\lambda^{3/2}(\tfrac{7}{9}-\tfrac{1}{2}\rho+\ldots)-\tfrac{1}{8}\lambda^2(1+2\rho+\rho^2)+\mathrm{O}(\lambda^{5/2})].$$

Asymptotic series are also possible; for $\zeta < \tfrac{1}{2}$, $\lambda > 1$

$$K^{(-1)} = -4h_0 N^{1/2}[(\tfrac{1}{4}\pi \ln 4 - 1)+\zeta(\tfrac{1}{4}\pi - \tfrac{1}{12}\lambda^{-3/2}+\ldots)-\tfrac{10}{9}\zeta^{3/2}+\tfrac{1}{36}\lambda^{-3/2}+\mathrm{O}(\lambda^{-5/2})]$$

and for $\lambda > \zeta > 1$

$$K_1^{(-1)} = -4h_0 N^{1/2}[\tfrac{1}{2}\pi(\ln 4 - 1)-\tfrac{1}{6}\lambda^{-1/2}+\tfrac{11}{360}\lambda^{-3/2}-\tfrac{1}{6}\zeta^{-1/2}$$
$$+\tfrac{11}{360}\zeta^{-3/2}+\tfrac{1}{6}(\zeta+\lambda)^{-1/2}-\tfrac{7}{120}(\zeta+\lambda)^{-3/2}+\mathrm{O}(\lambda^{-5/2})].$$

An interesting question arises when we wish to write the perturbation expansion in terms of the two-parameter excluded volume variable z. It is possible to define z in terms of N, the contour length of the central subchain, so that

$$\alpha^{-1}(h_0 N^{1/2} w) = 1 + C_1(h_0 N^{1/2} w) + \ldots$$

in which case C_1 is simply $K_1^{(-1)}$ divided by $h_0 N^{1/2}$. If z is defined in terms of n, the total contour length, then

$$\alpha^{-1}(h_0 n^{1/2} w) = 1 + D_1(h_0 n^{1/2} w) + \ldots$$

in which case D_1 is $K_1^{(-1)}$ divided by $h_0(1+\zeta+\lambda)^{1/2} N^{1/2}$. Both these functions are plotted against λ in figure 1 for two limiting values of ρ.

The most interesting feature of the coefficient is the effect of endchain length upon its limiting value. There are clearly three cases of interest: (i) no endchains, (ii) one

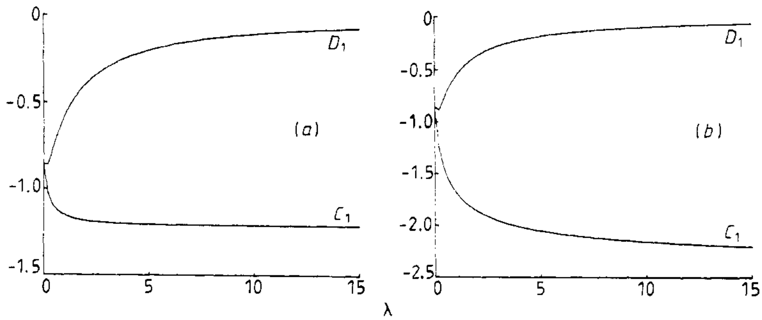


Figure 1. (*a*) C_1 and D_1 plotted against λ for $\rho = 0$. (*b*) C_1 and D_1 plotted against λ for $\rho = 1$.

endchain and (iii) two endchains. Des Cloizeaux (1980) has identified these as being three different 'universality classes'. This means that, if chain behaviour is assumed to be governed by power-law behaviour, then there will be differing exponents for each of the three cases. It is impossible to verify this, of course, from an examination of the series coefficients; however, the limiting behaviour of the coefficient is strikingly different for each case. If $\lambda \to \infty$, then

$$C_1 = \pi - 4 = -0.858\,407 \qquad \text{no endchains}$$

$$C_1 = \pi(1 - \ln 4) = -1.213\,580 \qquad \text{one endchain}$$

$$C_1 = 2\pi(1 - \ln 4) = -2.427\,160 \qquad \text{two endchains.}$$

It is important to realise that the last limit given holds for any finite $\rho > 0$, regardless of how small. This is a fascinating rigorous example of critical behaviour in a physical system.

A similar situation occurs for the first coefficient in the series for α_{ij}^2. This coefficient was computed years ago by Teramoto *et al* (1958). If their expression is rewritten in terms of ζ and λ, and the limit as $\lambda \to \infty$ taken, then one finds the three respective limiting values $\frac{4}{3}$, $\frac{16}{9}$, and $\frac{32}{9}$. Note that these are all rational, while the corresponding limits for C_1 are irrational.

6. The average value

By definition

$$\alpha_{\mathrm{H}}^{-1} = \langle R_{\mathrm{H}}^{-1}(z)\rangle / (\langle R_{\mathrm{H}}^{-1}(0)\rangle = 1 + E_1 z + \ldots.$$

The Albrecht–Stockmayer result for E_1 is easily obtained. The four contributing graphs are shown in table 2(*b*), and the final result is

$$E_1 = [4 - (\tfrac{27}{16} - \tfrac{3}{2}\ln\tfrac{3}{2})\pi].$$

7. Conclusions

A perturbation series has been developed for the contraction factor α_{ij}^{-1} of the Domb–Joyce model of a polymer chain. An exact expression has been calculated for the first coefficient in this series in the two-parameter limit.

From this brief study it is possible to draw a number of conclusions, valid for very long polymer chains under weak excluded volume conditions. It is clear for instance that the effect of endchains upon chain dimensions can be considerable (e.g. the limiting value of C_1 for two endchains is twice that for a single endchain). One should, therefore, exercise care when making approximations which ignore this effect. Furthermore, it can be seen that the approximation $\alpha_{ij}^{-1} = (\alpha_{ij}^2)^{-1/2}$ is not justified by the two-parameter expansion.

Finally, it is fascinating to discover that the Des Cloizeaux hypothesis of three universality classes finds support in the limiting behaviour of the perturbation series coefficients. It will be interesting to see if further evidence of this nature can be found for chains exhibiting strong excluded volume. Indeed, it will be interesting to discover how reliable the behaviour of the series coefficients is as a guide to a description of chains with large excluded volume.

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Appendix

From table 1, the generating function for graph 5 is

$$P(y)\Phi_T(s: x, y)P(z)$$

where

$$\Phi_T(s: x, y) = g^{-2}\int \mathrm{d}\boldsymbol{R}\, \mathrm{d}\boldsymbol{R}'\, P(\boldsymbol{R}', x)P(\boldsymbol{R}', y)(\boldsymbol{R}-\boldsymbol{R}', x)\, \mathrm{e}^{-sR}.$$

If s is set to 0, we obtain as the singular part of the generating function

$$2(\pi)^{1/2}h_0 t^{-1}u^{-1}v^{-1}/(u^{1/2}+t^{1/2})$$

where $u = 1-x$, $t = 1-y$ and $v = 1-z$.

The next step is to extract the coefficient of $x^N y^L z^M$ from this expression. This may be done by writing

$$(u^{1/2}+t^{1/2})^{-1} = t^{-1/2}(1+u^{1/2}/t^{1/2})^{-1}$$

assuming the ordering $u<t$, then expanding in Maclaurin series. The desired coefficient may then be determined term by term, using (2), and then summed to give the contribution of this graph to τ_1:

$$4h_0N^{1/2}[1+\zeta^{1/2}-(1+\zeta)^{1/2}]. \tag{A1}$$

The same result is obtained for any assumed ordering of u, v, t.

If we operate with I prior to setting $s=0$, we obtain, again from table 1, the singular function

$$2a^{-1}\sqrt{\pi}h_0 t^{-1}u^{-1}v^{-1}[\ln(2u^{1/2}+t^{1/2})-\ln(u^{1/2}+v^{1/2})].$$

Extraction of the coefficient of $x^N y^L z^M$ proceeds as above; however, in this case it is necessary to use a modification of (2) developed by Domb and Joyce. The coefficient of x^N in $u^\nu \ln u$ is, asymptotically,

$$\frac{N^{-\nu-1}}{\Gamma(-\nu)}[\psi(-\nu)-\ln N+\mathrm{O}(N^{-1}\ln N)].$$

$\psi(x)$ is the logarithmic derivative of $\Gamma(x)$. The resulting contribution to ν_1 from this graph is

$$4h_0N^{1/2}[\mathrm{Ti}_2((4\zeta)^{-1/2})-\mathrm{Ti}_2(\zeta^{1/2})+\tfrac{1}{4}\pi\ \ln(4\zeta)]. \tag{A2}$$

The contribution to $K_1^{(-1)}$ is found by subtracting (A1) from (A2).

The contribution from graph 6 may be obtained by replacing ζ by λ.

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