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On the Flory formula for the polymer size exponent ν

M A Moore and A J Bray

Department of Theoretical Physics, The University, Manchester, M13 9PL, UK

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Abstract. The average end-to-end distance R_N of a flexible polymer chain of N segments in a good solvent varies as N^ν , where, according to Flory, the size exponent $\nu = 3/(2+d)$ in d dimensions ($1 \leq d \leq 4$). The original derivation of this formula for the exponent ν has been shown by des Cloizeaux to be without foundation. We demonstrate that the Flory formula is valid in a model for which only a finite (but large) number of spherical harmonics are retained in the harmonic (partial wave) expansion of the propagator.

1. Introduction

The average end-to-end distance R_N of a flexible polymer chain in a good solvent varies with the number of links N as $R_N \sim bN^\nu$, $N \gg 1$, where b is a link length. All aspects of polymer behaviour in the dilute and semi-dilute concentration regimes involve ν . Hence it is not surprising that there have been many attempts at determining the value of this fundamental exponent. Reviews of these varied attempts are given by Yamakawa (1971), des Cloizeaux (1970, 1976) and McKenzie (1976). One of the oldest approaches is that of Flory (1953), which, when generalised to arbitrary dimensionality d (Fisher 1969), gives $\nu = 3/(2+d)$, ($1 \leq d \leq 4$). For $d = 1$, it predicts that $\nu = 1$ which is clearly the exact answer. For $d = 2$, the formula yields $\nu = 0.75$. Exact enumeration and Monte Carlo estimates of ν in two dimensions lie in the range $0.74-0.75$ (McKenzie 1976). In three dimensions, the Flory value for ν is 0.60 , while numerical estimates give values in the range $0.59-0.61$ (McKenzie 1976). Experimental determination of ν is, of course, possible in three dimensions; for example, Decker (1968) obtained $\nu = 0.59(5)$ in a light scattering experiment. Probably, the most precise estimate of ν in three dimensions is the renormalisation group calculation of Le Guillou and Zinn-Justin (1977) who quote $\nu = 0.588 \pm 0.001$.

Despite the numerical success of the Flory formula for ν it is certainly not exact (except for $d = 1$). This was first shown by de Gennes (1972). Universal properties of self-interacting walks are described by the Landau-Ginzburg-Wilson isotropic n -vector model in the limit $n \rightarrow 0$ (de Gennes 1972, Emery 1975). In the renormalisation group $\epsilon (= 4-d)$ expansion, $2\nu = 2\nu(n=0) = 1 + \epsilon/8 + O(\epsilon^2)$, whereas the Flory formula gives $2\nu = 1 + \epsilon/6 + O(\epsilon^2)$.

As the Flory formula for ν is so accurate, one might hope that it would be possible to provide a derivation of it which would at the same time provide an approach to polymers in solution which is conceptually simpler than one based on the renormalisation group. Unfortunately, the original derivation of the Flory formula is quite without foundation (des Cloizeaux 1976). Another approach which is supposed to

give the Flory result is the self-consistent field (SCF) method devised by Edwards (1965) (for a review see Freed 1972). We shall comment on this method in § 4.

Before describing our basic approximation some formalism must be introduced. As usual we shall be studying the Green function $\hat{G}(\mathbf{r}, \mathbf{r}', L)$ of a continuous flexible string of length L which has one end at \mathbf{r} and its other end at \mathbf{r}' . Its Laplace transform $G(\mathbf{r}, \mathbf{r}', E)$ is the generating function for these strings. Because of translational invariance, $G(\mathbf{r}, \mathbf{r}', E) = G(|\mathbf{r} - \mathbf{r}'|, E)$. In the absence of excluded volume forces, $G(\mathbf{r}, \mathbf{r}', E) = g(\mathbf{r}, \mathbf{r}', E)$ where the bare propagator g satisfies the differential equation

$$(E - \nabla^2)g(\mathbf{r}, \mathbf{r}', E) = \delta(\mathbf{r} - \mathbf{r}'). \tag{1}$$

(All lengths, etc, are expressed in terms of the segment length b to suppress b from the equations.) The solution of equation (1) gives the well known Gaussian behaviour of a random chain. The excluded volume interaction energy of two points at \mathbf{x} and \mathbf{y} on the string will be taken to be $k_B T v(\mathbf{x}, \mathbf{y})$ where $v(\mathbf{x}, \mathbf{y}) = u\delta(\mathbf{x} - \mathbf{y})$. The graphical perturbation expansion of G in powers of u is given in figure 1.

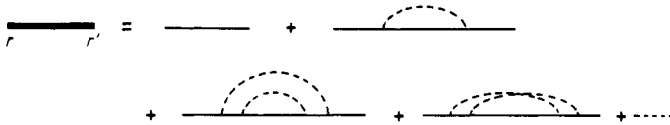


Figure 1. Graphical expansion of $G(\mathbf{r}, \mathbf{r}', E)$. The broken lines carry a factor $-u\delta(\mathbf{x} - \mathbf{y})$. The light full lines are bare propagators g . The bold line represents the full Green function $G(\mathbf{r}, \mathbf{r}', E)$.

Both the bare propagator $g(\mathbf{r}, \mathbf{r}', E)$ and the Green function $G(\mathbf{r}, \mathbf{r}', E)$ can be expanded in three dimensions in the spherical harmonics Y_{lm} :

$$g(\mathbf{r}, \mathbf{r}', E) = \sum_{l=0}^{\Lambda} \sum_{m=-l}^l Y_{lm}(\Omega) Y_{lm}^*(\Omega') g_l(\mathbf{r}, \mathbf{r}', E), \tag{2}$$

$$G(\mathbf{r}, \mathbf{r}', E) = \sum_{l=0}^{\Lambda} \sum_{m=-l}^l Y_{lm}(\Omega) Y_{lm}^*(\Omega') G_l(\mathbf{r}, \mathbf{r}', E), \tag{3}$$

as $\Lambda \rightarrow \infty$. Ω and Ω' denote the angular spherical polar coordinates of \mathbf{r} and \mathbf{r}' respectively.

Our basic approximation is not to let $\Lambda \rightarrow \infty$ but to keep it large but finite. Such an approximation destroys translational invariance so that now $G(\mathbf{r}, \mathbf{r}', E) \neq G(|\mathbf{r} - \mathbf{r}'|, E)$. In many ways it is as though there were a central potential at the origin. The loss of translational invariance makes the approximation unsuitable for constructing a simple intuitive theory of polymers in solution. On the other hand it defines a model for which the Flory result emerges relatively cleanly.

Because of the loss of translational invariance $G(\mathbf{r}, \mathbf{r}, E)$ now becomes a function of r . Scaling suggests that its r dependence at $E = 0$ should be $G(\mathbf{r}, \mathbf{r}, 0) \sim 1/r^{d-1/\nu}$. (In the translationally invariant system $G(\mathbf{r}, \mathbf{r}, E) \sim |E - E_c|^{d\nu-1}$ (McKenzie 1976), where E_c is the critical value of E . One expects, therefore, that in the non-translationally invariant system $G(\mathbf{r}, \mathbf{r}, E) \sim |E - E_c|^{d\nu-1} f(r|E - E_c|^\nu)$, so that as $|E - E_c| \rightarrow 0$, $G(\mathbf{r}, \mathbf{r}, E_c) \sim 1/r^{d-1/\nu}$. Explicit calculation in §§ 2 and 3 confirm this scaling prediction and also show that $E_c = 0$.) We shall find the Flory result for ν in the finite- Λ

approximation from the r dependence of $G(\mathbf{r}, \mathbf{r}, 0)$. A similar procedure for finding ν is used in the SCF theory (Freed 1972).

The expansions in equations (2) and (3) in terms of spherical harmonics are particular to three dimensions. In general dimensionality similar expansions exist, but in terms of the Gegenbauer polynomials. They will not be written down as their explicit form is not needed. In all cases our approximation consists of cutting off the summation over the partial waves at some finite Λ .

In § 2 the Green function $G(\mathbf{r}, \mathbf{r}', 0)$ is calculated in the self-consistent Fock approximation with finite Λ . It is shown explicitly that $G(\mathbf{r}, \mathbf{r}, 0)$ falls off as $r^{-2(d-1)/3}$, so that on setting $d - 1/\nu = 2(d - 1)/3$, one obtains the Flory result for ν . We prove in § 3 that the exponent dependence of $G(\mathbf{r}, \mathbf{r}, 0)$ remains as determined in the self-consistent Fock approximation to all orders in perturbation theory. In § 4 the mechanism by which the Flory result fails as the limit $\Lambda \rightarrow \infty$ is taken is exhibited. In addition we discuss the relation of our approximation to the SCF of Edwards.

2. The self-consistent Fock approximation

The Green function in this approximation, $\mathcal{G}(\mathbf{r}, \mathbf{r}', E)$, is given by the solution of the non-linear integral equation (see figure 2)

$$\mathcal{G}(\mathbf{r}, \mathbf{r}', E) = g(\mathbf{r}, \mathbf{r}', E) - \int d\mathbf{x} d\mathbf{y} g(\mathbf{r}, \mathbf{x}, E) \mathcal{G}(\mathbf{x}, \mathbf{y}, E) \mathcal{G}(\mathbf{y}, \mathbf{r}', E) v(\mathbf{x}, \mathbf{y}). \tag{4}$$

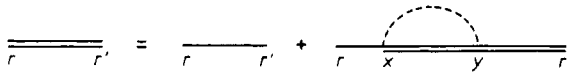


Figure 2. Graphical equation for the self-consistent Fock propagator $\mathcal{G}(\mathbf{r}, \mathbf{r}', E)$ (double line).

It is to be understood that g in this equation is the expression which arises from keeping Λ finite in equation (2). Only the special case of $E = 0$ will be studied. Let us make the *ansatz* that

$$v(\mathbf{x}, \mathbf{y}) \mathcal{G}(\mathbf{x}, \mathbf{y}, 0) = A \delta(\mathbf{x} - \mathbf{y}) / x^{d-1/\nu}, \tag{5}$$

where A and ν are to be determined self-consistently. Then \mathcal{G} is the solution of the differential equation

$$(-\nabla^2 + A/r^{d-1/\nu}) \mathcal{G}(\mathbf{r}, \mathbf{r}', 0) = \delta(\mathbf{r} - \mathbf{r}'). \tag{6}$$

Each individual harmonic $\mathcal{G}_l(\mathbf{r}, \mathbf{r}')$ of $\mathcal{G}(\mathbf{r}, \mathbf{r}', 0)$ satisfies the equation

$$\left(-\frac{d^2}{dr^2} - \frac{d-1}{r} \frac{d}{dr} + \frac{l(l+d-2)}{r^2} + \frac{A}{r^{d-1/\nu}} \right) \mathcal{G}_l(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathbf{r} - \mathbf{r}')}{r^{d-1}}. \tag{7}$$

Provided $d - 1/\nu < 2$, at sufficiently large r

$$\frac{A}{r^{d-1/\nu}} \gg \frac{l(l+d-2)}{r^2}, \quad \text{for all } l \leq \Lambda, \tag{8}$$

and in this region of space each \mathcal{G}_l satisfies the same equation, independent of l ,

$$\left(-\frac{d^2}{dr^2} - \frac{d-1}{r} \frac{d}{dr} + \frac{A}{r^{d-1/\nu}}\right) \mathcal{G}_l(r, r') = \frac{\delta(r-r')}{r^{d-1}}. \tag{9}$$

For values of r, r' which satisfy the inequality in equation (8) one can write

$$\mathcal{G}_l(r, r') = F(r, r') / (rr')^{(d-1)/2}, \tag{10}$$

where $F(r, r')$ satisfies the equation

$$\left(-\frac{d^2}{dr^2} + \frac{A}{r^{d-1/\nu}}\right) F(r, r') = \delta(r-r'). \tag{11}$$

The solution of equation (11) is (Abramowitz and Stegun 1965, p 362)

$$F(r, r') = (rr')^{1/2} I_{1/p}(2\sqrt{A}r^{p/2}/p) K_{1/p}(2\sqrt{A}r'^{p/2}/p), \quad r \leq r' \tag{12}$$

where $p = 2 - d + 1/\nu$. For $2\sqrt{A}r^{p/2} \gg 1$ and $2\sqrt{A}r'^{p/2} \gg 1$ (which is automatically true if equation (8) is satisfied), one may approximate the modified Bessel functions $I_{1/p}$ and $K_{1/p}$ by their large-argument expansions to obtain

$$F(r, r') = [(rr')^{1/2} p / 4\sqrt{A}(rr')^{p/4}] \exp(-2\sqrt{A}|r^{p/2} - r'^{p/2}|/p). \tag{13}$$

Hence

$$\mathcal{G}_l(r, r') = [p / 4\sqrt{A}(rr')^{(2d-4+p)/4}] \exp(-2\sqrt{A}|r^{p/2} - r'^{p/2}|/p) \tag{14}$$

for $l \leq \Lambda$.

The values of ν and A for which the *ansatz* is self-consistent can now be found. From (5) and (14),

$$\frac{A}{x^{d-1/\nu}} = u(p/4\sqrt{A}x^{(2d-4+p)/2}) \sum_{l=0}^{\Lambda} D_l^d / S_d, \tag{15}$$

where D_l^d is the degeneracy of the l th polynomial,

$$D_l^d = \frac{(l+d-3)!(2l+d-2)}{l!(d-2)!}, \tag{16}$$

(Balian and Toulouse 1974). (The appropriate values for 1, 2 and 3 dimensions are easily recovered from equation (16); $D_0^1 = 1 = D_1^1$, $D_l^1 = 0$ for $l \geq 2$; $D_0^2 = 1$, $D_l^2 = 2$ for $l \geq 1$; $D_l^3 = 2l + 1$.) The factor S_d , the surface area of a unit sphere in d dimensions, arises from the normalisation of the polynomials. In three dimensions for example

$$\sum_{m=-l}^l Y_{lm}(\Omega) Y_{lm}^*(\Omega) = 1/S_3 = 1/4\pi.$$

Equating the exponents of x on both sides of equation (15) gives

$$d - 1/\nu = (2d - 4 + p)/2 = d - 2 + (2 - d + 1/\nu)/2$$

and hence that $\nu = 3/(2 + d)$. Equating the constants on both sides of (15) yields

$$A^{3/2} = \frac{1}{6}\epsilon \left(u \sum_{l=0}^{\Lambda} D_l^d / S_d \right), \tag{17}$$

where $\epsilon = 4 - d$. Self-consistency can thus be achieved. Note that the calculation is

only valid for $d < 4$, when the central potential $A/r^{d-1/\nu}$ dominates the centrifugal term.

The calculation is analytically intractable for $E \neq 0$. However, it is still possible to see that $E_c = 0$ within this approximation for finite Λ , since if it had not been zero $\mathcal{G}(r, r, 0)$ would have been found to be a finite constant as $r \rightarrow \infty$. But $\mathcal{G}(r, r, 0) \sim r^{-2(d-1)/3}$ as $r \rightarrow \infty$ so $E_c = 0$.

3. Corrections to the self-consistent Fock theory

For Λ finite and r and r' satisfying the inequality of equation (8), the self-consistent Fock propagator $\mathcal{G}(r, r', 0)$ can be written $\mathcal{G}(r, r')f(\Omega, \Omega')$ where (substituting for p in equation (14))

$$\mathcal{G}(r, r') = [\epsilon/6\sqrt{A}(rr')^{(d-1)/3}] \exp(-3\sqrt{A}|r^{\epsilon/3} - r'^{\epsilon/3}|/\epsilon) \tag{18}$$

and

$$f(\Omega, \Omega') = \sum_{l=0}^{\Lambda} \sum_{m=-l}^l Y_{lm}(\Omega) Y_{lm}^*(\Omega'), \tag{19}$$

in three dimensions. We shall now determine the corrections to $\mathcal{G}(r, r, 0)$ which arise from graphs other than those implicitly summed in figure 2. A typical graph is shown in figure 3. As we are computing corrections to the Fock propagator the propagators in the graphs are Fock propagators. On inserting the δ function form of the excluded volume interaction the broken lines collapse to a four-point vertex to which there is associated a factor of $(-u)$. The sum over all such diagrams (excluding Fock-type insertions) gives the full Green function $G(r, r', 0)$.

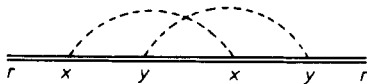


Figure 3. A higher-order correction to the Fock propagator.

For large Λ ,

$$\int d\Omega g(\Omega) f^n(\Omega, \Omega') \approx C_n^d f^{n-1}(0) g(\Omega'), \tag{20}$$

$$f(0) \equiv f(\Omega', \Omega') = \sum_{l=0}^{\Lambda} D_l^d / S_d, \tag{21}$$

and $g(\Omega)$ is an arbitrary function. C_n^d are numerical coefficients of order one. Essentially, $f(\Omega, \Omega')$ is a sort of delta function for large Λ . On using equations (20) and (21) the diagram of figure 3 becomes, after carrying out the integrations over Ω_x and Ω_y , of the order of

$$u^2 f^2(0) f(\Omega_r, \Omega_{r'}) \int_0^\infty dx x^{d-1} \int_0^\infty dy y^{d-1} \mathcal{G}(r, x) \mathcal{G}^3(x, y) \mathcal{G}(y, r').$$

The variable changes,

$$r^{\epsilon/3} = \tilde{r}, \quad r'^{\epsilon/3} = \tilde{r}', \quad x^{\epsilon/3} = \tilde{x}, \quad y^{\epsilon/3} = \tilde{y},$$

enable this expression to be rewritten as of order

$$u^2 f^2(0)(3/\epsilon)^2 f(\Omega_r, \Omega_{r'}) (rr')^{-(d-1)/3} \int_0^\infty d\tilde{x} \int_0^\infty d\tilde{y} \tilde{\mathcal{G}}(\tilde{r}, \tilde{x}) \tilde{\mathcal{G}}^3(\tilde{x}, \tilde{y}) \tilde{\mathcal{G}}(\tilde{y}, \tilde{r}') \tag{22}$$

where

$$\tilde{\mathcal{G}}(\tilde{x}, \tilde{y}) = (\epsilon/6\sqrt{A}) \exp(-3\sqrt{A}|\tilde{x} - \tilde{y}|/\epsilon). \tag{23}$$

Equations (22) and (23) show that the graph and propagator have been reduced to a form very close to what would be encountered in a one-dimensional problem. As both r and r' are large the error involved in extending the lower limits on the \tilde{x} and \tilde{y} integrations to minus infinity in equation (22) is exponentially small. If this is done the integrals in (23) are independent of r (if $r' = r$), so the graph gives a contribution to $G(r, r, 0)$ just equal to $r^{-2(d-1)/3}$ times a finite constant. In other words the graph of figure 3 does not alter the r dependence of $G(r, r, 0)$ found in the self-consistent Fock approximation of § 2.

This is just an example of a result which is true order by order in the perturbation expansion in u . After the angular integrations have been performed each graph becomes one-dimensional with a pre-factor $f(\Omega_r, \Omega_{r'})/(rr')^{(d-1)/3}$. A typical internal integration over a vertex labelled by z then proceeds as follows. There is an overall factor $1/z^{4(d-1)/3}$ coming from the four lines emanating from the vertex. The z integration is of the form

$$\int_0^\infty dz z^{d-1}/z^{4(d-1)/3} \times \text{exponentials.}$$

The substitution $z^{\epsilon/3} = \tilde{z}$ reduces the integration to

$$(3/\epsilon) \int_0^\infty d\tilde{z} \times \text{exponentials.}$$

The error in extending the lower limit on the \tilde{z} integration to minus infinity is always small for large r and r' . The graph is then basically that of the one-dimensional system with propagator as in equation (23). As the integrals are independent of r when $r = r'$ one can conclude that any graph will always give contributions to $G(r, r, 0)$ of the form $r^{-2(d-1)/3}$. Hence the higher-order corrections to the Fock propagator should not change the value of ν from the Flory result.

4. Discussion

It is obvious that the derivation of the Flory result in § 2 depended crucially on having Λ finite. Once this approximation had been made, the rest followed fairly directly. The manner in which the derivation breaks down as $\Lambda \rightarrow \infty$ is worth recording. The proof of self-consistency is confined to distances which satisfy the inequality in equation (8), that is, for

$$r \gg (\Lambda^2/A)^{3/2\epsilon}. \tag{24}$$

Using the large- l approximation that $D_l^d \sim l^{d-2}$, equation (17) shows that $A^{3/2} \sim u\Lambda^{d-1}$. Thus the region of validity of the calculation is for distances r such that

$$r > \Lambda u^{-1/\epsilon}. \tag{25}$$

For finite Λ a region can always be found in which the Flory result holds. As $\Lambda \rightarrow \infty$ no such region exists. In the region $r < \Lambda u^{-1/\epsilon}$ the Green function will not be as in equation (18), but close to that of the true Green function calculated for $\Lambda = \infty$. The situation is probably like that which occurs in certain models for phase transitions in which one embeds a cluster at the centre of a Bethe lattice. The exponents and transition temperature remains always those of the mean-field approximation, which fails only in the central cluster.

While the calculation presented here was couched in a language natural for polymers, there is nothing in it which precludes extension to a Landau-Ginzburg-Wilson isotropic n -vector model with n values other than zero (the value appropriate to polymers). The Flory result for the exponent ν would be obtained for all n .

In one dimension only D_0^1 and D_1^1 are non-zero, so only a finite number of harmonics occurs. This may explain why the finite Λ value of ν , namely the Flory result, is exact in one dimension.

We shall conclude with a discussion of the relationship between the finite- Λ approximation and the SCF theory of Edwards (1965) and Freed (1972). For both theories translational symmetry is broken. In our approximation this happens through the truncation of the partial wave expansion. In the SCF theory the chain ends are specified, which breaks the translational symmetry as the SCF field equations depend explicitly on these end points. The resulting SCF equations (Gillis and Freed 1975, Kosmas and Freed 1978) are intractable non-linear integral equations which cannot be solved analytically. A further approximation is resorted to in which only s-wave components are retained. It may therefore be the case that our finite- Λ approximation is in some senses a generalisation of the traditional SCF theories at the level at which they become analytically tractable. Our finite- Λ approximation has, however, the advantage of being explicitly soluble and its status as an approximation is manifest.

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