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Renormalization group calculation of polymer properties in dilute solution

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Abstract. The Riedel-Wegner phenomenological approach to crossover phenomena is used to calculate the temperature and molecular-weight dependence of the second virial coefficient and expansion factor of polymers in dilute solution both near the Θ temperature and at higher temperatures. The specific heat maximum of a single polymer chain in solution is predicted to diverge logarithmically as its molecular weight goes to infinity. The Θ temperature is assumed analogous to a tricritical point. It is shown that for problems involving the interaction of m polymers, one must work with an $(m \times n)$ -component field theory, and then take the limit $n \rightarrow 0$.

1. Introduction

The properties of polymer chains in dilute solution have been extensively studied both experimentally and theoretically for many years. A recent survey is given in the book by Yamakawa (1971). Among the main topics of interest are α , the expansion factor of an isolated polymer and A_2 , the second coefficient in the virial expansion of the osmotic pressure, and in this paper we shall use renormalization group methods to calculate both of them. The Θ temperature, the temperature at which the polymer chains behave ideally (and at which A_2 therefore vanishes), is analogous to a tricritical point (de Gennes 1975), and the exponents describing the behaviour at the Θ temperature have the mean-field or random-walk values. At higher temperatures in the good-solvent region a critical or non-trivial fixed point becomes dominant with a consequent change in the values of the exponents. Both α and A_2 can be written in terms of crossover functions which interpolate between the Θ point and good-solvent regions.

The polymer solution will be taken to be monodisperse, i.e. each polymer has the same molecular weight, M , corresponding to N flexible units. The molecular weight dependence of $\langle S^2 \rangle$, the mean-square size of a single polymer chain is

$$\langle S^2 \rangle \sim M^{2\nu}, \quad \text{as } M \rightarrow \infty. \quad (1.1)$$

At temperatures above the Θ temperature, in the good-solvent region, the exponent $\nu = \frac{3}{5}$. As the temperature of the solution is reduced, $\langle S^2 \rangle$ decreases and at the Θ temperature, where the short-range repulsive (excluded-volume) interaction between the monomers is exactly balanced by longer-range attractive forces, the exponent ν is

$\frac{1}{2}$ —the random-walk value (Cotton *et al* 1974). The expansion factor, α , is defined by

$$\alpha^2 = \frac{\langle S^2 \rangle}{\langle S^2 \rangle_{\Theta}}, \quad (1.2)$$

where $\langle S^2 \rangle_{\Theta}$ is the mean-square size at the Θ temperature. For dilute solutions, α^2 may be expressed as a universal function of the excluded-volume parameter, $z \sim uM^{1/2}$, where u is the effective interaction between the monomers, which varies with temperature, T , as $(1 - \Theta/T)$ (Yamakawa 1971); i.e.

$$\alpha^2 = W(z). \quad (1.3)$$

At the Θ temperature, $z = 0$ and $W(0) = 1$, but for large z , in the good-solvent region, $W(z) \sim z^{2/5}$, so as to recover (1.1).

The osmotic pressure, Π , of a dilute polymer solution has a virial expansion in the concentration ρ (molecules/unit volume) of the polymer:

$$\Pi = kT(\rho + A_2\rho^2 + A_3\rho^3 + \dots), \quad (1.4)$$

where the first term is just the 'ideal gas' term. A_2 would be expected to be proportional to the volume from which one molecule is excluded by the presence of another, i.e. $A_2 \sim \langle S^2 \rangle^{3/2}$. In the good-solvent region this is found to be the case and so

$$A_2 \sim M^{9/5}, \quad \text{as } M \rightarrow \infty. \quad (1.5)$$

However, as the temperature is lowered, A_2 decreases and eventually vanishes at the Θ temperature. A_2 may in fact be written as a universal function of z :

$$A_2 = \langle S^2 \rangle_{\Theta}^{3/2} f(z) = M^{3/2} X(z). \quad (1.6)$$

Near the Θ temperature $X(z) \sim z$, so $A_2 \sim (1 - \Theta/T)M^2$. For large z , $X(z) \sim z^{3/5}$ to be consistent with (1.5).

The fact that both $\langle S^2 \rangle$ and A_2 can be expressed in terms of two parameters ($\langle S^2 \rangle_{\Theta}$ and z) indicates that the details of the structure of polymer molecules are unimportant in dilute solutions. In concentrated solutions and solids, however, this is not the case and features, such as side chains, chemical nature, etc (short-range interferences), of the chains are important.

The layout of this paper is as follows. In § 2 we indicate how the $n \rightarrow 0$ limit of an n -component field theory can be used to model a polymer chain (de Gennes 1972), and how quantities familiar from magnetic systems are related to polymers (des Cloizeaux 1975). In particular, it is shown that correlation functions of the fields are generating functions of polymer properties, and that the field-theoretic Hamiltonian describes a random walk for $u = 0$ and a self-avoiding walk for $u \rightarrow \infty$. The generating functions are written in a form reminiscent of magnetic critical phenomena and the resulting exponents are shown to have the mean-field values for the random-walk case ($u = 0$). We show that the generalization of the original Hamiltonian of de Gennes (1972) to systems of m polymer chains requires the use of an $(m \times n)$ -component field. In § 3 the renormalization group approach is discussed. The functions $W(z)$ and $X(z)$ are interpreted as crossover functions, whose behaviours are governed by a tricritical fixed point in the Θ temperature region and a critical fixed point in the good-solvent region. The renormalization group differential recursion relations to order ϵ (where $\epsilon = 4 - d$ and d is the dimensionality of space) are written in terms of scaling fields, and, by

inserting the experimental values of the exponents into them we obtain the phenomenological crossover equations proposed by Riedel and Wegner (1974). In § 4 the Riedel-Wegner method for obtaining thermodynamic quantities from the phenomenological equations is closely followed to calculate A_2 . Unknown constants appearing in the calculation are determined by matching the result in the Θ temperature (small- z) region to the results of perturbation theory calculations in z . The calculated values for A_2 in the good-solvent (large- z) region are then found to agree well with experiment. By similar procedures α^2 is obtained in § 5. The same values of the constants determined in § 4 are used, and it is found that the first-order perturbation theory result for α^2 in z is not correctly obtained. The theory also does not fit the data particularly well in the high-temperature region. A discussion of the many possible reasons for these discrepancies is given. In § 6 the specific heat of a single polymer near the Θ temperature is calculated by determining the equation of the critical line from the renormalization group equations. The specific heat is found to diverge as $\ln(1 - \Theta/T)$ in the infinite-molecular-weight limit which is in reasonable agreement with some numerical results of Rapaport (1974). Finally, in § 7, we review the model employed for treating dilute polymer solutions and the calculations we have presented. In particular, the phenomenological nature of the Riedel-Wegner equations is highlighted, and the difficulties encountered when trying to compare results obtained from them with experiment are noted. The role of marginal operators such as the ' ϕ^6 ' term in three dimensions is also discussed. In an appendix, we calculate $W(z)$ and $X(z)$ to order ϵ using the results of Nelson and Rudnick (1975). This latter approach seems to have greater possibilities of systematic extension than that of Riedel and Wegner, although in low order its asymptotic predictions are in considerable error.

2. $n=0$ field theory and its magnetic analogy

De Gennes (1972) has shown that the limit $n \rightarrow 0$ of an n -component field theory is formally equivalent to a self-interacting chain, and hence to a single polymer in solution. Des Cloizeaux (1975) has extended this argument to polymer solutions at intermediate concentrations, and shown how the language used to describe magnetic systems may also be useful for polymers. Following these authors we construct a lattice model of the polymer solution, use the $n \rightarrow 0$ limit and work with functions whose properties in the magnetic analogue are well known.

The lattice-model field-theoretic effective Hamiltonian, H , is the $O(n)$ symmetric form:

$$H = -\beta \mathcal{H} = J \sum_{\langle ij \rangle} \sum_{p=1}^n \phi_i^p \phi_j^p - (\lambda/2) \sum_i \sum_{p=1}^n \phi_i^p \phi_i^p - (u/4!) \sum_i \left(\sum_{p=1}^n (\phi_i^p \phi_i^p) \right)^2 + \sum_i \sum_{p=1}^n \phi_i^p h_i^p + O(|\phi_i|^6), \quad (2.1)$$

where there is a field variable, $\phi_i = (\phi_i^1, \dots, \phi_i^n)$ at each lattice site, i ; $\beta = (kT)^{-1}$; $\langle ij \rangle$ represents all pairs of nearest-neighbour lattice sites; J is the (dimensionless) 'exchange' interaction in magnetic language; and h_i is an applied field.

The calculations of polymer properties are performed with the n -component Hamiltonian and the limit $n \rightarrow 0$ is taken, usually, as the final step in the calculation. In this limit J acts as a generating function parameter; $u \sim (1 - \Theta/T)$ describes the

interactions between monomers, and the properties of the polymer are given by the coefficients of the Taylor series expansion of the correlation functions in J .

As an example, consider the correlation function

$$\chi(J, u) = \sum_j \langle \phi_i^1 \phi_j^1 \rangle_c, \quad (2.2)$$

where subscript c denotes the cumulant or connected part. The Taylor expansion of

$$\chi(J, u) = \sum_{N=0} C_N(u) J^N \quad (2.3)$$

is the generating function of the partition function, $C_N(u)$, of a polymer of N flexible units (de Gennes 1972, Burch and Moore 1976). When $u = 0$, no interactions are present between the monomers and the chain is free to assume all the configurations of a random walk. Thus $C_N(0)$ is just q^N , the number of random walks of N steps on a lattice of coordination number q . The value of λ in the Hamiltonian is determined by setting $C_0(0) = 1$, which gives $\lambda = 1$. Thus

$$\chi(J, 0) = (1 - qJ)^{-1}. \quad (2.4)$$

Even for non-zero u , we expect from the magnetic analogue that the generating function $\chi(J, u)$ will be of the form

$$\chi(J, u) \sim (1 - J/J_c(u))^{-\gamma}, \quad \text{as } J \rightarrow J_c(u), \quad (2.5)$$

which implies (McKenzie and Moore 1971)

$$C_N(u) \sim N^{\gamma-1} (J_c(u))^{-N}, \quad \text{as } N \rightarrow \infty, \quad (2.6)$$

where $J_c(u)$ is the singularity of $\chi(J, u)$ nearest the origin. For the random walk $J_c(0) = q^{-1}$ and $\gamma = 1$.

As $u \rightarrow \infty$, $\lambda = -un/6$, the chain configurations become restricted to those of a self-avoiding walk. In this limit the Hamiltonian becomes

$$H = J \sum_{\langle ij \rangle} \sum_{p=1}^n \phi_i^p \phi_j^p + \sum_i \sum_{p=1}^n \phi_i^p h_i^p, \quad (2.7)$$

with the constraint at each lattice site, i ,

$$\sum_{p=1}^n \phi_i^p \phi_i^p = n. \quad (2.8)$$

It is found by numerical methods that $\gamma = \frac{7}{6}$ for the self-avoiding walk in three dimensions (Martin *et al* 1967).

The calculation of the second virial coefficient involves the interaction of two polymer chains. Each chain must be given its own generating function parameter, and the field theory must be generalized to contain $2n$ components. For two polymers labelled α and β , the Hamiltonian becomes

$$H = J_\alpha \sum_{\langle ij \rangle} \sum_{p=1}^n \phi_i^p \phi_j^p + J_\beta \sum_{\langle ij \rangle} \sum_{p=n+1}^{2n} \phi_i^p \phi_j^p \\ - (\lambda/2) \sum_i \sum_{p=1}^{2n} \phi_i^p \phi_i^p - (u/4!) \sum_i \left(\sum_{p=1}^{2n} (\phi_i^p \phi_i^p) \right)^2 + \sum_i \sum_{p=1}^{2n} \phi_i^p h_i^p. \quad (2.9)$$

In general, for systems of m polymer chains, the Hamiltonian must contain m

generating function parameters and be expressed in terms of an $m \times n$ -component field (Burch and Moore 1976).

The following correlation functions may be obtained from a study of the two-polymer Hamiltonian (2.9):

$$\chi(J_\alpha, u) = \sum_j \langle \phi_i^1 \phi_j^1 \rangle_c \quad (2.10)$$

$$\chi(J_\beta, u) = \sum_j \langle \phi_i^{n+1} \phi_j^{n+1} \rangle_c \quad (2.11)$$

$$G_4(J_\alpha, J_\beta, u) = \frac{1}{2} \sum_{jkl} \langle \phi_i^1 \phi_j^1 \phi_k^{n+1} \phi_l^{n+1} \rangle_c \quad (2.12)$$

$$G_4(J_\alpha, u) = \frac{1}{6} \sum_{jkl} \langle \phi_i^1 \phi_j^1 \phi_k^1 \phi_l^1 \rangle_c \quad (2.13)$$

$$G_4(J_\beta, u) = \frac{1}{6} \sum_{jkl} \langle \phi_i^{n+1} \phi_j^{n+1} \phi_k^{n+1} \phi_l^{n+1} \rangle_c \quad (2.14)$$

$\chi(J_\alpha, u)$ is independent of J_β in the limit $n \rightarrow 0$ and vice versa. Thus the generating functions $\chi(J_\beta, u)$, $\delta = \alpha$ or β , are identical to $\chi(J, u)$ calculated from the one-polymer Hamiltonian (2.1).

The three forms of G_4 are also useful generating functions:

$$G_4(J_\alpha, J_\beta, u) = - \sum_{MN} C_{M,N}(u) J_\alpha^M J_\beta^N \quad (2.15)$$

$$G_4(J_\beta, u) = - \sum_N g_N(u) J_\beta^N \quad (2.16)$$

$C_{M,N}(u)$ and $g_N(u)$ are related by

$$g_N(u) = \sum_{I=0}^N C_{I,N-I}(u). \quad (2.17)$$

We call $C_{M,N}(u)$ the 'two-polymer interaction' function. It is related to the second virial coefficient, A_2 , of a monodisperse dilute polymer solution by

$$A_2 = C_{N,N}(u) / C_N^2(u) \quad (2.18)$$

(McKenzie and Domb 1967). If the correct dependence of $C_{I,N-I}(u)$ on I and $N-I$ is known, then $C_{M,N}(u)$ can be deduced from $g_{M+N}(u)$. Field theories of two interacting polymers which do not contain $2n$ components and do not compensate for this deficiency by the use of the $(M+N)$ th term of the generating function $G_4(J_\beta, u)$, produce results with the correct exponent dependence, but cannot be relied upon to give correct numerical coefficients (Burch and Moore 1976).

$C_N(u)$ and $C_{M,N}(u)$ can be calculated from their generating functions by the inverse Laplace transforms:

$$C_N(u) = \frac{1}{2\pi i} \oint \frac{\chi(J_\beta, u)}{J_\beta^{N+1}} dJ_\beta \quad (2.19)$$

$$C_{M,N}(u) = \frac{1}{(2\pi i)^2} \oint \oint \frac{G_4(J_\alpha, J_\beta, u)}{J_\alpha^{M+1} J_\beta^{N+1}} dJ_\alpha dJ_\beta \quad (2.20)$$

To find α^2 , one introduces the second moment of the pair correlation function, $\Gamma_2(J_\delta, u)$, defined by

$$\Gamma_2(J_\delta, u) = \sum_j R_{ij}^2 \langle \phi_i^1 \phi_j^1 \rangle_c \quad (2.21)$$

where $R_{ij} = R_i - R_j$ is the separation vector of sites i and j . The Taylor series expansion is

$$\Gamma_2(J_\delta, u) = \sum_{N=0} a_N(u) J_\delta^N, \quad (2.22)$$

where

$$a_N(u) = \sum R_N^2(u), \quad (2.23)$$

$R_N^2(u)$ is the square size of a particular configuration of N flexible units, and the sum is over all such configurations. The mean-square size of a polymer of N flexible units is given by

$$\langle R_N^2(u) \rangle = a_N(u) / C_N(u). \quad (2.24)$$

As $J_\delta \rightarrow J_c(u)$,

$$\Gamma_2(J_\delta, u) \sim (1 - J_\delta / J_c(u))^{-(2\nu+\gamma)} \quad (2.25)$$

where $\nu = \frac{1}{2}$ for the random walk and $\nu = \frac{3}{5}$ for the self-avoiding walk in three dimensions (Domb 1969). For large N it follows from (2.5), (2.24) and (2.25) that

$$\langle R_N^2(u) \rangle \sim N^{2\nu}. \quad (2.26)$$

It should be noted that, in the limit $n \rightarrow 0$, the singularity nearest the origin of all the generating functions is always $J_c(u)$.

3. The renormalization group approach

The functions $W(z)$ and $X(z)$ defined by (1.3) and (1.6) for the square of the expansion factor, α^2 , and the second virial coefficient, A_2 , are typical of situations in which there is a crossover between the Gaussian fixed point and a non-trivial fixed point. Their argument, the excluded-volume parameter, has the general form $z \sim uM^{\phi_t}$ where the crossover exponent ϕ_t is $\epsilon/2$ for the Gaussian fixed point (Nelson and Rudnick 1975), which reduces to the value quoted (i.e. $\frac{1}{2}$) for $d = 3$. Since $u = 0$ at the Θ temperature, a tricritical or Gaussian fixed point (de Gennes 1975) will govern the behaviour of the crossover functions $W(z)$ and $X(z)$ in the poor-solvent region, that is for small z ; while the good-solvent, or large- z , region will be dominated by a non-trivial or critical fixed point.

The two-polymer Hamiltonian (2.9) may be written in the continuous limit as

$$H = \int dx \left[-\frac{1}{2} \sum_{p=1}^{2n} \nabla \phi^p(\mathbf{x}) \cdot \nabla \phi^p(\mathbf{x}) - (r_\alpha/2) \sum_{p=1}^n \phi^p(\mathbf{x}) \phi^p(\mathbf{x}) - (r_\beta/2) \sum_{p=n+1}^{2n} \phi^p(\mathbf{x}) \phi^p(\mathbf{x}) - (u/4!) \left(\sum_{p=1}^{2n} (\phi^p(\mathbf{x}) \phi^p(\mathbf{x})) \right)^2 + \sum_{p=1}^{2n} \phi^p(\mathbf{x}) h^p(\mathbf{x}) \right], \quad (3.1)$$

where $r_\delta = (1 - J_\delta/J_c(0))$. (3.1) is of the form of the anisotropic n -vector model investigated by Fisher and Pfeuty (1972). However, the renormalization group differential equations for r_α and r_β decouple in the $n \rightarrow 0$ limit because the terms in the equation for, say, r_α which involve r_β are always multiplied by the factor n . For small r_δ the equations for r_δ and u describing how they change under a renormalization group scale change of e^l are

$$\frac{dr_\delta(l)}{dl} = 2r_\delta(l) + Au(l) - Au(l)r_\delta(l) + O(u^2(l)) \quad (3.2)$$

$$\frac{du(l)}{dl} = \epsilon u(l) - Bu^2(l) + O(u^3(l)), \quad (3.3)$$

where u has been supposed to be of order ϵ , and $A = \pi^{-2}$, $B = 4\pi^{-2}$ (Nelson and Rudnick 1975). Linearization of these equations about the Gaussian fixed point $r_\delta^* = 0$, $u^* = 0$ yields eigenvalues 2 and ϵ . Hence the crossover exponent $\phi_t = \epsilon/2$ (Fisher 1974).

These equations may be written in terms of the usual scaling fields (Wegner 1972) $\mu_{1\delta}(l) = r_\delta(l) + Au(l)/(2 - \epsilon)$ and $\mu_2(l) = ku(l)$, where k is a constant:

$$d\mu_{1\delta}(l)/dl = 2\mu_{1\delta}(l) - (A/k)\mu_{1\delta}(l)\mu_2(l) + (A^2 - AB)/[(2 - \epsilon)k^2]\mu_2^2(l) \quad (3.4)$$

$$d\mu_2(l)/dl = \epsilon\mu_2(l) - (B/k)\mu_2^2(l). \quad (3.5)$$

Since (3.2) is only correct to order ϵ , we shall neglect the term in $\mu_2^2(l)$ in (3.4), although for $d = 3$ ($\epsilon = 1$), there is little justification in assuming this term is small. Without this term (3.4) and (3.5) are of identical form to the phenomenological equations proposed by Riedel and Wegner (1974) to describe crossover phenomena. For three-dimensional systems $\epsilon = 1$, and we shall choose $B/k = 1$, so that the critical fixed point is at $(\mu_{1\delta}^*, \mu_2^*) = (0, 1)$. By linearizing (3.4) about the critical fixed point, the correlation length exponent, ν_c , associated with this fixed point is given by $(2 - A/k)^{-1}$. However, we shall follow the phenomenological approach advocated by Riedel and Wegner (1974) and 'adjust' A to obtain the experimental value of $\frac{3}{5}$ for ν_c . This is equivalent to setting $A/k = \frac{1}{3}$. Linearization of (3.4) about the Gaussian fixed point $(0, 0)$ gives the mean-field value $\nu_t = \frac{1}{2}$.

Thus the phenomenological equations we shall use to calculate the crossover functions $W(z)$ and $X(z)$ are

$$d\mu_{1\delta}(l)/dl = 2\mu_{1\delta}(l) - \frac{1}{3}\mu_{1\delta}(l)\mu_2(l) \quad (3.6)$$

$$d\mu_2(l)/dl = \mu_2(l)(1 - \mu_2(l)), \quad (3.7)$$

where

$$\mu_{1\delta}(0) = (J_c(u)/J_c(0))(1 - J_\delta/J_c(u)), \quad (3.8)$$

and

$$J_c(u) = J_c(0)[1 + \frac{1}{3}\mu_2(0) + O(\mu_2^2(0))]. \quad (3.9)$$

Equations (3.8) and (3.9) follow from the definition of $\mu_{1\delta}(0)$ in terms of r_δ and u . $J_c(u)$ is the value of J_δ for which $\mu_{1\delta} = 0$.

4. The second virial coefficient

4.1. The partition function, $C_N(u)$

To obtain $C_N(u)$ we must calculate the generating function χ . This is a homogeneous function of the scaling fields μ_{1s} and μ_2 such that

$$\chi(\mu_{1s}, \mu_2) = e^{2l} \chi(\mu_{1s}(l), \mu_2(l)), \quad (4.1)$$

where the small exponent η is neglected as it is of order ϵ^2 , in which case $\gamma = 2\nu$, when (4.1) follows. μ_{1s} and μ_2 are the starting ($l=0$) values of $\mu_{1s}(l)$ and $\mu_2(l)$.

Equation (4.1) together with (3.6) and (3.7) allow the evaluation of the generating function χ provided it is known at a 'boundary' outside the critical region where it can be computed by mean-field or some other approximate procedure. We shall take the boundary at the value of $l = \hat{l}$ for which $\mu_{1s}(\hat{l}) = 1$, and assume

$$\chi(1, \mu_2(\hat{l})) = \bar{\chi} \quad (4.2)$$

where $\bar{\chi}$ is a constant independent of $\mu_2(\hat{l})$. In a more refined approximation one might replace the right-hand side of (4.2) by a power series in $\mu_2(\hat{l})$. Then, at the boundary

$$\chi(\mu_{1s}, \mu_2) = e^{2\hat{l}} \bar{\chi}. \quad (4.3)$$

\hat{l} may be determined in terms of μ_{1s} and μ_2 by solving (3.6) at $l = \hat{l}$, which reduces to solving either

$$f_t(C_{\mu_{1s}}) = (1 + C_{\mu_{1s}}^{-1/2} f(C_{\mu_{1s}}))^{1/6} \quad (4.4)$$

with

$$f_t(C_{\mu_{1s}}) = \mu_{1s}^{1/2} (1 - \mu_2)^{-1/6} e^{\hat{l}}, \quad (4.5)$$

or

$$f_c(C_{\mu_{1s}}) = (1 + C_{\mu_{1s}}^{3/5} f_c(C_{\mu_{1s}}))^{-1/5} \quad (4.6)$$

with

$$f_c(C_{\mu_{1s}}) = \mu_{1s}^{-3/5} \mu_2^{1/5} e^{-\hat{l}}, \quad (4.7)$$

where

$$C_{\mu_{1s}} = \mu_{1s}(l)(1 - \mu_2(l))^{5/3} \mu_2(l)^{-2} \quad (4.8)$$

is a renormalization group invariant, i.e. $dC_{\mu_{1s}}/dl = 0$.

Near the Gaussian fixed point, $C_{\mu_{1s}} \gg 1$. In this limit (4.4) can be expanded in powers of $C_{\mu_{1s}}^{-1/2}$. Substitution in (4.5) then gives

$$e^{\hat{l}} = \mu_{1s}^{-1/2} (1 - \mu_2)^{1/6} (1 + \frac{1}{6} C_{\mu_{1s}}^{-1/2} + O(C_{\mu_{1s}}^{-1})). \quad (4.9)$$

Similarly, near the critical fixed point $C_{\mu_{1s}} \ll 1$, and (4.6) and (4.7) produce

$$e^{\hat{l}} = \mu_{1s}^{-3/5} \mu_2^{1/5} (1 + \frac{1}{5} C_{\mu_{1s}}^{3/5} + O(C_{\mu_{1s}}^{6/5})). \quad (4.10)$$

Inserting (4.9) and (4.3) and performing the inverse Laplace transform (2.19), we find in the poor-solvent region (that is, near the Θ temperature)

$$C_N(u) = \left(\frac{J_c(0)}{J_c(u)} \right) \frac{\bar{\chi}(1 - \mu_2)^{1/3}}{(J_c(u))^N \Gamma(1)} \left(1 + \frac{1}{3} \frac{\Gamma(1)}{\Gamma(1.5)} X + O(X^2) \right) \quad (4.11)$$

where

$$X = (J_c(0)/J_c(u))(1 - \mu_2)^{-5/6} \mu_2 N^{1/2}. \quad (4.12)$$

Similarly in the good-solvent region, we obtain from (4.10), (4.3) and (2.19)

$$C_N(u) = \left(\frac{J_c(0)}{J_c(u)} \right)^{6/5} \frac{\tilde{\chi} \mu_2^{2/5} N^{1/5}}{(J_c(u))^N \Gamma(1.2)} \left(1 + \frac{2}{5} \frac{\Gamma(1.2)}{\Gamma(0.6)} X^{-6/5} + O(X^{-12/5}) \right). \quad (4.13)$$

The expression for $C_N(u)$ in (4.13) is of the form (2.6) but with $\gamma_c = \frac{6}{5}$ rather than the experimental value of $\frac{7}{6}$. The discrepancy arises because we have set $\eta = 0$ and so $\gamma_c = 2\nu_c$.

4.2. The two-polymer interaction function, $C_{N,N}(u)$

The calculation of $C_{N,N}(u)$ is similar to that for $C_N(u)$, but is complicated by the presence of the two scaling fields $\mu_{1\alpha}$ and $\mu_{1\beta}$. To clarify the situation we define new variables $P(l) = (\mu_{1\alpha}(l)\mu_{1\beta}(l))^{1/2}$ and $\Delta(l) = \mu_{1\alpha}(l) - \mu_{1\beta}(l)$, both of which satisfy the differential equation (3.6). G_4 is a homogeneous function of the variables $P(l)$, $\Delta(l)$ and $\mu_2(l)$, with

$$G_4(P, \Delta, \mu_2) = e^{7l} G_4(P(l), \Delta(l), \mu_2(l)), \quad (4.14)$$

when the small exponent η is neglected. (In general, G_4 diverges as $\xi^{(4+d-2\eta)}$, $\xi \rightarrow \infty$ when $J_\alpha = J_\beta$, where ξ = the 'coherence' length.)

We take the boundary at $l = \bar{l}$ given by $P(\bar{l}) = 1$, and assume that, at this boundary,

$$G_4(1, \Delta(\bar{l}), \mu_2(\bar{l})) = \bar{G}_4 \mu_2(\bar{l}), \quad (4.15)$$

where \bar{G}_4 is a constant independent of $\Delta(\bar{l})$ and $\mu_2(\bar{l})$. This boundary value for G_4 can be envisaged as being the leading term of a series in $\mu_2(\bar{l})$ and $\Delta(\bar{l})$. It is not easy to justify (4.15) except for the special case $\Delta = 0$, when J_α and J_β are small and equal, so $G_4(1, \Delta(\bar{l}), \mu_2(\bar{l}))$ becomes proportional to the 'bare' coupling constant in the Hamiltonian and hence to $\mu_2(\bar{l})$. At the boundary (4.14) and (4.15) give

$$G_4(P, \Delta, \mu_2) = e^{7\bar{l}} \bar{G}_4 \mu_2(\bar{l}). \quad (4.16)$$

In a similar fashion to the calculation of $C_N(u)$, the solutions of the differential equation (3.6) for $P(\bar{l})$ can be expressed near the Gaussian fixed point as

$$e^{\bar{l}} = P^{-1/2} (1 - \mu_2)^{1/6} [1 + \frac{1}{6} C_P^{-1/2} + O(C_P^{-1})], \quad (4.17)$$

with

$$C_P = P(l) (1 - \mu_2(l))^{5/3} \mu_2(l)^{-2}, \quad (4.18)$$

which is also a renormalization group invariant.

The value of $\mu_2(\bar{l})$ is obtainable from (4.18) for both large and small C_P . Near the Gaussian fixed point (at which $C_P \gg 1$) one finds

$$\mu_2(\bar{l}) = C_P^{-1/2} [1 - \frac{5}{6} C_P^{-1/2} + O(C_P^{-1})]. \quad (4.19)$$

Inserting (4.17) and (4.19) into (4.16) and performing the Laplace transform (2.20) we obtain, in the poor-solvent region;

$$C_{N,N}(u) = \left(\frac{J_c(0)}{J_c(u)} \right)^4 \frac{\bar{G}_4 \mu_2 (1 - \mu_2)^{1/3} N^2}{(J_c(u))^{2N} (\Gamma(2))^2} \left[1 + \frac{1}{3} \left(\frac{\Gamma(2)}{\Gamma(2.25)} \right)^2 X + O(X^2) \right]. \quad (4.20)$$

A similar treatment for the good-solvent region ($C_p \ll 1$) yields

$$C_{N,N}(u) = \left(\frac{J_c(0)}{J_c(u)} \right)^{21/10} \frac{\bar{G}_4 \mu_2^{7/5} N^{11/5}}{(J_c(u))^{2N} (\Gamma(2.1))^2} \left[1 + \frac{2}{5} \left(\frac{\Gamma(2.1)}{\Gamma(1.8)} \right)^2 X^{-6/5} + O(X^{-12/5}) \right]. \quad (4.21)$$

4.3 The second virial coefficient, A_2

A_2 for a monodisperse solution is calculated in the poor-solvent region by inserting (4.20) and (4.11) into (2.18). Thus near the Θ point

$$A_2 = \frac{\bar{G}_4}{\bar{\chi}^2} \left(\frac{J_c(0)}{J_c(u)} \right)^2 \mu_2 (1 - \mu_2)^{-1/3} N^2 [1 - 0.4926X + O(X^2)]. \quad (4.22)$$

In the good-solvent region, (4.21), (4.12) and (2.18) yield

$$A_2 = 0.7698 \frac{\bar{G}_4}{\bar{\chi}^2} \left(\frac{J_c(0)}{J_c(u)} \right)^{-3/10} \mu_2^{3/5} N^{9/5} [1 + 0.0117X^{-6/5} + O(X^{-12/5})]. \quad (4.23)$$

Equations (4.22) and (4.23) are not in the crossover form of (1.6), unless we replace $(1 - \mu_2)$ by 1 —even in the good-solvent region. We view the experimental evidence for (1.6) as a strong argument that $\mu_2 = ku \ll 1$, in which case $J_c(u) = J_c(0) + O(\mu_2)$. Near the Θ temperature, setting $B_2 = A_2 N_A / M^2$, where N_A is Avogadro's number, one has

$$B_2 M^{1/2} / z = D(1 - 2.865z + O(z^2)), \quad z < 0.1, \quad (4.24)$$

where D is a constant and $z = b\mu_2 N^{1/2}$. The constant, b , has been adjusted so that the coefficient of z in (4.24) is the value derived from perturbation theory (Yamakawa 1971, § 21a). Using this value of b ($= 0.1719$) in (4.23) produces, for the good-solvent region

$$B_2 M^{1/2} / z = 0.381 D z^{-2/5} [1 + 0.0014z^{-6/5} + O(z^{-12/5})], \quad z > 0.75. \quad (4.25)$$

Equations (4.24) and (4.25) are both asymptotic expansions. The sizes of the successive terms in (4.24) are such that it is only valid for $z < 0.1$. Inclusion of higher terms in (4.25) would only be justifiable when $z > 9$.

Figure 1 is a plot of $X(z)/z (= B_2 M^{1/2} / Dz)$ against z . Also shown is the experimental data for polystyrene in decalin (Berry 1966) and the internally consistent non-renormalization group calculations of Flory and Krigbaum (1950) and Orifino and Flory (1957), its modification by Stockmayer (1960), and of Kurata *et al* (1964), Yamakawa (1968) and Yamakawa and Tanaka (1967). (All of these theories are summarized by Yamakawa (1971).) The small discrepancy at large z is partly due to the crudeness of the boundary conditions (4.2) and (4.15), which are only the leading terms of series expansions. Notice also that improvements in the boundary conditions would alter the value of the constant b . Another possible source of the small discrepancy at large z is that the relation $u \sim (1 - \Theta/T)$, assumed by Berry (1966) in presenting his data may not be valid when T is not close to Θ (Yamakawa 1971, p 375).

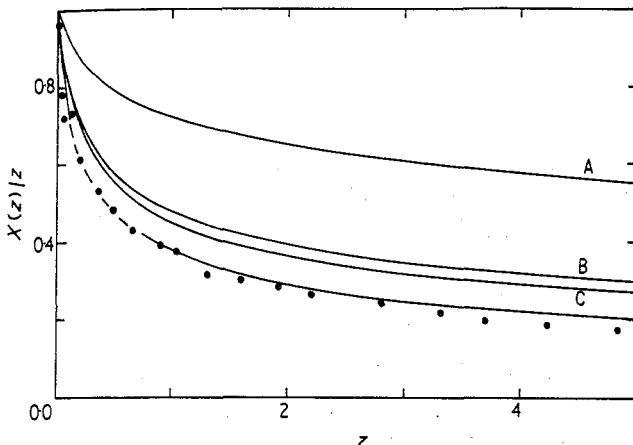


Figure 1. Plot of $X(z)/z$ against z . The data points are for polystyrene in decalin (Berry 1966). The broken curve is an interpolation of (4.23) and (4.24) for $0.1 < z < 0.75$. Also shown for comparison are the results of the theories of Flory and Krigbaum (1950) and Orifino and Flory (1957), curve A; its modification by Stockmayer (1960), curve B; and of Kurata *et al* (1964), Yamakawa (1968) and Yamakawa and Tanaka (1967), curve C.

5. The expansion factor

5.1. The mean-square size, $\langle R_N^2(u) \rangle$

The correlation function Γ_2 , needed to obtain $\langle R_N^2(u) \rangle$, will also be a homogeneous function of the scaling fields:

$$\Gamma_2(\mu_{1\delta}, \mu_2) = e^{4l} \Gamma_2(\mu_{1\delta}(l), \mu_2(l)), \tag{5.1}$$

where the small exponent η is again neglected (see (2.25)).

Using the Riedel-Wegner procedure, the boundary value for $\Gamma_2(\mu_{1\delta}(l), \mu_2(l))$ at $l = \hat{l}$ is taken as

$$\Gamma_2(1, \mu_2(\hat{l})) = \bar{\Gamma}_2, \tag{5.2}$$

where $\bar{\Gamma}_2$ is a constant, which again might represent the leading term of a series in $\mu_2(\hat{l})$.

The calculation of $a_N(u)$, defined by (2.22), now follows exactly that of the partition function $C_N(u)$ in § 4.1. In the Θ temperature region

$$a_N(u) = \left(\frac{J_c(0)}{J_c(u)} \right)^2 \frac{\bar{\Gamma}_2 (1 - \mu_2)^{2/3} N}{(J_c(u))^N \Gamma(2)} \left(1 + \frac{2}{3} \frac{\Gamma(2)}{\Gamma(2.5)} X + O(X^2) \right), \tag{5.3}$$

while at higher temperatures

$$a_N(u) = \left(\frac{J_c(0)}{J_c(u)} \right)^{12/5} \frac{\bar{\Gamma}_2 \mu_2^{4/5} N^{7/5}}{(J_c(u))^N \Gamma(2.4)} \left(1 + \frac{4}{5} \frac{\Gamma(2.4)}{\Gamma(1.8)} X^{-6/5} + O(X^{-12/5}) \right). \tag{5.4}$$

$\langle R_N^2(u) \rangle$ in both regions may now be found by dividing the expressions (5.3) and (5.4) for $a_N(u)$ by (4.11) and (4.13) for $C_N(u)$ respectively, according to (2.24).

5.2. The square of the expansion factor, α^2

The value of $\langle R_N^2(u) \rangle$ at the Θ temperature has the form

$$\langle R_N^2(0) \rangle = c^2 N \quad (5.5)$$

where c is a constant of the order of the length of a segment.

In the Θ temperature region, from (1.2), (5.3) and (5.5)

$$\alpha^2 = 1 + 0.7292z + O(z^2), \quad z < 0.1, \quad (5.6)$$

where we have set $\bar{\Gamma}_2/(c^2 \bar{\chi}) = 1$ to ensure $\alpha^2 = 1$ at $z = 0$. Similarly from (1.2), (5.4) and (5.5), the result in the good-solvent region is

$$\alpha^2 = 1.4948z^{2/5} [1 + 0.0992z^{-6/5} + O(z^{-12/5})], \quad z > 0.75. \quad (5.7)$$

The value of b determined in the calculation of A_2 has been used in (5.6) and (5.7), and $(1 - \mu_2)$ has again been replaced by 1 to obtain the crossover form (1.3). Equations (5.6) and (5.7) are again asymptotic expansions.

Figure 2 is a plot of (5.7) against z . Also shown are experimental data for the radius of gyration expansion factor of polystyrene in decalin (Berry 1966), and several non-renormalization group calculations, summarized by Yamakawa (1971). The expansion factor calculated here applies to the end-to-end distance of the polymer which is expected to be larger than that deduced from the radius of gyration (Yamakawa *et al* 1966). The coefficient of z in (5.6) does not agree with the perturbation theory values of 1.333 for the end-to-end distance expansion factor (Yamakawa 1971, § 13) or 1.276 for the radius of gyration expansion factor (Yamakawa 1971, § 14). This is, perhaps, to be expected because the boundary conditions (4.2) and (5.2) are only the leading terms in series in $\mu_2(\bar{l})$ and the value of b derived from A_2 is only approximate. The discrepancy at large z is larger than that expected merely from the difference between the end-to-end distance and radius of gyration expansion factors (Yamakawa

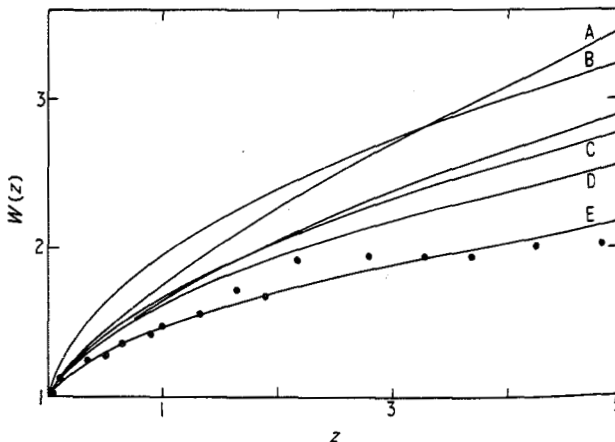


Figure 2. Plot of $W(z)$ from equation (5.7) against z . The data points are for the radius of gyration expansion factor of polystyrene in decalin (Berry 1966). Also shown for comparison are the results of the theories of the radius of gyration expansion factor of Ptitsyn (1961), curve A; Flory (1949), curve B; Yamakawa and Tanaka (1967), curve C; the modification of the Flory (1949) theory by Stockmayer (1960), curve D; and of Flory and Fisk (1966), curve E.

et al 1966). This may also be ascribed to the crudeness of the boundary conditions and possible defects in the definition of z assumed by Berry (1966) in the presentation of his data (Yamakawa 1971, p 375). In addition marginal operators, like the $|\phi_i|^6$ in (2.1) when $\epsilon = 1$ (Wegner and Riedel 1973) may be a cause of some of the discrepancy.

6. The specific heat near the Θ temperature

The reduced specific heat C may be calculated from the partition function $C_N(u)$ as

$$C = d^2 \ln C_N(u) / d\tau^2, \quad (6.1)$$

where τ is the inverse temperature (Rapaport 1974).

Near the Θ temperature and in the good-solvent region $C_N(u) \sim N^{\gamma-1} (J_c(u))^{-N}$ for large N (see (2.6)), and the dominant term in the reduced specific heat is just

$$C = -N d^2 \ln J_c(u) / d\tau^2. \quad (6.2)$$

The first two terms of the series in u of $J_c(u)$ can be calculated from the renormalization group equations (3.2) and (3.3), provided we retain the term in $u^2(l)$ in (3.2). The equations to be solved are

$$dr_\delta/dl = 2r_\delta + Au - Aur_\delta + Eu^2 \quad (6.3)$$

$$du/dl = u - Bu^2 \quad (6.4)$$

where E is a constant. The critical fixed point of these equations is at $(r_\delta^*, u^*) = (r_c^*, B^{-1})$ where $r_c^* = -(AB + E)/(2B^2 - AB)$. Dividing (6.3) by (6.4) and integrating with respect to u gives r_δ as a function of u :

$$\begin{aligned} r_\delta(u) &= u^2(1 - Bu)^{(A-2B)/B} \int du \frac{(A + Eu)(1 - Bu)^{(B-A)/B}}{u^2} \\ &= u^2(1 - Bu)^{(A-2B)/B} (K + f_1(u) + f_2(u)) \end{aligned} \quad (6.5)$$

where K is a constant of integration and

$$f_1(u) = \int du \frac{A(1 - Bu)^{(B-A)/B}}{u^2} \quad (6.6)$$

$$f_2(u) = \int du \frac{E(1 - Bu)^{(B-A)/B}}{u}. \quad (6.7)$$

The only line in (r_δ, u) space which passes through both the critical and Gaussian fixed points has $K = 0$. This is the critical line upon which J_δ has its critical value $J_c(u)$. Denoting the values of r_δ and u on the critical line by r_c and u_c , (6.5) yields

$$r_c \sim u_c + Fu_c^2 \ln u_c + O(u_c^3), \quad (6.8)$$

and

$$J_c(u_c) = J_c(0) + Gu_c + Hu_c^2 \ln u_c + O(u_c^3), \quad (6.9)$$

where F , G and H are constants.

Substituting (6.9) in (6.2) shows that the reduced specific heat at the Θ temperature diverges as $N \ln(1 - \Theta/T)$. Rapaport (1974) has determined the maximum specific

heat of chains of finite N and suggests that $C = N \ln N$, which is consistent with (6.9) (Ferdinand and Fisher 1967, Moore 1971).

7. Discussion

The theory developed in this paper has certain apparent defects. Firstly, the renormalization group equations (3.2) and (3.3) are valid only for small r_δ , but, in the subsequent calculations, the boundary conditions (4.2), (4.14) and (5.2) have been taken at $\mu_{1s}(\hat{l}) = 1$. Secondly, (3.6) and (3.7) have had the experimental values of the exponents inserted into them. Thus (3.6) and (3.7) should be viewed as the phenomenological equations proposed by Riedel and Wegner (1974) and not as equations derived from systematic renormalization group procedures like the ϵ expansion. Thirdly, only the leading terms of series in $\mu_2(\hat{l})$ have been taken for the boundary values of χ , G_4 and Γ_2 , with consequent inaccuracies in the second terms of (4.21) and (5.6) and both terms of (4.24) and (5.7). Our attempts to improve the boundary values have either produced undetermined constants within the theory, or nonsensical equations. (It should be possible to choose boundary conditions to give an empirical fit to the data for both A_2 and α^2 both at small and large values of z , but a more revealing test of the theory is to determine the constants in the Θ -temperature region, and predict the results at higher temperatures, as done in this paper.) Fourthly, the Θ temperature has been taken as being analogous to a Gaussian fixed point. For a tricritical fixed point a term of the order $v|\phi(x)|^6$ should have been included in the Hamiltonian (3.1). Near the critical fixed point v is an irrelevant field but near the tricritical fixed point it is a marginal field for $d = 3$. Thus we expect that logarithmic corrections are needed to our results near the Θ temperature (Wegner and Riedel 1973).

We conclude that the approach of Riedel and Wegner (1974) to crossover problems seems useful in the description of the properties of polymers in dilute solution. In spite of the semi-phenomenological nature of the method, quantitative predictions for α^2 and A_2 in reasonable agreement with experiment have been obtained. The form of the calculations is very close to that in an ϵ expansion taken to order ϵ (Nelson and Rudnick 1975) (except where the coefficients in the differential equations were adjusted to give the experimental values of the indices). Because systematic improvement of the boundary conditions is not easy within the phenomenological Riedel–Wegner procedure, we believe that further work using the ϵ expansion directly but taken to order ϵ^2 probably offers the best scope for further improvement. In an appendix, we give the calculation of the crossover functions correct to order ϵ .

The predicted logarithmic divergence of the specific heat maximum of a single chain in solution as its molecular weight is increased could not have been made within the strict confines of an ϵ expansion. The apparent existence of such a divergence (Rapaport 1974) is an argument for the utility of the semi-phenomenological approach.

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Appendix

We shall give here the results of calculations, correct to order ϵ , for the crossover functions $W(z)$ and $X(z)$. The calculation is based on the work of Nelson and Rudnick (1975), which is very similar in form to the Riedel-Wegner approach, except that no attempt is made to adjust the coefficients in the equations for the scaling variables ((3.4) and (3.5)) to obtain the experimentally known asymptotic behaviour. Stephen (1975) has indeed already calculated the crossover function for α^2 using this procedure. His result is

$$\alpha^2 = \left(1 + \frac{\bar{u}_d}{6\pi^2 \epsilon} N^{\epsilon/2}\right)^{1/4}, \quad (\text{A.1})$$

where $\bar{u}_d \propto u + \alpha_d u_6 c^{2-d}$, α_d is a numerical factor, and $u_6 c^{6-2d}$ corresponds to a three-particle potential between three links of the chain. If for $d=3$ or $\epsilon=1$, we again remove the unknown constants from α^2 by demanding that its expansion in z matches up with the leading term of the conventional expansion of α^2 in powers of z , (A.1) becomes

$$\alpha^2 = \left(1 + \frac{16}{3}z\right)^{1/4} = W(z). \quad (\text{A.2})$$

For small z , (A.2) predicts

$$\alpha^2 = 1 + \frac{4}{3}z - \frac{8}{3}z^2 + \frac{224}{27}z^3 \dots, \quad (\text{A.3})$$

whereas the perturbation theory result is (Yamakawa 1971)

$$\alpha^2 = 1 + \frac{4}{3}z - 2.075z^2 + 6.459z^3 \dots$$

For large z , (A.2) gives, $\alpha^2 \sim 2(z/3)^{1/4}$. The correct asymptotic dependence on z is probably closer to $\frac{2}{3}$. In the region of z -values accessible to experiment and plotted in figure 2, the expression (A.2) gives a good fit to the data.

The crossover function for A_2 to order ϵ is trivially evaluated from the expression which Nelson and Rudnick derive for the free energy. It is

$$X(z)/z = \left(1 + \frac{16}{3}z\right)^{-1/2}. \quad (\text{A.4})$$

For small z , (A.4) predicts

$$X(z)/z = \left(1 - \frac{8}{3}z + \dots\right), \quad (\text{A.5})$$

in contrast to the exact result

$$X(z)/z = (1 - 2.865z + \dots). \quad (\text{A.6})$$

Notice that the leading term in z in (A.5) is at variance with the exact result, and that a similar problem was encountered in the Riedel-Wegner calculation, where it was found impossible to ensure simultaneously valid expansions for both the crossover functions of α^2 and A_2 . This discrepancy is not hard to understand with an expansion procedure only correct to order ϵ , as the term in z in (A.5) is really a term of order \bar{u}_d^2 in the original calculation of A_2 , and so is of order ϵ^2 .

For large z , (A.4) takes the form

$$X(z)/z = (\sqrt{3}/4)z^{-1/2}, \quad (\text{A.7})$$

whereas the probable z dependence is as the $-\frac{2}{3}$ power. However, in the range of z -values 0-5 as in figure 1, (A.4) gives a very good fit to the data.

It clearly would be of interest and value to extend these calculations to higher order in ϵ .

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