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Virial Expansion for a Polymer with a Realistic Pair-Potential Interaction

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No modern theory of polymer excluded volume adequately describes the crossover from poor solvent to good solvent conditions; a fundamental difficulty is a singularity in the binary cluster integral. Mayer expansion techniques are applied to a model with a pair interaction between monomers to clarify the distinction between "geometric" and "solvent" contributions to excluded volume. Detailed calculations are undertaken for a hard-core potential and a mimic Lennard-Jones potential. The significance of the singularity in the binary cluster integral for calculations in the crossover regime is discussed.

KEY WORDS: Binary cluster integral; Domb–Joyce model; hard-core potential; Lennard-Jones potential; pair potential; polymer chain; two-parameter model.

1. INTRODUCTION

Tremendous progress over the last 25 years would lead some to believe that the polymer excluded-volume problem has been solved. Others would disagree. The renormalization group has not provided a satisfactory description of a polymer in the poor-solvent (weak-coupling) regime, perturbation methods are hopelessly incapable of describing the good-solvent (strong-coupling) regime, there is no entirely satisfactory description of the crossover from poor solvent to good solvent conditions, and the limits in which excluded-volume chains exhibit universality are not fully understood.

It is interesting to examine the obstacles to formulating an adequate description of the crossover regime. Modern theories describe an excluded-volume polymer using three fundamental quantities: a chain length parameter, an excluded-volume strength parameter which accounts for both

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"geometric" and "solvent" effects, and a cutoff length which ensures that certain integrals are finite.(1–3) By "geometric" effects we mean those arising from monomer–monomer interactions and by "solvent" or "temperature" effects we mean those arising from monomer–solvent interactions. The strength of excluded volume may be adjusted using any one of three possible mechanisms: the effective binary cluster integral,(4) a statistical weight,(5) or the cutoff length.(1) None of the modern theories has yet established satisfactory correspondences between its parameters and those used by the other theories. This is a great difficulty. None of the recent efforts to bridge the poor-solvent regime with the good-solvent regime(6–9) has been entirely successful. The problems here, we believe, are far from trivial.

The matter becomes more complicated when the excluded-volume parameter is examined more closely. A recent study by Barrett and Benesch(10) revealed that, for a freely jointed stick–bead model, the geometric contribution to the effective binary cluster integral is singular when bead diameter is equal to one-half the bond length. No such singularity is expected for the solvent contribution. The geometric and solvent effects are therefore very different. When viewed from the good-solvent or strong-coupling limit, this detail is absorbed with other geometric details into the excluded-volume strength parameter and is therefore "irrelevant." When viewed from the poor-solvent or weak-coupling limit, however, this "irrelevant" detail becomes a matter of some importance since, unlike the other geometric details, it cannot be described by a smoothly-varying parameter. We shall discuss this question in greater detail in the final section.

Our limited aim in this paper is to clarify the relation of the geometric and temperature contributions in the poor-solvent regime. We shall apply the familiar techniques of the Mayer expansion for a condensing gas to the Domb–Joyce model(5) for a freely jointed stick–bead chain with realistic intermonomer interaction. The original Domb–Joyce paper shows explicitly how the model is applied for a δ-function interaction, but states that for the more realistic "Rayleigh model of steps of fixed length..., the details require further investigation."(5) Over the 20 years or so that the model has been in use, this has never been done.

2. PERTURBATION EXPANSION FOR A PAIR-POTENTIAL MODEL

The classic description of the poor-solvent regime is the perturbation expansion of Teramoto, Zimm, and Fixman(3, 4):

$$\alpha^2 = 1 + \tfrac{4}{3}z + \left(\tfrac{28}{27}\pi - \tfrac{16}{3}\right)z^2 + \cdots \tag{1}$$

The *excluded-volume variable* z is traditionally defined as

$$z = \left(\frac{3}{2\pi a^2}\right) N^{1/2}\beta$$

and thus incorporates the number of bonds N and the effective binary cluster integral β. The length of a single bond is a. The third parameter, the cutoff length, is implicitly applied in the evaluation of the coefficients. The expression (1) has been amply demonstrated by experiment.

Domb and Joyce redefine z to include a *weight factor* w, as follows:

$$z = \left(\frac{3}{2\pi a^2}\right) N^{1/2}\beta w; \qquad 0 \leqslant w \leqslant 1 \tag{2}$$

As discussed above, polymer excluded volume is a combination of geometric excluded volume and solvent condition. Increasing solvent temperature increases chain size, and lowering solvent temperature collapses the polymer. The Θ temperature is defined to be the point where geometric excluded volume is balanced exactly by solvent condition, and chain dimensions are ideal. In (2), β represents geometric excluded volume and w represents the solvent effect.

In the Domb–Joyce model, the coefficients of (1) are computed using generating functions. Two of the simplest of these are

$$R(z) = \sum_{N=2}^{\infty} u_N z^N \tag{3}$$

and

$$W_3(z) = \sum_{N=3}^{\infty} w_N^{(3)} z^N$$

The numbers u_N and $w_N^{(3)}$ represent the number of N-step polygons and N-step theta graphs, respectively. The function $R(z)$ represents the simplest *ladder* graph and $W_3(z)$ represents the simplest *nonladder* graph (see ref. 11 for a thorough explanation of these terms).

If we write $u = 1 - z$, then for small values of u, these functions have the Darboux expansions$^{(5)}$

$$R(z) = e_0 + e_1 u + \cdots + u^{1/2}(f_0 + f_1 u + \cdots)$$

and

$$W_3(z) = e_0^{(3)} + e_1^{(3)} u + \cdots + \ln u (f_0^{(3)} + f_1^{(3)} u + \cdots)$$

The dominant contribution to the generating function arises from the term with the least noninteger exponent. To obtain the dominant contribution, then, it suffices to write

$$R(z) \sim f_0 u^{1/2}$$

and

$$W_3(z) \sim f_0^{(3)} \ln u$$

Recipes for extracting u_N and $w_N^{(3)}$ from these expressions may be found in ref. 11.

We follow Yamakawa's[4] development for the partition function of the polymer. We have

$$\mathscr{Z} = \int e^{-U(\mathbf{R}_1,\ldots,\mathbf{R}_N)} \, d^3R_1 \cdots d^3R_N$$

with U the potential energy of $N+1$ linearly linked monomers at $\mathbf{R}_0,\ldots, \mathbf{R}_N$. We assume that U may be decomposed as follows:

$$U = \sum_{j=1}^{N} u(\mathbf{r}_j) + W(\mathbf{R}_1,\ldots, \mathbf{R}_N)$$

with u the effective bonding potential that links the monomers, and W the potential of mean force due to excluded volume. For convenience, we define

$$\mathbf{r}_j = \mathbf{R}_j - \mathbf{R}_{j-1}; \qquad \tau(\mathbf{r}_j) = e^{-u(\mathbf{r}_j)/kT}$$

At this point we make the usual superposition approximation and define Mayer functions f_{ij}, incorporating the weight factor w. The partition function may be written

$$\mathscr{Z} = \int \left[\prod_{i=1}^{N} \tau(\mathbf{r}_i) \right] \prod_{0 \leqslant j < k \leqslant N} [1 - w f_{jk}] \, d^3r_1 \cdots d^3r_N$$

Developing the second product, we obtain the usual cluster expansion with w as the expansion parameter:

$$\prod_{i,j} (1 - w f_{ij}) = 1 - w \sum_{i<j} f_{ij} + w^2 \sum_{i<j} \sum_{k<l} f_{ij} f_{kl} - \cdots \tag{4}$$

Each term in the expansion is represented by a set of Domb–Joyce diagrams. We shall be content to study the contributions to the partition function from two selected diagrams for three potentials: the usual

δ-function interaction, a hard-sphere potential, and a hard core with an attractive tail. We have selected only one *ladder* diagram and one *nonladder* diagram, since the techniques and results are applicable to *all* diagrams.

3. TWO DIAGRAMMATIC CONTRIBUTIONS

There is only one diagram that contributes to the term in w; its contribution is

$$-w \sum_{i<j} \int \left[\prod_{i+1}^{j} \tau(\mathbf{r}_k) \right] f(\mathbf{R}_{ij})\, d^3r_{i+1} \cdots d^3r_j$$

Multiplying by z^N and summing over all N, we easily see that the coefficient of w in (4) is the coefficient of z^N in the usual generating function P^2R, where

$$P(z) = (1-z)^{-1} = u^{-1}$$

and R is defined in Eq. (3). The number u_N is defined as

$$u_N = \int \left[\prod_{i=1}^{N} \tau(\mathbf{r}_i) \right] f(\mathbf{R})\, \delta\left(\mathbf{R} - \sum_{i=1}^{N} \mathbf{r}_i \right) d^3r_1 \cdots d^3r_N\, d^3R \tag{5}$$

Continuing with the procedure outlined by Yamakawa,(4) we represent the δ-function by a Fourier integral:

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3k\, e^{-i\mathbf{k}\cdot\mathbf{r}}$$

Substituting into (5), we obtain

$$u_N = \frac{1}{(2\pi)^3} \int d^3R\, d^3k\, e^{-i\mathbf{k}\cdot\mathbf{R}} f(\mathbf{R})\, Q(\mathbf{k}) \tag{6}$$

where

$$Q(\mathbf{k}) = \prod_{i=1}^{N} \int d^3r_i\, e^{i\mathbf{k}\cdot\mathbf{r}_i} \tau(\mathbf{r}_i)$$

If we represent $\tau(\mathbf{r})$ by a δ-function, then(4)

$$Q(\mathbf{k}) = \left[\frac{\sin ak}{ak} \right]^N$$

We may now substitute this, and carry out the integrals with respect to angles. Finally, multiplying by z^N and summing over all $N \geqslant 2$, we obtain

$$R(z) = \frac{z^2}{2\pi^2 a^2} \int_0^\infty \frac{F(k) \sin^2 ak}{1 - z(\sin ak)/ak}\, dk \tag{7}$$

where

$$F(\mathbf{k}) = F(k) = \int d^3r\, e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})$$

Note that we have exploited the fact that $F(\mathbf{k})$ is a function only of the modulus of $\mathbf{k}$ and that $F(k) = F(-k)$.

There is only one nonladder graph that contributes to the coefficient of w^2 in (4). The contribution of this diagram is the coefficient of z^N in the generating function $P^2 W_3$, with

$$\begin{aligned} w_N^{(3)} = \sum_{0<i<j<N} \int \left[\prod_1^i \tau(\mathbf{r}_m)\, d^3r_m \right] \left[\prod_{i+1}^j \tau(\mathbf{r}_p)\, d^3r_p \right] f(\mathbf{R}_{0j}) \\ \times \left[\prod_{j+1}^N \tau(\mathbf{r}_q)\, d^3r_q \right] f(\mathbf{R}_{iN}) \end{aligned}$$

Again inserting Fourier representations of δ-functions, integrating, and summing over N, we obtain

$$\begin{aligned} W_3(z) = (2\pi)^{-6} \int F(k_1)\, F(k_2)\, d^3k_1\, d^3k_2 \\ \times \left[\left(1 - z \frac{\sin ak_1}{ak_1}\right) \left(1 - z \frac{\sin a\,|\mathbf{k}_1 + \mathbf{k}_2|}{a\,|\mathbf{k}_1 + \mathbf{k}_2|}\right) \left(1 - z \frac{\sin ak_2}{ak_2}\right) \right]^{-1} \end{aligned} \tag{8}$$

Now, F may be expanded as a power series in k^2:

$$F(k) = F_0 + F_1 k^2 + F_2 k^4 + \cdots \tag{9}$$

If this expansion is substituted into (7) and (8), then the dominant parts of R and W_3 are obtained by retaining only the first term F_0. The higher-order terms provide the subdominant contributions if desired.

4. COMPARISON OF THREE POTENTIALS

We are interested in three specific potentials:

(i) $f(\mathbf{r}) = \beta\delta(\mathbf{r})$

$$\text{(ii)}\quad V(\mathbf{r})=\begin{cases}\infty & \text{if } r<r_0\\ 0 & \text{if } r>r_0\end{cases}$$

$$\text{(iii)}\quad V(\mathbf{r})=\begin{cases}\infty & \text{if } r<r_0\\ -U_0\left(\dfrac{r_0}{r}\right)^6 & \text{if } r>r_0\end{cases}$$

The first of these is the standard assumed δ-function interaction for continuum models of linear polymers. The constant β represents an *effective* binary cluster integral. For this model, $F_0=F=\beta$. We may therefore write, from (7),

$$R(z)=\frac{\beta z^2}{2\pi^2a^2}\int_0^{\infty}\frac{\sin^2 ak}{1-z(\sin ak)/ak}\,dk$$

It is immediately clear that this integral does not exist, but it is not hard to show that the singular behavior arises from the contribution of $N=2$ step returns. The difficulty is usually avoided by invoking the cutoff or, equivalently, using the Gaussian model expression for u_N:

$$u_N\sim\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta N^{-3/2}$$

The nonladder contribution may be treated in a similar way. Substituting $F(k)=\beta$ into the integral (8) yields the expression

$$W_3(z)=\beta^2(2\pi)^{-6}\int d^3k_1\,d^3k_2$$
$$\times\left[\left(1-z\frac{\sin ak_1}{ak_1}\right)\left(1-z\frac{\sin|\mathbf{k}_1+\mathbf{k}_2|}{|\mathbf{k}_1+\mathbf{k}_2|}\right)\left(1-z\frac{\sin ak_2}{ak_2}\right)\right]^{-1}$$

Following through calculations done elsewhere,(11) we obtain the perturbation series (1), with z defined in Eq. (2).

These results are not new, but are useful for the calculations to follow. In particular, we note that the same series (1) will be obtained for *any* potential, if β is replaced by F_0 in the definition of z. It follows that the natural definition of z is Eq. (2), with β replaced by F_0.

The δ-function interaction provides a simplified approach to the excluded-volume problem. The singular integrals that arise are purely an artifact of the model, as can be seen from the corresponding integrals for the more realistic potentials.

For the hard-sphere potential, the Fourier transform is

$$F(k)=\frac{4\pi r_0}{k^2}\left(\frac{\sin r_0k}{r_0k}-\cos r_0k\right) \tag{10}$$

When this is substituted into (6), we obtain the expression

$$u_N=\frac{2r_0}{\pi}\int_0^\infty dk\left(\frac{\sin r_0k}{r_0k}-\cos r_0k\right)\left(\frac{\sin ak}{ak}\right)^N$$

Note that this integral is well-defined for all N, and can be performed for any given N to give a polynomial in (r_0/a) with rational coefficients. We have used the symbolic language MAPLE to evaluate u_N for several N; for $r_0=ba$, we obtain

$$u_2=\frac{b^2}{4},\qquad u_3=\frac{b^3}{6},\qquad u_4=\frac{b^3}{6}-\frac{3b^4}{64}$$

$$u_5=\frac{5b^3}{48}-\frac{b^5}{80},\qquad u_6=\frac{b^3}{12}-\frac{b^5}{80}+\frac{5b^6}{2304}$$

We have not yet found a general formula.

We are also interested in the asymptotic formula for $R(z)$ and $W_3(z)$. If (10) is expanded in powers of k, we obtain

$$F_0=\tfrac{4}{3}\pi r_0^3 \tag{11}$$

Since r_0 represents the *diameter* of the hard sphere, we simply replace the binary cluster integral by eight times the hard-sphere volume.

The dominant contribution to $W_3(z)$ is obtained by substituting (11) into (8). The result is the same integral as obtained with the δ-function model, with β again replaced by $4\pi r_0^3/3$.

It is not hard to see that this procedure will have the same result for the contributions of all diagrams. In consequence, the appropriate definition of z for a hard-sphere chain is

$$z=\left(\frac{3}{2\pi a^2}\right)^{3/2}(8V_0)\,N^{1/2}w$$

where V_0 is the volume of the hard sphere.

We have chosen the third potential as a conveniently tractable function that nonetheless exhibits all the essential features of the true intermonomer potential. It closely resembles, for instance, a Lennard-Jones function. We find for this choice

$$F(k) = F(\text{hard sphere}) + \frac{4\pi}{k}\int_{r_0}^{\infty} r \sin kr \left\{1 - \exp\left[\left(\frac{r_0}{r}\right)^6 \frac{U_0}{kT}\right]\right\} dr$$

The leading contribution, obtained by keeping only the first terms in the expansions of the sine and exponential in the integrand, is

$$F_0 = 8V_0\left(1 - \frac{U_0}{kT}\right)$$

5. DISCUSSION

Application of Mayer expansion techniques to a freely jointed stick–bead model with a realistic potential shows that the effective binary cluster integral is written as the product of two factors, one which represents the geometric excluded volume and another which accounts for solvent or temperature effect. This distinction, of little consequence in the good-solvent regime, is important in the poor-solvent regime because of the singularity in the effective binary cluster integral β and is particularly important in any attempt to describe the crossover from poor- to good-solvent conditions.

There is a fascinating example of the effect of the singularity. DesCloizeaux *et al.*(8) and Muthukumar and Nickel(9) have summed the perturbation series (1) to obtain the asymptotic formula.

$$\alpha^2 = 1.53z^{0.354} \tag{12}$$

which is clearly at odds with numerical data for stick–bead chains(12) and renormalization group results,(1) which suggest that

$$\alpha^2 = 1.75z^{0.3544}$$

We suggest that the discrepancy arises because β, and therefore z, *has a different meaning* in the good-solvent regime than in the poor-solvent regime. If, instead of z, one chooses as the relevant variable

$$x = N^{1/2}V_0$$

with V_0 the volume of the hard sphere, then (12) can be written

$$\alpha^2 = 2.157x^{0.354}$$

and the agreement with the data of ref. 12 is remarkably good. It would be very interesting to test this suggestion on other models.

Two-parameter theories still provide the best description of the poor-solvent regime. For these theories, the appropriate definition of the excluded-volume variable is

$$z = \left(\frac{3}{2\pi a^2}\right)^{3/2} N^{1/2} F_0 w$$

Here F_0 represents the dominant contribution to the effective binary cluster integral, obtained from the expansion (9). Subdominant corrections may be obtained from the higher-order terms. For a dilute polymer solution with small excluded volume, the binary cluster integral is exactly what it would be for a dilute gas whose particles are subject to the same interaction. For a chain with large excluded volume, the binary cluster integral will be very different. However, as we have shown, the perturbation series remains valid for small w. That is, even with a large geometric excluded volume, the perturbation series still provides an accurate description near the Θ point.

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