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Excluded Volume Effects in the Θ Regime. 1. Perturbation Formulation for a Repulsive–Attractive Potential†

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ABSTRACT: Perturbation methods are used to develop a theory of dilute polymer solutions in the Θ regime. The theory assumes that a polymer can be represented as a Gaussian random walk that interacts through a pairwise potential. The formulation is graph theoretical and is developed in a way that is independent of polymer topology. Various properties are treated: scattering and pair correlation functions, the end-to-end vector, the radius of gyration, the hydrodynamic radius, and the second virial coefficient. Unlike δ-function theory, the excluded volume potential used here is bounded and contains repulsive and attractive interactions. These interactions persist at the Θ temperature and give a reference state that is non-Gaussian, except in the δ-function limit of the theory. Several conclusions are reached: (1) the Θ chain is swollen relative to the unperturbed chain (no interactions) but this swelling does not affect the ratio of the radius of gyration to the end-to-end vector; (2) the swelling is greater for the hydrodynamic radius than the radius of gyration (non-Gaussian behavior); (3) a universal excluded volume parameter (hence a two-parameter theory) is found only in the δ-function limit. Finally, it is shown that in the short-range interaction limit the theory can be generalized to arbitrary excluded volume potentials by introducing a dimensionless parameter that is related to the second moment of the cluster formation.

I. Introduction

The δ-function perturbation theory of the excluded volume effect, due to Fixman,[1] has come under close scrutiny in recent years. Most of the recent interest has centered on the convergence properties of the cluster series and on the assumption that two-body interactions provide an adequate description of the Θ regime. In this connection it has been suggested by Edwards[2] and Gordon et al.[3] that the perturbation series for expansion factors is actually divergent (this does not necessarily limit its utility for calculations, however, since the series appears to be asymptotic). Aronowitz and Eichinger[4] have explicitly demonstrated the presence of divergences in the series for expansion factors of small chains. They trace this difficulty to the δ-function potential (a preaveraged cluster function) and estimate a radius of convergence of order $1/N^{1/2}$ for the cluster series. Oono[5] has demonstrated that the perturbation series is an expansion about a singular point (a collapse transition for infinite chains) and has also estimated a radius of convergence of order $1/N^{1/2}$.

Oyama and Oono[6] have expressed doubt that the many-body interactions in a real polymer chain can be expressed in terms of the segment binary cluster integral alone—a measure of binary contacts. They include the effect of three-body interactions and find that these tend to swell the polymer at the Θ point (a specific solvent effect), without affecting exponents.

Monte Carlo simulations of lattice and continuum chains have been done for poor, marginal, and good solvents. These studies represent a polymer chain as an interacting walk whose many-body potential can be approximated by a sum of pairwise interactions between segments. The potential has a temperature-dependent parameter that can be adjusted to achieve the desired solvent condition. Excluded volume potentials chosen for such studies differ in two ways from the δ potential: they are of nonvanishing width and do not identically vanish at the Θ temperature. In these studies the Θ condition is achieved by balancing the repulsive core interaction against an attractive interaction that occurs at larger distances. We will refer to this chain as the Θ chain so as to distinguish it from the unperturbed chain (no excluded volume interactions).

Baumgartner[7] and Webman et al.[8] have simulated continuum chains with Lennard-Jones interactions. Baumgartner has found that at the Θ point, defined by the vanishing of the second virial coefficient, the exponent for the polymer radius is $^1/_2$ but the chain is swollen relative to the unperturbed state. In fact, for the width of the excluded volume potential chosen by Baumgartner, $\langle R^2\rangle_\Theta/\langle R^2\rangle_0 \sim 1.7$, where the subscripts refer to the Θ and unperturbed chain, respectively.

It would seem that this swelling is not of any real significance in itself, since an appropriately renormalized unperturbed chain would be equivalent to the Θ chain insofar as the radius of gyration is concerned. It is not clear, however, that this renormalized chain is equivalent to the Θ chain in all its properties. For example, obvious differences between these models would arise in the calculation of exponents for the radius in 1 and 2 dimensions.

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The unperturbed chain gives an exponent of $^1/_2$ in all dimensions, whereas Oono[9] has obtained 1, $^2/_3$, $^1/_2$,... in 1, 2, 3,... dimensions for a real Θ chain.

The nonequivalence of the unperturbed chain and the Θ chain has been demonstrated by Guttman et al.[10] in three-dimensional Monte Carlo simulations of lattice chains with nearest-neighbor interactions. Working in the nondraining limit of the Kirkwood approximation to the hydrodynamic radius, Guttman et al. found the ratio of the radius of gyration to the hydrodynamic radius to be ~1.40. For the unperturbed chain this ratio is ~1.50[11] and experimental values tend to be in the range 1.26–1.43.[10,12]

The purpose of the present paper is to present a treatment of the Θ regime that can account for some of these observations. The theory describes a polymer in the Θ regime as a Gaussian walk whose segments interact through an excluded volume potential that has the same general characteristics as those used in Monte Carlo simulations: a repulsive core followed by an attractive interaction. The temperature-dependent parameter is chosen such that the potential does not identically vanish at the Θ point, and the model is thus of the Θ-chain type.

The formulation is graph theoretical and is generalized to arbitrary polymer topology. Results are obtained by cluster expansion perturbation series and are valid only for finite chains near the Θ temperature. In order to obtain a consistent theory of dilute polymer solutions, several properties are treated: the expansion factors for the radius of gyration, the hydrodynamic radius, and the end-to-end vector, the second virial coefficient, and light scattering and pair correlation functions and their exponents. In this paper only first-order results are given, but even to this order it is clear that a description of the Θ regime depends not only on the segment binary cluster integral but upon the width of the excluded volume potential as well. This general conclusion is in agreement with the three-body interaction theory of Oyama and Oono and with Monte Carlo simulations.

II. Gaussian Chain and Excluded Volume Potential

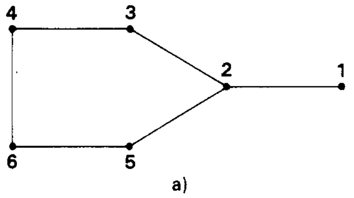
Consider a canonical ensemble of a dilute polymer, whose configurational degrees of freedom are given by the coordinates **P**, immersed in a bath of solvent molecules whose collective configurational degrees of freedom are given by **S**. The ensemble average of a global polymer property $\psi(\mathbf{P})$ (weakly dependent on "local" coordinates) can be written in terms of the configurational part of the many-body Hamiltonian $H(\mathbf{S},\mathbf{P})$. Integration over the solvent coordinates and the local polymer coordinates defines a temperature-dependent function $H'(\mathbf{P}',T)$ as follows:

$$\langle\psi\rangle = \int \mathrm{d}\mathbf{P}\int \mathrm{d}\mathbf{S}\ \psi(\mathbf{P})e^{-H(\mathbf{S},\mathbf{P})/kT} \Big/ \int \mathrm{d}\mathbf{P}\int \mathrm{d}\mathbf{S}\ e^{-H(\mathbf{S},\mathbf{P})/kT} \equiv \int \mathrm{d}\mathbf{P}'\ \psi(\mathbf{P}')e^{-H'(\mathbf{P}',T)/kT} \Big/ \int \mathrm{d}\mathbf{P}'\ e^{-H'(\mathbf{P}',T)/kT} \qquad (1)$$

The function $H'(\mathbf{P}',T)$ is the configurational part of the effective polymer Hamiltonian. For a homopolymer near the Θ point, the Boltzmann factor can be approximated by

$$e^{-H'(\mathbf{P},T)/kT} = [\prod_{i=1}^{N-1}\Omega(\mathbf{r}_{i+1}-\mathbf{r}_i)]e^{-\sum_{ij}v(\mathbf{r}_i-\mathbf{r}_j,T)/kT} \qquad (2)$$

where $\Omega(\mathbf{r}_{i+1}-\mathbf{r}_i)$ is the bond probability for a simple Markoff process with step ends (vertices) at $\mathbf{r}_{i+1}$ and $\mathbf{r}_i$. The product of these $N-1$ transition probabilities represents the ideal part of a random flight polymer. Considered alone this always gives a polymer radius $\sim N^{1/2}$, where N is proportional to the degree of polymerization.



$$\begin{pmatrix} 1 & -1 & 0 & 0 & 0 & 0 \\ -1 & 3 & -1 & 0 & -1 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & -1 & 2 & 0 & -1 \\ 0 & -1 & 0 & 0 & 2 & -1 \\ 0 & 0 & 0 & -1 & -1 & 2 \end{pmatrix}$$

b)

Figure 1. (a) Graphical representation of the topology of a polymer with a single circuit. (b) Kirchhoff matrix for this graph.

The function $v(\mathbf{r}_i - \mathbf{r}_j,T)$ is a temperature-dependent potential of mean force, called the excluded volume potential, and represents solvent-mediated nonbonded interactions between monomers on the polymer chain. The physical reasons for the temperature dependence of v are clear enough: spatial and angular correlation functions between monomers and solvent molecules are temperature dependent. Such local ordering of the solvent field greatly affects solvent-screened monomer–monomer interactions.

In the absence of strong external fields, it is valid to use a Gaussian transition probability in eq 2. In compact notation[13]

$$\prod_{i=1}^{N-1}\Omega(\mathbf{r}_{i+1}-\mathbf{r}_i) = e^{-\gamma\mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t} \qquad (3)$$

where $\mathbf{R} = (x_1, y_1, z_1, x_2, ..., z_N)$ is a $1 \times 3N$ row vector containing the coordinates of the vertices of the walk, $\mathbf{R}^t$ is the transpose of $\mathbf{R}$, and $\mathbf{K}$ is a symmetric $N \times N$ Kirchhoff matrix describing the connectivity of the walk. The matrix $\mathbf{E}_3$ is the identity of order 3, ⊗ denotes the tensor product, and the constant $\gamma = 3/2\langle l^2\rangle$, where $\langle l^2\rangle$ is the mean square step length of the walk.

Formulation in terms of **K** allows generalization to polymers with circuits and branches, e.g. circular chains, comb polymers, and star polymers. Although discussed extensively elsewhere,[13] it is convenient to describe the construction of the Kirchhoff matrix for a general walk. First label the vertices from 1 to N as in Figure 1. If vertex i is connected to vertex j with a multiplicity m, then $\mathbf{K}_{ij} = \mathbf{K}_{ji} = -m$: otherwise, $\mathbf{K}_{ij} = 0$. The diagonal element $\mathbf{K}_{ii}$ is the functionality of the ith vertex. The construction of a Kirchhoff matrix for a simple walk is shown in Figure 1.

The choice of a suitable excluded volume potential is more difficult. A schematic drawing of the actual solvent-mediated monomer–monomer potential is in Figure 2; a hard-core repulsive interaction is followed by an attractive interaction, moderated by small liquid packing ripples.

In the two-parameter theory of the excluded volume effect, a convenient choice is made for the potential. Introducing the cluster function $\zeta\chi_{ij} \equiv 1 - e^{-v(\mathbf{r}_{ij},T)/kT}$, Fixman[1] let

$$\zeta\chi_{ij} = \beta\delta^3(\mathbf{r}_i - \mathbf{r}_j) \qquad (4a)$$

$$\beta \equiv \int (1 - e^{-v(\mathbf{r}_{ij})/kT})\ \mathrm{d}^3\mathbf{r}_{ij} \qquad (4b)$$

where the temperature-dependent parameter $\beta(T)$ is called the segment binary cluster integral and $\delta^3(r)$ is the

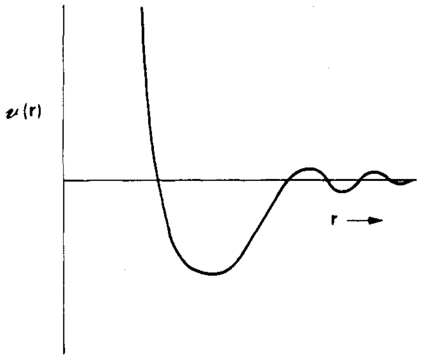


Figure 2. Excluded volume potential for a real polymer chain in dilute solution.

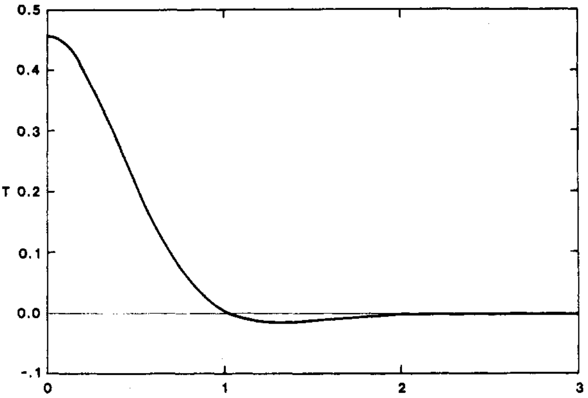


Figure 3. Approximate excluded volume potential of eq 7.

three-dimensional Dirac δ function. For reasons that will later become apparent, we will define the Θ temperature, Θ, as the temperature at which $\beta(T) = 0$.

The δ-function potential suffers from two defects: the width of the interaction, δr, is zero and $\lim_{T\to\Theta} v(\mathbf{r}_{ij}) = 0$; i.e., the excluded volume potential identically vanishes at the Θ point. This is physically untenable, since it is clear that at the Θ point the hard-core interaction must persist. In some sense then, this must be compensated for by a strong attractive interaction. The δ-function approximation must lead to a description of the Θ regime which is not entirely correct.

An excluded volume potential of finite width and nonvanishing amplitude at $T = \Theta$ should give a better description of the Θ regime. A potential that satisfies the first condition is

$$v(\mathbf{r}_{ij}) = -kT \ln \left(1 - \left(\frac{\gamma\epsilon}{\pi} \right)^{3/2} \beta e^{-\epsilon\gamma \mathbf{r}_{ij}^2} \right) \tag{5a}$$

$$\zeta\chi_{ij} = \left(\frac{\gamma\epsilon}{\pi} \right)^{3/2} \beta e^{-\epsilon\gamma \mathbf{r}_{ij}^2} \tag{5b}$$

where ϵ is a width parameter and $\delta r^2 \sim \langle l^2 \rangle / \epsilon$. This potential is similar to the first-order quantum statistical potential[14] of free fermions if β is >0 or free bosons if β is <0. The potential suffers from the defect of being either purely repulsive ($\beta > 0$) or purely attractive ($\beta < 0$) and therefore must vanish at Θ. In fact, in the limit $\epsilon \to \infty$, this cluster function reduces to the δ function $\zeta\chi_{ij} = \beta\delta^3(\mathbf{r}_{ij})$.

It has been shown[15] that singularities can occur in expressions based on this δ function. Consider the configuration integral

$$Z = \int \dots \int \mathrm{d}^{3N}\mathbf{R}\ e^{-\gamma \mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t} \prod_{i<j} \left(1 - \left(\frac{\gamma\epsilon}{\pi} \right)^{3/2} \beta e^{-\epsilon\gamma \mathbf{r}_{ij}^2} \right) \tag{6}$$

Since Z appears as the denominator in ensemble averages, roots of Z must be avoided. A lower bound on the region where $Z > 0$ is $\beta < (\pi/\epsilon\gamma)^{3/2}$. This domain is restricted (but not actually zero) in the limit $\epsilon \to \infty$ ($\delta r \to 0$). Singularities have been observed for the expansion factor of the radius of gyration in this δ-function limit.

Although singularities are avoided with this potential, the zero amplitude at the Θ temperature approximation persists; but it is nonetheless instructive to do calculations based on eq 5. A more physically acceptable potential is

$$v(\mathbf{r}_{ij}) = -kT \ln \left(1 + \sigma \left(\frac{\gamma\epsilon}{\pi} \right)^{3/2} (e^{-\epsilon\gamma \mathbf{r}_{ij}^2} - 8^{1/2} c e^{-2\epsilon\gamma \mathbf{r}_{ij}^2}) \right) \tag{7a}$$

$$\zeta\chi_{ij} = -\sigma \left(\frac{\gamma\epsilon}{\pi} \right)^{3/2} (e^{-\epsilon\gamma \mathbf{r}_{ij}^2} - 8^{1/2} c e^{-2\epsilon\gamma \mathbf{r}_{ij}^2}) \tag{7b}$$

$$\beta = \sigma(c(T) - 1) \tag{7c}$$

Figure 3 shows the behavior of this potential near the Θ point. The repulsive core is compensated by a short-range attractive interaction. The parameter c is taken to be the temperature-dependent parameter, ϵ is again a width parameter, and σ is an amplitude parameter.

Development of cluster expansion equations is possible with this potential, and a more realistic description of the Θ regime emerges from such a treatment.

III. Cluster Expansion Equations

The development of cluster equations for polymers of arbitrary connectivity is easily accomplished in the Gaussian approximation. First expand the excluded volume potential as

$$e^{-\sum_{ij} v(\mathbf{r}_{ij},T)/kT} = \prod_{i>j}(1 - \zeta\chi_{ij}) = 1 - \zeta \sum_{i>j} \chi_{ij} + \zeta^2 \sum_{k<l} \sum_{m<n} \chi_{kl}\chi_{mn} - \dots (-\zeta)^{N(N-1)/2} \prod_{i>j} \chi_{ij} \tag{8}$$

where the sums are over all nonidentical cluster diagrams.

Now define $\xi_0(\zeta)$ and the operation "$\cdot$" by

$$\xi_0(\zeta)\cdot\psi(\mathbf{R}) \equiv \int \dots \int \mathrm{d}^{3N}\mathbf{R}\ e^{-\gamma \mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t} \prod_{i<j} (1 - \zeta\chi_{ij}) \psi(\mathbf{R}) \delta^3(\sum_{i=1} \mathbf{r}_i) \tag{9}$$

where $\psi(\mathbf{R})$ is a function of the polymer coordinates and the δ function serves to fix the coordinate origin at the polymer center of gravity. It is convenient to define a normalized operator $\xi(\zeta)$ through

$$\xi(\zeta)\cdot\psi(\mathbf{R}) \equiv (\xi_0(\zeta)\cdot\psi(\mathbf{R}))/(\xi_0(0)\cdot\psi(\mathbf{R})) \tag{10}$$

Finally, define the expansion factor of property $\psi(\mathbf{R})$ as the ratio of its ensemble average in the perturbed state to that in its unperturbed state.

$$\alpha_\psi \equiv \xi(\zeta)\cdot\psi(\mathbf{R})/\xi(\zeta)\cdot 1 = \langle \psi \rangle / \langle \psi \rangle_0 \tag{11}$$

There is no a priori reason to assume that this unperturbed (no excluded volume) reference state is physically attainable, but it is a convenient state nonetheless.

The numerator and denominator of eq 11 can be expanded as two finite polynomials

$$\xi(\zeta)\cdot 1 = \sum_{p=0}^{N(N-1)/2} (-\zeta)^p Z_p \tag{12a}$$

$$\xi(\zeta)\cdot\psi(\mathbf{R}) = \sum_{p=0}^{N(N-1)/2} (-\zeta)^p \psi_p \tag{12b}$$

where the coefficients ψ_p are given by

$$\psi_p = \left[\int\ldots\int \mathrm{d}\mathbf{R}^{3N}\, e^{-\gamma\mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t}\psi(\mathbf{R})\delta^3(\textstyle\sum\mathbf{r}_j)\sum\ldots\sum\chi_{kl}\cdots\chi_{mn}\right]\Big/\left[\int\ldots\int \mathrm{d}^{3N}\mathbf{R}\, e^{-\gamma\mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t}\psi(\mathbf{R})\delta^3(\textstyle\sum\mathbf{r}_j)\right] \quad (13)$$

Expanding the polynomial in the denominator of eq 11 gives an expression for the expansion factor:

$$\alpha_\psi = \left[1 + \sum_{p=1}^{N(N-1)/2}(-\zeta)^p\psi_p\right]\left[1 + \sum_{m=1}^{\infty}(-1)^m \sum_{\substack{\{m_j\}\\ \sum m_j = m}} (-\zeta)^{\sum_1^{N(N-1)/2} j m_j}\left(\prod_1^{N(N-1)/2} Z_k^{m_k}\right)\frac{m!}{\prod_{l=1}^{N(N-1)/2} m_l!}\right] = \sum_{p=0}^{\infty} b_p(\zeta)^p \quad (14)$$

The first few coefficients of this polynomial are

$$b_0 = 1$$

$$b_1 = Z_1 - \psi_1$$

$$b_2 = Z_1^2 - Z_2 - \psi_1 Z_1 + \psi_2$$

$$b_3 = Z_3 - 2Z_1Z_2 + Z_1^3 - \psi_1(Z_1^2 - Z_2) + \psi_2 Z_1 - \psi_3$$

$$b_4 = Z_1^4 - 3Z_1^2Z_2 + Z_2^2 + 2Z_1Z_3 - Z_4 - \psi_1(Z_3 - 2Z_1Z_2 + Z_1^3) + \psi_2(Z_1^2 - Z_2) - \psi_3 Z_1 + \psi_4$$

Evaluation of these coefficients is not simple for an arbitrary cluster function, but much progress can be made with the potentials given in eq 5 and 7. This is part of the motivation in the selection of these potentials.

IVa. Configuration Integral

The above equations allow the computation of expansion factors for the ensemble average of any polymer property $\psi(\mathbf{R})$. It is useful to define a cluster function χ_{ij} that allows computation of the ψ_p of eq 13 for the χ_{ij} of both eq 5b and 7b. Let the product of p cluster functions for the p-contact term be

$$\chi_{kl}\cdots\chi_{mn} = (\alpha_1\epsilon\gamma/\pi)^{3/2}e^{-\alpha_1\epsilon\gamma r_{kl}^2}\ldots(\alpha_p\epsilon\gamma/\pi)^{3/2}e^{-\alpha_p\epsilon\gamma r_{mn}^2} \quad (15)$$

where the α_j are either 1 or 2. Substitution of this product into eq 13 defines $\psi_p(\alpha_1, \alpha_2, ..., \alpha_p) = \psi_p(\{\alpha\})$. In terms of this function, the coefficient ψ_p for cluster function eq 5b is

$$\zeta^p\psi_p = \beta^p\psi_p(\{\alpha\})|_{\alpha_1=\alpha_2=\ldots=\alpha p=1} \quad (16)$$

ψ_p for the cluster function of eq 7b is

$$\zeta^p\psi_p = (-\sigma)^p \sum_{\alpha_1,\alpha_2,\ldots,\alpha_p}\ldots\sum(-c)^{\sum_{j=1}^p(\alpha_j-1)}\psi_p(\{\alpha\}) \quad (17)$$

Equation 13 gives $\psi_p(\{\alpha\})$ as a sum over all p-contact terms, each term defining a cluster diagram or graph. There are just $\binom{N(N-1)/2}{p}$ graphs for the p-contact term in the perturbation expansion. An example of a double-contact graph for a star polymer is given in Figure 4. Note that the edges (lines indicating excluded volume contacts have a relative weighting $\alpha_j\epsilon$ in this graph. Usually such cluster diagrams serve only to indicate the interacting molecules or monomers; in the context of this treatment, their graphical nature will be exploited to evaluate the ψ_p.

To determine $\psi_p(\{\alpha\})$, a variable Kirchhoff matrix is constructed for each cluster diagram. Define the k–l "contact" matrix

$$\mathbf{C}(k-l)_{\omega\nu} = \delta_{\omega k}\delta_{\nu k} + \delta_{\omega l}\delta_{\nu l} - \delta_{\omega k}\delta_{\nu l} - \delta_{\omega l}\delta_{\nu k} \quad (18)$$

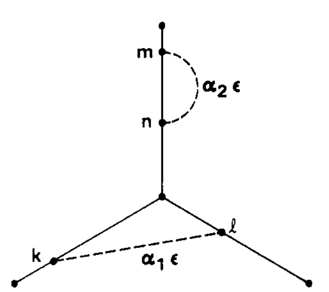


Figure 4. Double-contact cluster diagram for a star polymer. Note the weightings (bond multiplicities) given to the contacts (dashed lines).

where $\delta_{\omega k}$ is the Kronecker δ. The variable Kirchhoff matrix for a p-contact graph with vertex k interacting with vertex l, etc., is then

$$\mathbf{K}(\{\alpha\}, k-l, ..., m-n) = \mathbf{K} + \alpha_1\epsilon\mathbf{C}(k-l) + \ldots + \alpha_p\epsilon\mathbf{C}(m-n) \quad (19)$$

Here, $\mathbf{K}$ is the Kirchhoff matrix for the graph descriptive of polymer connectivity (the o-contact graph). In terms of this variable Kirchhoff matrix

$$\psi_p(\{\alpha\}) = \sum_{k<l}\ldots\sum_{m<n}\prod_1^p(\alpha_j\epsilon\gamma/\pi)^{3/2} \times \left[\int\ldots\int \mathrm{d}^{3N}\mathbf{R}\psi(\mathbf{R})e^{-\gamma\mathbf{R}(\mathbf{K}(\{\alpha\},k-l,\ldots,m-n)\otimes\mathbf{E}_3)\mathbf{R}^t}\delta^3(\textstyle\sum\mathbf{r}_i)\right]\Big/\left[\int\ldots\int \mathrm{d}^{3N}\mathbf{R}\,\psi(\mathbf{R})e^{-\gamma\mathbf{R}(\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}^t}\delta^3(\textstyle\sum\mathbf{r}_i)\right] \quad (20)$$

The configuration integral is readily evaluated. Diagonalization of the real symmetric quadratic forms gives $Z_p(\{\alpha\})$ ($\equiv\psi_p(\{\alpha\})$ with $\psi(\mathbf{R}) = 1$) as a sum of determinants:

$$Z_p(\{\alpha\}) = \prod_{j=1}^p(\alpha_j\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\ldots\sum_{m<n}(|\mathbf{K}_i(\alpha, k-l, ..., m-n)|/|\mathbf{K}_i|)^{-3/2} \quad (21)$$

$\mathbf{K}_i$ is the $N-1 \times N-1$ matrix formed by striking the ith row and column of $\mathbf{K}$. The Binet–Cauchy theorem[13] gives $|\mathbf{K}_i|$ as the number of spanning trees rooted at the ith vertex of the graph. A spanning tree of graph G may be defined as a connected graph without circuits that covers G (visits all vertices) using only the edges of G. For a connected graph $|\mathbf{K}_i|$ is independent of i. Any spanning tree of G can be formed by removing edges from G.

In this way the evaluation of the configuration integral is reduced to a graphical problem. In section Vb the configuration integral will be evaluated by this method for linear and circular chains.

IVb. Radius of Gyration

In the unperturbed reference state (no excluded volume interactions), the mean square radius of gyration, $\langle S^2\rangle_0$, of a polymer having a Kirchhoff matrix $\mathbf{K}$ can be expressed as the trace of the inverse of an $N-1 \times N-1$ diagonal matrix, Λ_0, of the $N-1$ nonzero eigenvalues of $\mathbf{K}$.[15] This result is

$$\langle S^2\rangle_0/\langle l^2\rangle = N^{-1}\,\mathrm{Tr}\,(\Lambda_0^{-1}) \quad (22)$$

Letting $\psi(\mathbf{R}) = N^{-1}\mathbf{R}\mathbf{R}^t$, $S_p(\{\alpha\}) \equiv \psi_p(\{\alpha\})$, and using the conventional notation for the expansion factor of the mean square radius of gyration, $\alpha_S^2 = \alpha_\psi$, eq 20 becomes

$$S_p(\{\alpha\}) = \left(\prod_1^p\alpha_j\epsilon\gamma/\pi\right)^{3/2}\sum_{k<l}\ldots\sum_{m<n}[|\mathbf{K}_i(\{\alpha\}, k-l, ..., m-n)|^{-3/2} \times \mathrm{Tr}\,(\Lambda_0^{-1}(\{\alpha\}, k-l, ..., m-n))]/[|\mathbf{K}_i|^{-3/2}\,\mathrm{Tr}\,(\Lambda_0^{-1})] \quad (23)$$

A somewhat more tractable form for $S_p(\{\alpha\})$ will be developed in the treatment of scattering functions.

IVc. Hydrodynamic Radius

Let $\psi(R) = a_{\mathrm{h}}^{-1} = (2/N^2)\sum_{i<j}|\mathbf{r}_{ij}|^{-1}$, the Kirkwood[16,17] approximation to the inverse hydrodynamic radius in the nondraining limit. Define a Moore–Penrose or generalized inverse,[18] **A**, of the Kirchhoff matrix (a singular matrix) through three conditions:[13]

(i) $\mathbf{KA} = \mathbf{E}_N - N^{-1}\mathbf{U}$

(ii) $\mathbf{A}^{\mathrm{t}} = \mathbf{A}$

(iii) $\mathbf{AU} = \mathbf{0}$

where the $N \times N$ matrix **U** is a matrix of ones. Let **T** be the $N \times N$ transformation matrix that diagonalizes **K**, $\mathbf{T}^{\mathrm{t}}\mathbf{K}\mathbf{T} = \Lambda$. Form the $N \times N - 1$ matrix $\mathbf{T}_0$ from **T** by deleting the constant column of **T** (the eigenvector corresponding to the zero eigenvalue). It is readily verified that the matrix $\Lambda = \mathbf{T}_0\Lambda_0^{-1}\mathbf{T}_0^{\mathrm{t}}$ satisfies the above conditions and is the generalized inverse of **K**. In a previous paper[19] it has been shown that $a_{ij} = (\mathbf{A})_{ij} = \langle \mathbf{r}_i\cdot\mathbf{r}_j\rangle_0/\langle l^2\rangle$. Define the elements of a matrix **G** by $g_{ij} = a_{ii} + a_{jj} - 2a_{ij}$ so $g_{ij} = \langle|\mathbf{r}_i - \mathbf{r}_j|^2\rangle_0/\langle l^2\rangle$. In the unperturbed reference state[13]

$$(\langle a_{\mathrm{h}}\rangle_0/\langle l^2\rangle^{1/2})^{-1} = (2/N^2)(6/\pi)^{1/2}\sum_{i<j} g_{ij}^{-1/2} \tag{24}$$

Now let α_{h}^{-1} denote the expansion factor for the inverse hydrodynamic radius and let $H_p(\{\alpha\}) = \psi_p(\{\alpha\})$ with $\psi(\mathbf{R}) = a_{\mathrm{h}}^{-1}$. From eq 20

$$H_p(\{\alpha\}) = \prod_1^p(\alpha_j\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\ldots\sum_{m<n}\frac{|\mathbf{K}_i(\{\alpha\}, k-l, \ldots, m-n)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}} \times \frac{\sum_{i<j} g_{ij}^{-1/2}(\{\alpha\}, k-l, \ldots, m-n)}{\sum_{i<j} g_{ij}^{-1/2}} \tag{25}$$

It will be shown that the elements g_{ij} are not difficult to calculate and do not require knowledge of the eigenvalues, Λ_0, and eigenvectors, $\mathbf{T}_0$.

IVd. Pair Correlation Function $p(\mathbf{r})$

To investigate $p(r)$, let $\psi = (2/N(N-1))\sum_{i<j}\delta^3(\mathbf{r}_{ij} - \mathbf{r})$. In the unperturbed state this gives[20]

$$p_0(\mathbf{r}) = (2/N(N-1))\sum_{i<j} p_{0ij}(\mathbf{r}) = (2/N(N-1))\sum_{i<j}(\gamma/\pi g_{ij})^{3/2}e^{-\gamma r^2/g_{ij}} \tag{26}$$

where $p_{0ij}(\mathbf{r})$ is the distribution function in the unperturbed state for vertices i and j. Let the expansion factor for $p(\mathbf{r})$ be $\alpha(\mathbf{r}) = \alpha_\psi$ and let $P_p(\{\alpha\}) \equiv \psi_p(\{\alpha\})$. Then

$$P_p(\{\alpha\}) = \prod_1^p(\alpha_j\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\ldots\sum_{m<n}\frac{|\mathbf{K}_i(\{\alpha\}, k-l, \ldots, m-n)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}} \times \Big[\sum_{i<j}(\gamma/\pi g_{ij}(\{\alpha\}, k-l, \ldots, m-n))^{3/2} \times e^{-\gamma r^2/g_{ij}(\{\alpha\},k-l,\ldots,m-n)}\Big]\Big/\sum_{i<j}(\gamma/\pi g_{ij})^{3/2}e^{-\gamma r^2/g_{ij}} \tag{27}$$

To first order, with cluster function eq 5b, this gives

$$p(\mathbf{r}) = (2/N(N-1))\sum_{i<j}(\gamma/\pi g_{ij})^{3/2}e^{-\gamma r^2/g_{ij}} + \beta(\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\frac{|\mathbf{K}_i(\epsilon, k-l)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}}\Big[\sum_{i<j}(\gamma/\pi g_{ij})^{3/2}e^{-\gamma/\pi g_{ij}} - (\gamma/\pi g_{ij}(\epsilon, k-l))^{3/2}e^{-\gamma r^2 g_{ij}(\epsilon,k-l)}\Big] \tag{28}$$

This first-order pair correlation function is valid only for small β and large $|\mathbf{r}|$.

IVe. Scattering Function

The scattering function can be obtained by taking the Fourier transform of the pair correlation function or by letting $\psi(\mathbf{R}) = (2/N(N-1))\sum_{i<j}e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}$. The scattering wavevector **q** has a modulus $|\mathbf{q}| = (4\pi/\lambda)\sin(\theta/2)$, where λ is the radiation wavelength in the scattering medium and θ is the scattering angle. In the Gaussian approximation the unperturbed scattering function[20] is

$$S(u) = (2/N(N-1))\sum_{i<j} e^{-g_{ij}u} \tag{29}$$

where $u \equiv q^2\langle l^2\rangle/6$. At large wavevectors, it is known that $S(u)$ assumes a power law form $S(u) \sim u^{-\nu}$. In the asymptotic region where ν varies slowly with u

$$\nu = -\frac{\mathrm{d}\ln S(u)}{\mathrm{d}\ln u} \tag{30}$$

Differentiation of eq 29 gives

$$\nu = \overline{g_{\alpha\beta}u} = \frac{\sum_{\alpha<\beta} g_{\alpha\beta}u e^{-g_{\alpha\beta}u}}{\sum_{\alpha<\beta} e^{-g_{\alpha\beta}u}} \tag{31}$$

The coefficients of the perturbation expansion of $S(u)$ are easily computed. Letting $Q_p(\{\alpha\}) \equiv \psi_p(\{\alpha\})$, eq 13 becomes

$$Q_p(\{\alpha\}) = \prod_{j=1}^p(\alpha_j\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\ldots\sum_{m<n}\frac{|\mathbf{K}_i(\{\alpha\}, k-l, \ldots, m-n)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}} \times \frac{\sum_{i<j} e^{-g_{ij}(\{\alpha\},k-l,\ldots,m-n)u}}{\sum_{i<j} e^{-g_{ij}u}} \tag{32}$$

The first-order scattering function for the cluster function of eq 5b is

$$S(u) = (2/N(N-1))\sum_{i<j} e^{-g_{ij}u} + \beta(\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\frac{|\mathbf{K}_i(\epsilon, k-l)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}}\sum_{i<j}(e^{-g_{ij}u} - e^{-g_{ij}(\epsilon,k-l)u}) \tag{33}$$

This expression is valid for small β and u.

Differentiation of the scattering function gives the mean square radius of gyration. In the unperturbed state

$$\frac{\langle S^2\rangle}{\langle l^2\rangle} = -\frac{1}{2}\frac{\mathrm{d}S(u)}{\mathrm{d}u} = (2/N(N-1))\sum_{i<j} g_{ij} \tag{34}$$

In fact, this is simply Lagrange's theorem[21] and gives another expression for the expansion coefficients of the radius of gyration:

$$S_p(\{\alpha\}) = \prod_{j-1}^p(\alpha_j\epsilon\gamma/\pi)^{3/2}\sum_{k<l}\ldots\sum_{m<n}\frac{|\mathbf{K}_i(\{\alpha\}, k-l, \ldots, m-n)|^{-3/2}}{|\mathbf{K}_i|^{-3/2}} \times \frac{\sum_{i<j} g_{ij}(\{\alpha\}, k-l, \ldots, m-n)}{\sum_{i<j} g_{ij}} \tag{35}$$

This form of $S_p(\{\alpha\})$ is convenient for computations.

IVf. Second Virial Coefficient

The first-order expression for the second virial coefficient can be derived without recourse to a particular model. To show this, it is convenient to start with the cluster expansion expression for A_2 derived by Zimm.[22]

$$A_2 = -(N_A/2VM^2)\int F(1)F(2)[\prod_{i_1,i_2}(1-\zeta\chi_{i_1,i_2})-1]\,\mathrm{d}(1)\,\mathrm{d}(2) \tag{36a}$$

$$\cong (N_A/2VM^2)\int F(1)F(2)\zeta\sum_{i_1}\sum_{i_2}\chi_{i_1,i_2}\,\mathrm{d}(1)\,\mathrm{d}(2) \tag{36b}$$

$F(1)$ is the probability distribution for the internal and external coordinates, (1), of polymer 1 in the perturbed state, M is the molecular weight, N_A is Avogadro's number, and V is the volume of solution. The cluster function $\zeta\chi_{i_1,i_2}$ acts between monomers on different polymers. The normalization of $F(1)$ is

$$\int F(1)\,\mathrm{d}(1) = V \tag{37}$$

The cluster function is a function of the vector $\mathbf{r}_{i_1,i_2}$. Factor the volume element as $\mathrm{d}(1)\,\mathrm{d}(2) = \mathrm{d}(1)_{\mathrm{int}}\,\mathrm{d}(2)_{\mathrm{int}}\,\mathrm{d}(1+2)\,\mathrm{d}(1-2)$ and integrate the first-order expression, eq 36b, over the internal coordinates $(1)_{\mathrm{int}}$ and $(2)_{\mathrm{int}}$. Let $\mathrm{d}(1-2) = \mathrm{d}^3\mathbf{r}_{i_1,i_2}$ and $\mathrm{d}(1+2) = \mathrm{d}^3(\mathbf{r}_{i_1}+\mathbf{r}_{i_2})$. Integration over $\mathrm{d}(1+2)$ gives a factor V and

$$A_2 = -(N_A/2m_S^2)\int \zeta\chi_{i_1,i_2}\,\mathrm{d}^3\mathbf{r}_{i_1,i_2} = N_A\beta/2m_S^2 \tag{38}$$

where m_S is the segment molecular weight. The definition of β, eq 4b, has been used to obtain the last result. To first order the polymeric nature of the problem does not enter into the calculation. Equation 38 is just the virial coefficient for a solution of free polymer segments. No such model-independent calculation can be made for higher order terms.

A simplification is made in applying our model to higher order terms. Let $F(1)F(2)$ by given by the unperturbed normalized Gaussian function

$$F(1)F(2) = (\pi/\gamma)^{-3(N-1)}|\mathbf{K}_i|^3 e^{-\gamma\mathbf{R}_T(\mathbf{E}_2\otimes\mathbf{K}\otimes\mathbf{E}_3)\mathbf{R}_T{}^t} \tag{39}$$

The $1\times 6N$ row vector $\mathbf{R}_T = (\mathbf{R}_1, \mathbf{R}_2)$ and $\mathbf{K}$ is the $N\times N$ Kirchhoff matrix for each identical polymer.

The pth-order term requires the construction of the $2N\times 2N$ matrix

$$\mathbf{V}(\{\alpha\}, k_1-k_2, ..., m_1-m_2) = \mathbf{E}_2\otimes\mathbf{K} + \epsilon\alpha_1\mathbf{C}(k_1-k_2) + ... + \epsilon\alpha_p\mathbf{C}(m_1-m_2) \tag{40}$$

where $\mathbf{C}(k_1-k_2)$ is a $2N\times 2N$ matrix that specifies an interaction between vertex k_1, $1\le k_1\le N$, on polymer 1, and vertex k_2, $N+1\le k_2\le 2N$, on polymer 2. Explicitly, the $\omega\nu$ element is

$$\mathbf{C}(k_1-k_2)_{\omega\nu} = \delta_{\omega k_1}\delta_{\nu k_1} + \delta_{\omega k_2}\delta_{\nu k_2} - \delta_{\omega k_1}\delta_{\nu k_2} - \delta_{\omega k_2}\delta_{\nu k_1} \tag{41}$$

Note that $\mathbf{V}$ is a variable Kirchhoff matrix for a connected graph (one zero eigenvalue). If A_2 is expanded as

$$A_2 = -(N_A/2M^2)\sum_{p=1}^{N^2}(-1)^p a_p \tag{42a}$$

then a formula for the a_p can be obtained. Substituting the cluster function product, eq 15, with eq 39 into eq 36a, and making use of the matrix $\mathbf{V}(\{\alpha\}, k_1-k_2, ..., m_1-m_2)$ gives

$$a_p(\{\alpha\}) = (\gamma/\pi)^{3(p-1)/2}\epsilon^{3p/2}(\prod_{j=1}^{p}\alpha_j{}^{3/2}) \times \sum_{k_1,k_2}\cdots\sum_{m_1,m_2}\frac{|\mathbf{V}_i(\{\alpha\}, k_1-k_2, ..., m_1-m_2)|^{-3/2}}{|\mathbf{K}_i|^{-3}} \tag{42b}$$

The a_p for cluster function eq 5b or eq 7b can be obtained by using eq 16 or eq 17, respectively, with $\psi_p(\{\alpha\}) = a_p(\{\alpha\})$.

Va. Matrix Elements and Determinants for Cluster Diagram Graphs

The cluster expansion equations developed in section IV contain certain variable Kirchhoff matrices, their determinants, and elements of their Moore–Penrose inverses. These matrices will now be specialized to the linear-chain polymer of N vertices.

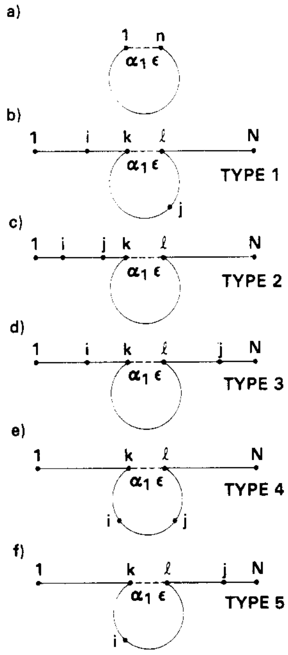


Figure 5. Single-contact cluster diagrams for the linear polymer. Each of the five types corresponds to a matrix element given in eq 46.

The Kirchhoff matrix for this linear chain has the following structure: the diagonal elements are 2 (except $k_{11} = k_{NN} = 1$), and the codiagonal elements are -1. All other elements are zero. In Kronecker δ notation

$$k_{ij} = 2\delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1} + \delta_{i,1}\delta_{j,N} + \delta_{i,N}\delta_{j,1} - \delta_{i,1}\delta_{j,1} - \delta_{i,N}\delta_{j,N} \tag{43}$$

In a previous paper, the conditions of section IVc are applied to $\mathbf{K}$ to find the Moore–Penrose inverse. Remembering that $g_{ij} = a_{ii} + a_{jj} - 2a_{ij}$, the result is

$$a_{ij} = -(2N)^{-1}[i(N-i+1) + j(N-j+1) + N|i-j| - (N+1)(2N+1)/3] \tag{44a}$$

$$g_{ij} = |i-j| \tag{44b}$$

Equation 44b is the well-known result $\langle|\mathbf{r}_i - \mathbf{r}_j|^2\rangle_0 = |i-j|\langle l^2\rangle$. The determinant of the $N-1\times N-1$ matrix $\mathbf{K}_i$ is readily computed, from the Binet–Cauchy theorem (section IVa) $|\mathbf{K}_i| = 1$, since there is only one spanning tree on the linear-chain graph (or any other graph lacking circuits).

Graph matrices for single-contact diagrams are more interesting. The single-contact matrix for the linear chain is $\mathbf{K}(\alpha_1, k-l) = \mathbf{K} + \alpha_1\epsilon\mathbf{C}(k-l)$ (eq 18 and 19), where the contact vertices are labeled k and l. The single-contact graph described by $\mathbf{K}(\alpha_1, k-l)$ is in Figure 5b. To calculate the g_{ij} for this graph, it will suffice to calculate the a_{ij} for the graph of Figure 5a. Label the vertices of this graph from 1 to n and give the bond connecting vertex 1 to vertex n a weighting $\alpha_1\epsilon$. A direct but lengthy calculation gives

$$a_{ij} = -(2n)^{-1}[i(n-i+1) + j(n-j+1) + n|i-j| - (n+1)(2n+1)/3] - \alpha_1\epsilon(n-2i+1)(n-2j+1)/4(1+(n-1)\alpha_1\epsilon) \tag{45a}$$

$$g_{ij} = |i-j| - |i-j|^2/(n-1+1/\alpha_1\epsilon) \tag{45b}$$

Letting $\alpha_1\epsilon = 0$ gives eq 44a and 44b, the linear-chain

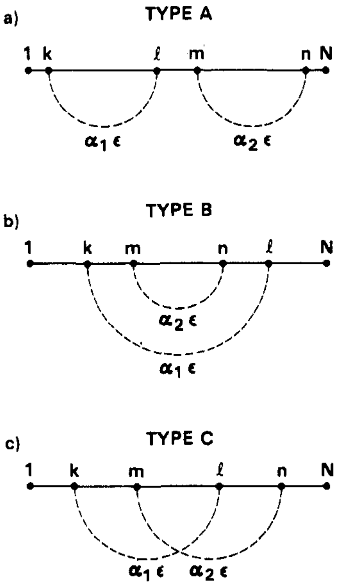


Figure 6. Double-contact cluster diagrams for the linear chain. Each of the three types corresponds to a determinant in eq 48.

results, and letting $\alpha_1\epsilon = 1$ gives a set of equations for the circular chain.

The g_{ij} for the single-contact graph are found in the following way: $g_{ij} = \langle|\mathbf{r}_i - \mathbf{r}_j|^2\rangle/\langle l^2\rangle = (\langle|\mathbf{r}_i - \mathbf{r}_k|^2\rangle + \langle|\mathbf{r}_j - \mathbf{r}_k|^2\rangle)/\langle l^2\rangle$ for the example of Figure 5b. Calculation of $\langle|\mathbf{r}_i - \mathbf{r}_k|^2\rangle$ requires g_{ij} for the linear chain and calculation of $\langle|\mathbf{r}_j - \mathbf{r}_k|^2\rangle$ requires eq 45b. Other factorizations are useful for other vertex pairs i and j. Combining eq 44b and 45b gives the g_{ij} for each of the graphs shown in Figure 5:

Type 1:

$$g_{ij} = |k - i| + |j - k|\left(1 - \frac{|j - k|}{|k - l| + 1/\alpha_1\epsilon}\right) \tag{46a}$$

Type 2:

$$g_{ij} = |i - j| \tag{46b}$$

Type 3:

$$g_{ij} = |k - i| + |j - l| + \frac{|k - l|}{\alpha_1\epsilon|k - l| + 1} \tag{46c}$$

Type 4:

$$g_{ij} = |i - j|\frac{|k - l| - |i - j| + 1/\alpha_1\epsilon}{|k - l| + 1/\alpha_1\epsilon} \tag{46d}$$

Type 5:

$$g_{ij} = |j - l| + |l - i|\left(1 - \frac{|l - i|}{|l - k| + 1/\alpha_1\epsilon}\right) \tag{46e}$$

where we have followed the convention $k < l$ as in Figure 5.

The determinant of $\mathbf{K}_i(\alpha_1, k - l)$ is found by enumerating the spanning trees of Figure 5b. Cutting the k–l bond gives 1 tree. There are just $|k - l|$ ways to cut the single bonds in the loop, but each of these graphs has a weighting of $\alpha_1\epsilon$ since the multiple k–l bond can be cut $\alpha_1\epsilon$ ways. The result is

$$|\mathbf{K}_i(\alpha_1, k - l)| = \alpha_1\epsilon|k - l| + 1 \tag{47}$$

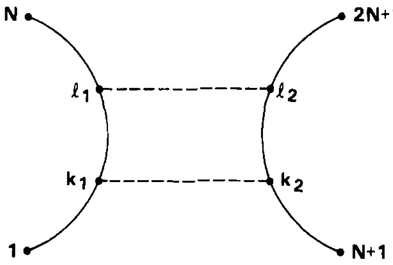


Figure 7. Double-contact cluster diagram for two identical linear chains. The associated determinant appears in eq 49.

Consider the double-contact graph for the linear chain. There are three types, as shown in Figure 6. Enumeration of the spanning trees gives the following determinants:

Type A:

$$(1 - \alpha_1\epsilon|k - l|)(1 + \alpha_2\epsilon|m - n|) \tag{48a}$$

Type B:

$$1 + \alpha_1\epsilon|k - l| + \alpha_2\epsilon|m - n| + \alpha_1\alpha_2\epsilon^2|m - n|(|k - l| - |m - n|) \tag{48b}$$

Type C:

$$1 + \alpha_1\epsilon|k - l| + \alpha_2\epsilon|m - n| + \alpha_1\alpha_2\epsilon^2(|n - l||m - k| + |l - m||n - l| + |l - m||m - k|) \tag{48c}$$

Finally, a calculation of the second-order term in the expansion of A_2 requires the determinant of $\mathbf{V}_i(\{\alpha\}, k_1 - k_2, ..., m_1 - m_2)$ for the double-contact graph shown in Figure 7. This determinant

$$|\mathbf{V}_i(\alpha_1, \alpha_2, k_1 - k_2, l_1 - l_2)| = (|k_1 - l_1| + |k_2 - l_2|)\alpha_1\alpha_2\epsilon^2 + \alpha_2\epsilon + \alpha_1\epsilon \tag{49}$$

These matrix elements and determinants will now be used to calculate properties of Θ chains.

Vb. Configuration Integral

The first-order expression for the configuration integral of the linear chain is obtained from eq 21 and 47. Letting $\Delta \equiv 1/\epsilon$

$$\begin{aligned} Z_1(\alpha_1) &= (\gamma/\pi)^{3/2}\sum_{k<l}(|k - l| + \Delta/\alpha_1)^{-3/2} \\ &\cong (\gamma/\pi)^{3/2}2N(1 - \Delta/2\alpha_1) \end{aligned} \tag{50}$$

where only terms of order N and Δ have been retained in evaluating $Z_1(\alpha_1)$. For cluster functions eq 5b and 7b this gives, respectively

$$\begin{aligned} \zeta Z_1 &\cong 2N\beta(\gamma/\pi)^{3/2}(1 - \Delta/2) \\ &\cong 2N\beta(\gamma/\pi)^{3/2} - N(\gamma/\pi)^{3/2}(\beta - \sigma)\Delta/2 \end{aligned} \tag{51}$$

In the δ-function limit, $\Delta \rightarrow 0$ and eq 51a and 51b reduce to $Z_1 = 2N\beta(\gamma/\pi)^{3/2}$.

The Θ-point behavior of Z_1, defined by $\beta = 0$, is nontrivial for the cluster function of eq 7b. In the δ-function limit, or for cluster function eq 5b, $\lim_{\beta\rightarrow 0} Z_j = 0$ ($j \geq 1$). The reason for this is clear; $\chi(\mathbf{r}_{ij}) \equiv 0$ at this temperature. However, from eq 51b

$$\lim_{\beta\rightarrow 0}(\zeta Z_1) = N(\gamma/\pi)^{3/2}\sigma\Delta/2 \tag{52}$$

In fact, Z_1 vanishes at $\beta \cong -\Delta\sigma/(4 - \Delta)$ (valid for small Δ), which is beneath the Θ temperature. Z_1 is not directly measurable, but this result gives an indication of how the formulas for the expansion factors might change with a cluster function that is nonvanishing at the Θ temperature.

Similar results are obtained for the circular chain. A count of the spanning trees gives

$$Z_1(\alpha_1) = (\gamma/\pi)^{3/2}\sum_{k<l}(|k-l|(N-|k-l|)/N+\Delta/\alpha_1)^{-3/2} \cong (\gamma/\pi)^{3/2}2N(1-\Delta/2\alpha_1) \quad (53)$$

which, to this order, is the linear-chain result. To terms of order N and Δ, eq 53 is probably independent of chain topology, although proof of this conjecture is lacking.

The second-order term, Z_2, can be calculated from the determinants given in eq 48. A Cray digital computer was used to compute the necessary sums exactly. Z_2 for eq 7b is a quadratic in C, but at finite molecular weight and potential width, Z_2 is never zero. Instead, Z_2 reaches a minimum at a temperature near the temperature where $Z_1 = 0$. In the δ-function limit these Z_p have a distinctly different behavior; $\lim_{\beta\to 0} Z_1 = Z_2 = ... = Z_p = 0$.

VIa. Results for Expansion Factors: Specific Solvent Effects

Expansion factors for the end-to-end vector and the radius of gyration are easily computed and demonstrate the qualitative features of this treatment. The mean square unperturbed vector $\langle R_{ij}^2\rangle_0$ is given by the matrix element $g_{ij}\langle l^2\rangle_0$. $\psi_1(\alpha_1)$ for the expansion factor of this vector is just

$$(\gamma/\pi)^{3/2}\sum_{k<l}(|k-l|+\Delta/\alpha_1)^{-3/2}g_{ij}(\alpha_1, k-l)/g_{ij} \quad (54)$$

The first-order expression for the expansion factor of the end-to-end vector of a polymer chain, $\alpha_R^2 = \langle R^2\rangle/\langle R^2\rangle_0$, is found for cluster function eq 5b by using eq 16, 21, 46 (type 3 with $i,j = 1, N$), and 54.

$$\alpha_R^2 - 1 = \beta\frac{(\gamma/\pi)^{3/2}}{N-1}\sum_{k<l}(|k-l|+\Delta)^{-3/2}|k-l| \times \left[1-\frac{\Delta}{|k-l|+\Delta}\right] \equiv ze_1(\Delta) \quad (55)$$

Here, $z = (\gamma/\pi)^{3/2}\beta N^{1/2}$ is the usual excluded volume parameter.[11] The expression for cluster function eq 7b can be formulated in terms of $e_1(\Delta)$. From eq 16 and 17 it can be shown that for any first-order expansion factor coefficient $\upsilon_1(\Delta)$, the expressions for eq 5b and 7b are, respectively

$$\alpha_\upsilon^2 - 1 = z\upsilon_1(0) - z\delta\upsilon_1(\Delta) \quad (56a)$$

$$\alpha_\upsilon^2 - 1 = z\upsilon_1(0) - z\delta\upsilon_1(\Delta/2) + \sigma(\gamma/\pi)^{3/2}N^{1/2}(\upsilon_1(\Delta/2) - \upsilon_1(\Delta)) \quad (56b)$$

where $\delta\upsilon_1(\Delta) = \upsilon_1(0) - \upsilon_1(\Delta)$. Written in this way, the δ-function result appears as the first term, i.e., $z\upsilon_1(0)$.

First-order expressions for the expansion factor of the radius of gyration depend on the constant $c_1(\Delta)$, where

$$c_1(\Delta) = \sum_{k<l}(|k-l|+\Delta)^{-3/2}\left[1-\frac{\sum_{i<j}g_{ij}(\Delta, k-l)}{\sum_{i<j}g_{ij}}\right] \quad (57)$$

The coefficients $e_1(\Delta)$ and $c_1(\Delta)$ are of the form $\upsilon_1(\Delta) = \upsilon_1(0) - f(\Delta)/N^{1/2} + \mathcal{O}(1/N)$, where $\lim_{\Delta\to 0} f(\Delta) = 0$. After some algebra the terms of order unity are shown to be (let $t \equiv |k-l|/N$)

$$e_1(0) = \int_0^1 \frac{1-t}{t^{1/2}}\,dt = \frac{4}{3}$$

$$c_1(0) = \int_0^1\left(t-\frac{t^3}{2}\right)\frac{1-t}{t^{3/2}}\,dt = \frac{134}{105}$$

These coefficients were originally derived by Fixman,[1] using the Wang–Uhlenbeck method of multivariate Gaussian distributions. Expanding $f(\Delta)$ as a power series in Δ and retaining only terms of order Δ gives

$$e_1(\Delta) = 4/3 - 1.46/N^{1/2} - \Delta 5\zeta(3/2)/2N^{1/2} \quad (58a)$$

$$c_1(\Delta) = 134/105 - 1.46/N^{1/2} - \Delta 5\zeta(3/2)/2N^{1/2} \quad (58b)$$

where $\zeta(x)$ is the Riemann ζ function ($\zeta(3/2) \sim 2.612$) and the coefficient 1.46 was obtained as $\lim_{N\to\infty} \sum_{k=1}^{N}k^{-1/2} - 2N^{1/2})$.

It is observed that expansion factors for cluster function eq 5b are uninteresting, the result being $\alpha_R^2 - 1 = (4/3)z(1 - (1.01 + 4.90\Delta)/N^{1/2}$ with a similar expression for $\alpha_S^2 - 1$. It is seen that a purely repulsive potential of nonvanishing width is quantitatively similar to a δ function except for the magnitude of finite molecular weight corrections to $e_1(\Delta)$, which are of order $1/N^{1/2}$. These corrections increase with the width of the potential. It is clear that calculations based on purely repulsive potentials (which must vanish at the Θ point), e.g. hard-core potentials, are not worth pursuing.

The finite chain length correction has been studied by Gupta et al.,[23] for branched and linear chains in the pseudopotential approximation. Using a numerical fitting procedure they estimated the correction to be $-0.885z/N^{0.462}$ for the radius of gyration, in good agreement with exact results. Direct comparisons are not easy however, since Gupta et al. represent a power series in $1/N^{1/2}$ by an effective exponent. It should be pointed out that this correction factor is not small; for polystyrene of molecular weight 10^5, $N \sim 10^2$. If the range of the potential is given by $\Delta \sim 0.3$, then $e_1 \sim 1.0$. Use of this factor would lead to a 30% change in the calculated value of z.

The excluded volume potential of eq 7a is of real interest here since it presents a picture of the Θ regime that is markedly different. From eq 56 it is seen that for large N

$$\alpha_R^2 - 1 = \frac{4}{3}z + \frac{5}{4}\zeta(3/2)\phi \quad (59a)$$

$$\alpha_S^2 - 1 = \frac{134}{105}z + \frac{5}{4}\zeta(3/2)\phi \quad (59b)$$

where $\phi = \Delta\sigma(\gamma/\pi)^{3/2}$ is a dimensionless parameter. Two limits are of interest:

$$\lim_{\beta\to 0}(\alpha_R^2 - 1) = \lim_{\beta\to 0}(\alpha_S^2 - 1) = \frac{5}{4}\zeta(3/2)\phi$$

$$\lim_{\beta\to a}(\alpha_R^2 - 1) = \lim_{\beta\to a'}(\alpha_S^2 - 1) = 0$$

where

$$a = -\frac{15}{16}\zeta(3/2)\frac{\Delta\sigma}{N^{1/2}}$$

and

$$a' = -\frac{105}{134}\,\frac{5}{4}\zeta(3/2)\frac{\Delta\sigma}{N^{1/2}}$$

The first limit defines a temperature where the polymer is ideal, i.e., $\langle R^2\rangle \sim N$, but swollen relative to the reference unperturbed chain. This swelling increases with the width of the excluded volume potential; Θ-state dimensions are seen to be

$$\langle R^2\rangle_\Theta = N\langle l^2\rangle\left(1+\frac{5}{4}\zeta(3/2)\phi\right) \quad (60a)$$

$$\langle S^2\rangle_\Theta = \frac{N\langle l^2\rangle}{6}\left(1 + \frac{5}{4}\zeta(3/2)\phi\right) \qquad (60b)$$

This swelling has no effect on the ratio $\langle R^2\rangle_\Theta/\langle S^2\rangle_\Theta = 6$ and thus is in agreement with Monte Carlo simulations of Θ chains. Calculations based on three-body interactions give similar predictions.

The second limit is physically unimportant. It simply states that a Θ chain will attain its unperturbed dimensions at a temperature that is of order $1/N^{1/2}$ beneath the Θ temperature. In the laboratory this has little significance. The term $(5/4)\zeta(3/2)\phi \cong 3.27\phi$ represents a specific solvent effect. Such variations in unperturbed dimensions are well documented experimentally, as can be seen from tables of "unperturbed" dimensions. As an example, consider the Θ dimensions reported by Schulz and Bauman.[24] These data were obtained from viscosity measurements very close to the Θ temperature: butyl formate (Θ = −9 °C), $\langle R^2\rangle_\Theta/M$ = 0.429 Å^2 g^{-1} mol; methylcyclohexane (Θ = 68 °C), $\langle R^2\rangle/M$ = 0.429 Å^2 g^{-1} mol; cyclohexanol (Θ = 83.5 °C), $\langle R^2\rangle/M$ = 0.331 Å^2 g^{-1} mol.

No simple picture of a temperature dependence of $\langle l^2\rangle$ emerges from these data. Three effects are probably of importance in explaining these results. First, rotational potential barriers are typically larger than kT, giving an appreciable temperature effect in the conformational Boltzmann factors. This should lead to an effective increase in the chain flexibility at higher temperatures and therefore decrease $\langle R^2\rangle_\Theta/M$. Second, variations in the solvent type could have an effect on rotational potential barriers, due to solvent screening of local interactions, or more efficient packing in some conformations. These effects are local in nature; the third effect is due to the excluded volume potential and is global in nature. It is of some interest that a long-range interaction need not perturb the Markoff nature of the chain.

In the laboratory it is not possible to measure the above expansion factors since they are relative to the unmeasurable unperturbed state. The experimentally observed expansion factors are relative to the Θ state and for large N are

$$\tilde\alpha_R^2 - 1 = \frac{4}{3}z\Big/\left(1 + \frac{5}{4}\zeta(3/2)\phi\right) \qquad (61a)$$

$$\tilde\alpha_S^2 - 1 = \frac{134}{105}z\Big/\left(1 + \frac{5}{4}\zeta(3/2)\phi\right) \qquad (61b)$$

Now suppose that a researcher is concerned only with the Θ-state dimensions $\langle R^2\rangle_\Theta$ and $\langle S^2\rangle_\Theta$ and their expansion factors. We then renormalize our results to a two-parameter theory (let $\lambda = N\langle l^2\rangle$) in the following way: $\tilde\lambda = \lambda(1 + 5\zeta(3/2)\phi/4)$; $\tilde z = z/(1 + 5\zeta(3/2)\phi/4)$. In terms of these new parameters

$$\langle R^2\rangle_\Theta = \tilde\lambda; \qquad \langle S^2\rangle_\Theta = \tilde\lambda/6$$

$$\tilde\alpha_R^2 - 1 = (4/3)\tilde z; \qquad \tilde\alpha_S^2 - 1 = (134/105)\tilde z$$

The experimental conclusion would be that two-parameter theory is "correct". In the next sections, however, it will be shown that a larger set of experimental data, e.g., measurements of diffusion coefficients and second virial coefficients, does not admit to such a two-parameter renormalization.

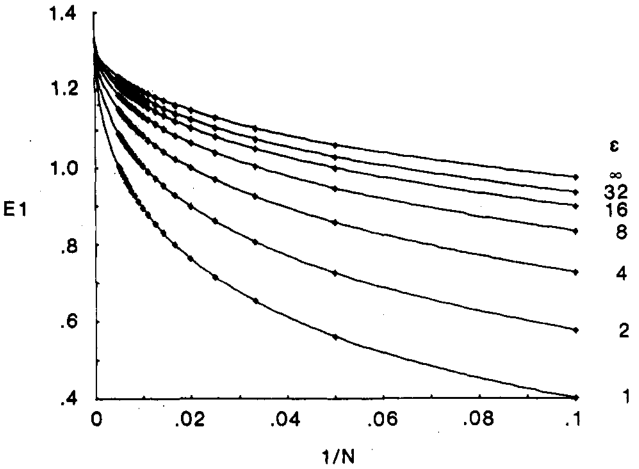


Figure 8. Results of numerical computations for the first-order expansion factor of the end-to-end vector of the linear chain. The value of Δ is given to the right of each curve. The lines are the result of numerical fits to the data, the coefficients of which are in Table I. The intercept was 1.3333 for all values of Δ.

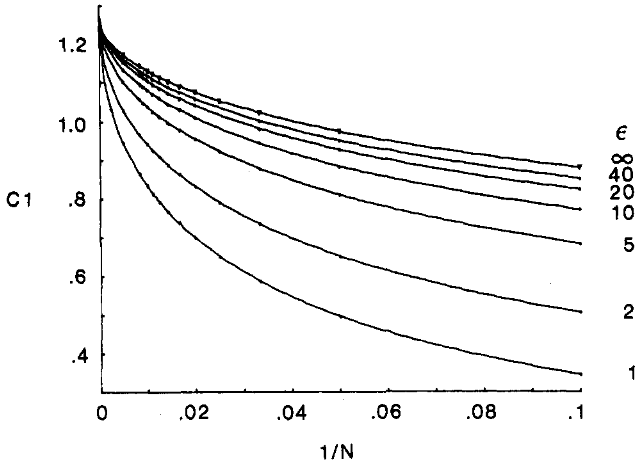


Figure 9. Results of numerical computations for the first-order expansion factor of the radius of gyration of the linear chain. The coefficients of the polynomial fits to the data are in Table I. The intercept was 1.276 for all values of Δ.

Table I
Results of Numerical Computations

ϵ	a_0	a_1	quantity
1	1.33331	−5.3427	end-to-end vector
2	1.33333	−3.8195	end-to-end vector
4	1.33333	−2.8134	end-to-end vector
8	1.33333	−2.1975	end-to-end vector
16	1.33332	−1.8468	end-to-end vector
32	1.33332	−1.6585	end-to-end vector
10^6	1.33333	−1.4602	end-to-end vector
1	1.27618	−5.3432	radius of gyration
2	1.27618	−3.8193	radius of gyration
4	1.27618	−2.8129	radius of gyration
8	1.27619	−2.1973	radius of gyration
16	1.27619	−1.8474	radius of gyration
32	1.27620	−1.6593	radius of gyration
10^6	1.27618	−1.4600	radius of gyration
1	0.61219	−2.2611	hydrodynamic radius
2	0.61072	−1.3701	hydrodynamic radius
4	0.60998	−0.80264	hydrodynamic radius
8	0.60963	−0.46303	hydrodynamic radius
16	0.60944	−0.27179	hydrodynamic radius
10^6	0.60926	−0.06242	hydrodynamic radius

VIb. Numerical Results for Expansion Factors

Exact numerical calculations of $e_1(\Delta)$ and $c_1(\Delta)$ for N = 10, 20, ..., 200 are shown in Figures 8 and 9. Since it is known that these coefficients are polynomials in $1/N^{1/2}$, data sets for each value of Δ were fit to polynomials of this type; these are the curves given in the figures. χ^2 for these fits was always less than 10^{-15}. In Table I are the first two

Table II
Numerical Data on the Relative Θ Dimensions of the Hydrodynamic Radius and the Radius of Gyration

ϵ	$L_R(\Delta)/\Delta$	$L_S(\Delta)/\Delta$	$2L_h(\Delta)/\Delta$	
1	1.522	1.524	1.782	0.259
2	2.012	2.013	2.270	0.258
4	2.464	2.462	2.717	0.254
8	2.806	2.800	3.068	0.257
16	3.013	3.010		
∞	$\xi_R \sim 3.25^a$	$\xi_S \sim 3.25^a$	$\xi_h \sim 3.50^a$	$\Delta\xi \sim 0.25$

[a] Based on numerical extrapolation (the exact theoretical value for the end-to-end vector and the radius of gyration is 3.265).

coefficients of the polynomials for various values of ϵ. The extrapolations to infinite molecular weight gave the coefficients 4/3 and 134/105 to within 0.0017% and 0.0007%, respectively, in the worst cases. The second coefficient is the term of order $1/N^{1/2}$. Within numerical error, this coefficient is the same for the end-to-end vector and the radius of gyration and is seen to extrapolate to the predicted value 1.46 for $\epsilon \rightarrow \infty$. Define the function $L_v(\Delta) = v_1(\Delta/2) - v_1(\Delta)$, which is the swelling term in eq 56b. This function is given as $L_v(\Delta)/\Delta$ in Table II and is seen to be identical, within numerical error, for the radius of gyration and the end-to-end vector. Previously, it was concluded that to terms of order Δ specific solvent effects were the same for $\langle R^2\rangle_\Theta$ and $\langle S^2\rangle_\Theta$; it is now clear that these effects are identical for all Δ. Thus $\langle R^2\rangle_\Theta/\langle S^2\rangle_\Theta = 6$ is a universal constant for all flexible polymers, and the renormalization to a Gaussian chain is generally valid for these quantities.

Finally, it is noted that extrapolation of $f(\Delta)/\Delta$ to $\Delta = 0$ gives the coefficient ξ_R in the expression $\langle R^2\rangle_\Theta = \langle R^2\rangle_\Theta(1 + \xi_R\phi)$. Numerical extrapolation of the data in Table II gives $\xi_R = \xi_S = 3.25$, which agrees quite well with the analytical value $5\zeta(3/2)/4 = 3.265$. This gives confidence that our numerical techniques are accurate.

VIc. Expansion Factor for the Hydrodynamic Radius

If Kirkwood's formula for the hydrodynamic radius is correct in the nondraining limit, then the formulation of section IVc should yield equations that are not renormalizable to the unperturbed chain. Kirkwood's derivation includes two major approximations: use of the Oseen tensor to estimate hydrodynamic interactions and preaveraging the Oseen tensor in the calculations. It may well be the case that these assumptions cancel to some extent. In this section it will be seen that the divergence in the Oseen tensor (of order $1/r$) causes a divergence in the expansion factor of the hydrodynamic radius in the finite molecular weight δ-function limit.

Working in the δ-function limit, Stockmayer and Albrecht[25] first calculated the exact single-contact expression for the expansion factor; $\alpha_h = 1 + 0.609z$. This result was based on Kirkwood's nondraining formula and should agree with our formulation with $\Delta = 0$. From eq 16, 21, and 25 we obtain a formula for $h(\Delta,N)$, defined by $\alpha_h = 1 + h_1(\Delta,N)z$, an expression valid for cluster function eq 5b. This function can then be used to calculate first-order expressions for the expansion factor, in a manner analogous to eq 60 for the end-to-end vector.

$$\alpha_h - 1 = zh_1(\Delta,N) \tag{62a}$$

$$\alpha_h - 1 = zh_1(\Delta/2,N) + \sigma(\gamma/\pi)^{3/2}N^{1/2}[h_1(\Delta/2,N) - h_1(\Delta,N)] \tag{62b}$$

These are valid for cluster function eq 5b and 7b, respectively.

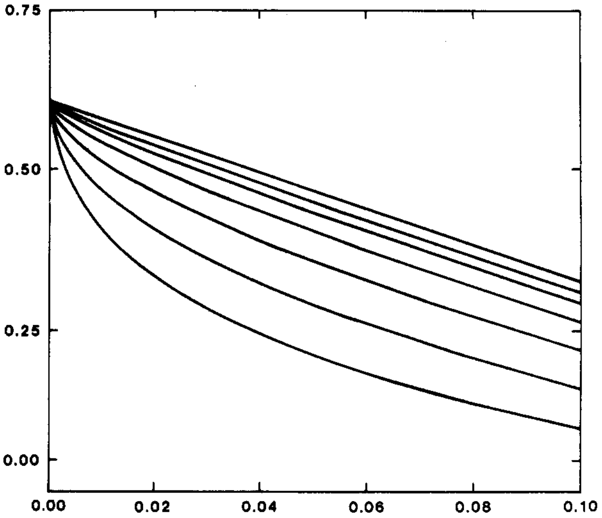


Figure 10. Results of numerical computations for the nonsingular part of the expansion factor of the hydrodynamic radius. The coefficients of the polynomial fits are in Table I.

Numerical computation of $h_1(\Delta,N)$ is troubled by divergent terms in eq 25. Two limits are of interest:

$$\lim_{N\to\infty}\lim_{\Delta\to 0} h_1(\Delta,N) = \infty$$

$$\lim_{\Delta\to 0}\lim_{N\to\infty} h_1(\Delta,N) = 0.609$$

To isolate the divergent part let $h_1(\Delta,N) = A(\Delta,N) + B(\Delta,N)$, where $\lim_{N\to\infty}\lim_{\Delta\to 0} A(\Delta,N) = \lim_{\Delta\to 0}\lim_{N\to\infty} A(\Delta,N) = 0.609$, $\lim_{\Delta\to 0}\lim_{N\to\infty} B(\Delta,N) = 0$ and $\lim_{N\to\infty}\lim_{\Delta\to 0} B(\Delta,N) = \infty$. Isolating the divergent terms in eq 25 gives

$$B(\Delta,N) = N^{-1/2}\sum_{k>l}(|k-l| + \Delta)^{-3/2}g_{kl}(\Delta, k-l)^{-1/2}\Big/\sum_{i<j}g_{ij}^{-1/2} = (3/4N)[\zeta(3/2)/\Delta^{1/2} - \zeta(5/2)\Delta^{1/2}] \tag{63}$$

This result is exact for large N and small Δ. It should be noted that in the large molecular weight limit only terms of order unity and $1/N^{1/2}$ contribute to the first-order expression for the expansion factor; the divergent part of $h_1(\Delta,N)$ makes no contribution in this limit.

Numerical results for $A(\Delta,N)$ are shown in Figure 10 for a wide range of Δ. These data were fit to a polynomial in $1/N^{1/2}$: the coefficients of order unity and $1/N^{1/2}$ appear in Table I. The term of $\mathcal{O}(1)$ is within 0.5% of the exact value 0.60927 for all values of Δ. The numerical value for $\Delta = 10^{-6}$ is 0.60925, which agrees quite well with the exact value. Numerical extrapolation to $\Delta = 0$ of the term of $\mathcal{O}(1/N^{1/2})$ gives a Θ-point swelling term of 0.350ϕ for the square of the hydrodynamic radius. This is larger than the value 0.326ϕ obtained for mean square dimensions and indicates that a polymer chain is non-Gaussian even at the Θ point.

Since a theoretical value of the Θ-point swelling term of the hydrodynamic radius is not available, it seems worthwhile to do a more direct numerical computation of this term. To this end the analytical expression for $A(\Delta,N)$ was differentiated with respect to Δ and evaluated at $\Delta = 0$. The result, which is in terms of sums of the usual matrix elements and their derivatives, is just the Θ-point swelling term for the hydrodynamic radius. Numerical evaluation of the resultant sum was done for N = 100, 110, ..., 200 and these data were extrapolated to $1/N = 0$. This gave a value of 3.45ϕ for the Θ-point swelling term. The

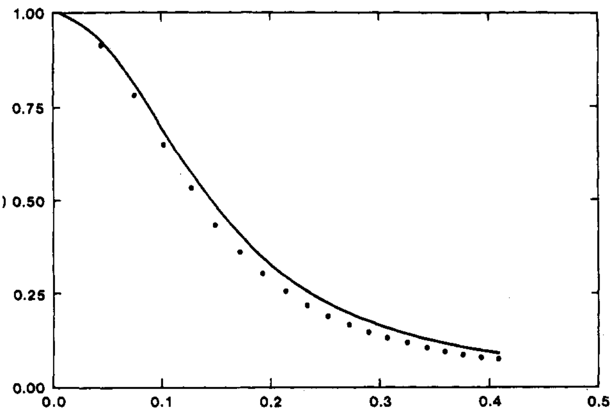


Figure 11. Scattering functions for the linear chain. The curve is for the unperturbed chain with $N = 200$ and the points are for the unperturbed chain with $z = 0.2$.

first-order expansion factor and the Θ-point hydrodynamic radius are then just

$$\tilde{\alpha}_h^2 - 1 = 1.218z/(1 + 0.345\phi) \tag{64a}$$

$$\langle a_h \rangle_\Theta^2 = \langle a_h \rangle_0^2 (1 + 0.345\phi) \tag{64b}$$

Although these numerical results indicate that the Θ chain is non-Gaussian, they do not constitute proof. Hopefully, future theoretical work will provide an exact value for the Θ-point swelling term.

Defining the ratio of the mean square radius of gyration to the hydrodynamic radius squared by $\rho = \langle R^2 \rangle_\Theta / \langle a_h \rangle_\Theta^2 = (\langle R^2 \rangle_0 / \langle a_h \rangle_0^2)(1 - \Delta\xi\phi)$ the numerical value of $\Delta\xi$ is seen to be $3.45 - 3.26 \sim 0.2$. These numerical results can be compared to the Monte Carlo simulations of Guttman et al. Their simulations of lattice chains with nearest-neighbor interactions give 1.69 for the value of the characteristic ratio $C_n = \langle S^2 \rangle_\Theta / \langle S^2 \rangle_0$. Their interaction potential extends over a range of one lattice site. Using $1.69 = 1 + 3.26\phi$ gives $\rho \sim 1.44$ for the ratio of the radius of gyration to the hydrodynamic radius. This estimate, though approximate, agrees well with the Monte Carlo value of 1.40 found by Guttman et al.

VId. Scattering Functions and Pair Correlation Functions

Scattering and pair correlation functions can be numerically computed from the equations given in sections IVd and IVe. Unfortunately, eq 28 and 33 represent long calculations even for very large digital computers. In fact, the computation time for $S(u)$ is $\mathcal{O}(N^4)$, and the asymptotic "Debye" limit is attained only for very large values of N. It is well to reflect on what can be learned from such computations.

In Figure 11 are shown three wavevector regimes of a scattering function. The Gunier regime is defined by $q^2\langle S^2 \rangle < 1$ and contains information about particle size. The initial slope of the scattering curve is specified by the radius of gyration of the scatterers and thus yields no new theoretical information about dilute polymer solutions.

Greater motivation for computing scattering functions comes from region II, the Porod region. For our purposes the Porod region is defined by $q^2\langle S^2 \rangle > 1$ and $q^2\langle l^2 \rangle < 1$. The Porod region contains information about segment correlations within a polymer, and these can be roughly quantified by the exponent in the relation $S(q) \sim q^{-2\nu}$. Since this exponent, 2ν, varies from 2 in a Θ solvent to $^5/_3$ in a good solvent, an understanding of the temperature dependence of this exponent is a reasonable motivation for computing scattering functions. It is not clear, however, that a first-order perturbation treatment of this intermediate region is valid. Higher order terms may make significant contributions to $S(q)$ in the Porod region.

Calculation of exponents in the unperturbed reference state gives some insight into the graphical methods used here and so is a logical prelude to the Θ chain. Equation 31 relates the scattering exponent to elements of the matrix **G**. As previously noted, the physical interpretation of these elements is simple enough; $g_{ij} = \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle$. Noting this, it is possible to give a somewhat more general form of eq 31 by passing to an integral and letting $g_{ij} = |i - j|^p = x^p$ (the swollen Gaussian approximation). The result is

$$\nu = \frac{\int_0^N u x^p \rho(x) e^{-x^p u} \, \mathrm{d}x}{\int_0^N \rho(x) e^{-x^p u} \, \mathrm{d}x} \tag{65}$$

where $\rho(x)$ is a path length distribution function and gives the number of paths of length x on the polymer graph. For the linear chain $\rho(x) = N - x$ and

$$\nu \cong p^{-1}[1 - \bar{u}^{-1}\Gamma(2/p)/\Gamma(1/p)] \tag{66}$$

Here, $\Gamma(x)$ is the Γ function and $\bar{u} = Nu$, the variable normally used in the Debye function. In the large $\bar{u}$ limit the result $\nu = p^{-1}$ is obtained. the $p = 1$ case can also be obtained by direct differentiation of the Debye function.

The dependence of the scattering exponent on chain topology is illustrated by a specific example, the regular f-functional star. If this star has just n vertices per arm, then the path length distribution function is

$$\rho(x) = f(f-1)(2n + 1 - x)/2 \qquad x \geq n + 1$$

$$\rho(x) = f[n + (f-3)(x-1)/2] \qquad x \leq n + 1$$

Substitution of this into eq 63 gives $\nu = p^{-1}$ in the limit of large nu. It appears that a universal region still exists and that the scattering exponent is insensitive to chain topology.

The pair correlation function exponent, η, can be treated in the same manner. Within the region $1 < \gamma r^2 < N$, it has been shown that $p(r) \sim r^{-\eta}$. In this region $\eta = -\mathrm{d} \ln p(r)/\mathrm{d} \ln r$. Differentiation of eq 26 gives

$$\eta = \sum_{i<j} 2\gamma r^2 g_{ij}^{-5/2} e^{-\gamma r^2/g_{ij}} \Big/ \sum_{i<j} g_{ij}^{-3/2} e^{-\gamma r^2/g_{ij}} \tag{67}$$

Passing to an integral gives a pair of equations that relates the three exponents discussed here

$$\eta = 3 - 2\nu$$
$$p = 1/\nu \tag{68}$$

A few familiar examples, first derived by Edwards,[26] are the Θ chain, $p = \nu = \eta = 1$, the good solvent chain, $p = {}^6/_5$, $\nu = {}^5/_6$, and $\eta = {}^4/_3$, and the rigid rod, $p = 2$, $\nu = {}^1/_2$, and $\eta = 2$.

Numerical results for scattering functions are shown in Figures 11 and 12. Computations were carried out for as large a value of N as possible, in order to increase the Porod region, $N^{-1} < u < {}^1/_6$. In Figure 12 it is seen that the initial slope of the perturbed scattering function is greater ($z = 0.2$), indicating a larger radius of gyration, as expected.

Figure 12 is a plot of the first-order scattering exponent vs. u. The calculation of ν was exact to first order; the values were obtained by analytically differentiating eq 32 and numerically evaluating the resultant sum. It is seen that in the Porod region the perturbed chain exponent is smaller than the unperturbed chain exponent. Even on a smaller length scale (large u) there seems to be no

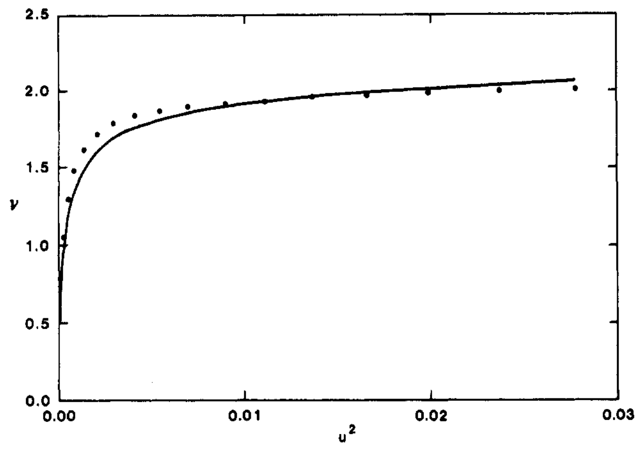


Figure 12. Scattering exponent for the unperturbed (curve) and perturbed chain. As expected, in the intermediate wavevector regime the exponent for the perturbed chain is somewhat smaller than the unperturbed chain.

tendency for the perturbed exponent to approach that of the ideal chain. This is in contradiction to the kind of behavior that might be expected for the blob model[27] but is in qualitative agreement with experiment. It is hoped that it will be possible to develop an analytical first-order expression for the scattering exponent in the large molecular weight limit. This should provide a useful basis for comparison with experimental results.

VIe. Results for the Second Virial Coefficient

The first-order expression for the second virial coefficient, $A_2 = N_A\beta/2m_S^2$, was shown to be model independent in section IVf. This can be explicitly shown by substituting the determinant of the single-contact matrix, $|\mathbf{V}_i(\alpha_1, k_1 - k_2)| = \alpha_1\epsilon$ into eq 42b with $p = 1$ and applying either eq 16 or eq 17.

Calculation of the second-order term ($p = 2$) proceeds from eq 49 and 42b. In this connection it is convenient to introduce the variable $\mu = \Delta(\alpha_1^{-1} + \alpha_2^{-1})$ and to define $B_1(\mu) = a_2(\alpha_1,\alpha_2)/(\gamma/\pi)^{3/2}N^{5/2}$. Letting $i = |k_1 - l_1|$ and $j = |k_2 - l_2|$ gives

$$B_1(\mu) = 2N^{-5/2}\left[\sum_{i=1}^{N-1}\sum_{j=1}^{N-1}\frac{(N-i)(N-j)}{(i+j+\mu)^{3/2}} + \sum_{i=1}^{N-1}\frac{N(N-i)}{(i+\mu)^{3/2}}\right] \cong (32/15)(7-4(2^{1/2})) - 3\zeta(3/2)\mu/N^{1/2} \quad (69)$$

$B_1(0)$ was evaluated by converting eq 69 to an integral; the result $B_1(0) = (32/15)(7 - 4(2^{1/2})) \cong 2.865$ represents the δ-function limit and is already familiar from the work of Zimm.[22] The coefficient $3\zeta(3/2) \cong 7.84$.

Numerical results for $B_1(\mu,N)$ are in Figure 13. Fitting these data to polynomials in $1/N^{1/2}$ gives $B_1(\mu,N) = 2.865 - 7.84\mu/N^{1/2} + ...$, in good agreement with analytical results. Use of eq 17 gives the second-order expression for A_2. In the large-N limit

$$A_2 = (\beta N_A/2m_S^2)[1 - 7.87\phi - 2.865z] \quad (70)$$

where we have neglected terms of order $1/N^{1/2}$ in 2.865. It is seen that even to second order the second virial coefficient vanishes at the Θ temperature in the large molecular weight limit. This is in agreement with the Monte Carlo computations of Baumgartner. More interesting is the very small β behavior of A_2. It is rather a surprise that the near-Θ behavior of A_2 is not given by the first-order term alone but includes a term of order ϕ from the second-order calculation. Clearly, the molecular weight independence of A_2 is preserved in this very near-Θ regime, but once again it is seen that the quantity that is measured is not β.

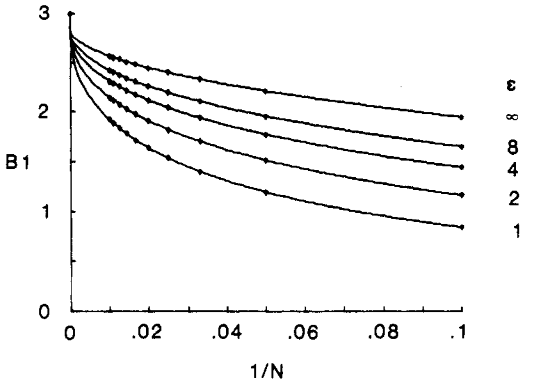


Figure 13. Numerical results for the second virial coefficient. Coefficients of the polynomial fits appear in Table III. For all values of Δ the curves extrapolated to 2.865.

Table III
Numerical Data for the Second Virial Coefficient

μ	a_0	a_1	
0.5	2.86549	−11.3711	4.2242
1	2.86543	−8.1476	5.2249
2	2.86541	−5.9877	6.1300
4	2.86537	−4.6261	6.8136
8	2.86543	−3.8324	7.2776
16	2.86538	−3.3919	7.5072
∞	2.86542	−2.9227	~7.79[a]

[a] Based on numerical extrapolation (exact value is 7.84, indicating a 0.6% error).

VII. Generalization to Arbitrary Interaction Potentials

It may seem that the conclusions drawn here are dependent upon the particular form of the cluster functions chosen and contain no general validity. That this is not the case is indicated by the following (a derivation of these results will be given in a forthcoming paper). Let

$$\alpha_R^2 - 1 = \frac{4}{3}N^{1/2}\chi_0 - \frac{5\pi}{3}\zeta(3/2)\chi_2 \quad (71)$$

where χ_0 and χ_2 are dimensionless moments of the cluster function $\chi(r)$

$$\chi_0 = (\gamma/\pi)^{3/2}\int \chi(r)\,\mathrm{d}^3r \quad (72a)$$

$$\chi_2 = (\gamma/\pi)^{5/2}\int r^2\chi(r)\,\mathrm{d}^3r \quad (72b)$$

Substitution of either eq 5b or eq 7b (let $\zeta = 1$) into these equations retrieves the results of section VIa. Thus we conjecture that the parameter $\phi = (-4\pi/3)\chi_2$ as long as the interaction potential is reasonably short ranged. In this light the theory of Fixman is a zeroth moment theory.

It is possible to derive in a general way some of the conclusions reached in this paper. Introduce a scaled cluster function $\epsilon^{3/2}\chi(\epsilon^{1/2}r)$, where the squared width of the interaction $\delta r^2 \sim 1/\epsilon$. By construction, the zeroth moment of the cluster function is independent of ϵ.

$$\chi_0 \sim \epsilon^{3/2}\int \chi(\epsilon^{1/2}r)\,\mathrm{d}^3r = \int \chi(s)\,\mathrm{d}^3s$$

The second moment, however, scales like $1/\epsilon = \Delta$.

$$\chi_2 \sim \epsilon^{5/2}\int r^2\chi(\epsilon^{1/2}r)\,\mathrm{d}^3r = \frac{1}{\epsilon}\int s^2\chi(s)\,\mathrm{d}^3s$$

These general scaling properties are in agreement with the results obtained explicitly for our potentials.

From eq 60 it is seen that Θ-state dimensions are given by $\langle R^2\rangle_\Theta = N\langle l^2\rangle(1 + 5\zeta(3/2)/3\chi_2)$, where χ_2 is to be evaluated at the Θ temperature. For a purely repulsive potential all the moments vanish when the zeroth moment vanishes; for a repulsive–attractive potential these moments will not simultaneously vanish. In fact, the second moment will always be negative when the zeroth moment vanishes: the Θ chain is always swollen relative to its unperturbed reference state.

VIII. Conclusions

It is seen that purely repulsive potentials give a description of the Θ regime that is quantitatively similar to δ-function theory, except for certain correction terms of order $z/N^{1/2}$. Repulsive–attractive potentials give Θ behavior that is inconsistent with the Gaussian chain but that seems to be consistent with Monte Carlo results.

A few remarks are in order concerning the application of this method to topologically complex polymers, e.g., branched polymers. It is likely that the swelling of the Θ chain (relative to the unperturbed state) is dependent on polymer topology. In fact it might be expected that this swelling increases with the extent of branching. This would increase calculated values of Zimm–Stockmayer contraction factors. Let the radius of gyration for the branched polymer be $\langle S^2\rangle_\Theta{}^b = \langle S^2\rangle_0{}^b/(1 + \xi\phi)$. The contraction in dimensions at the Θ point is thus

$$\hat{g} \equiv \frac{\langle S^2\rangle_\Theta{}^b}{\langle S^2\rangle_\Theta} = g(1 + (\xi - 3.27)\phi)$$

where g is the contraction factor in the unperturbed state. It has been implicitly assumed by many investigators that $\hat{g} = g$. This may be a good approximation if $g \sim 1$ but is known to be without merit for polymers with many circuits. An extreme example of the inapplicability of the unperturbed calculation occurs for networks—the phenomenon of network collapse.[28] Network collapse is characterized by $g \sim N^{-1}$, whereas physical considerations dictate that for real networks $g \sim N^{-1/3}$. The inclusion of an excluded volume potential is critical for networks.

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Excluded Volume Effects in the Θ Regime. 2. Extension of Perturbation Results to Arbitrary Potentials[†]

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ABSTRACT: The excluded volume effects treated in paper 1 are generalized to arbitrary interaction potentials by a moment expansion of the cluster function. In the first part of the paper the end-to-end vector is treated by a bond renormalization formulation that is shown to be essentially equivalent to first-order perturbation theory. These results show that perturbation theory is incorrect in one and two dimensions since no reference state is found in which the perturbation is small. The moment expansion method is shown to be qualitatively similar to three-body interaction theories but differs in its dependence on the excluded volume potential width. The formulation is extended to the second virial coefficient, and a relation is found between the dimensionless interaction width parameter introduced in paper 1 and the second moment of the cluster function. Finally, the results of the previous paper are presented as a three-parameter theory of Θ chains.

I. Introduction

In paper 1 a specific form of the excluded volume potential was used to obtain first-order perturbation theory results for polymers in the Θ regime. This approach to the excluded volume problem gave some interesting results for expansion factors, scattering functions, and second virial coefficients but lacked generality. In the present paper these results are generalized, via a moment expansion of the cluster function, to arbitrary well-localized interaction potentials.

In section II a heuristic bond renormalization approach is taken in the calculation of the first-order expansion

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