Crossover behaviour between Gaussian and self-avoiding limits of a single polymer chain:

conformational space renormalisation for polymers. VI

Crossover behaviour between Gaussian and self-avoiding limits of a single polymer chain: conformational space renormalisation for polymers VI

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Abstract. The Gell-Mann–Low style conformational space renormalisation method for polymers is generalised to describe the crossover between the random walk and self-avoiding walk limits, i.e., to describe the excluded volume dependence. Explicit calculations are provided to order $\varepsilon = 4 - d$ (d the spatial dimensionality) for the full end-to-end vector distribution function, the coherent elastic scattering function, the second virial coefficients and $\langle R^2 \rangle$ and $\langle S^2 \rangle$. The crossover functions are required therefore to exhibit the correct asymptotic limits of both the random and self-avoiding walks. The theory demonstrates that the latter choice implies that the expansion factors, α^2 and α_s^2, for the mean square end-to-end vector $\langle R^2 \rangle$ and radius of gyration $\langle S^2 \rangle$, respectively, are not universal functions of the single scaling variable describing the strength of the excluded volume interactions. Nevertheless, much of the available experimental data on long chain polymers appears to involve small renormalised dimensionless excluded volume, and therefore α^2 and α_s^2 are approximately universal quantities. Comparisons between our theoretical predictions and experimental data on the second virial coefficient and α_s^2 show good agreement.

1. Introduction

The polymer excluded volume (or self-interaction) problem is one which can be studied by the use of renormalisation group methods. The present paper extends the conformational space renormalisation group method, developed in the preceding papers III (Oono *et al* 1981) and V (Ohta *et al* 1981), to the calculation of the crossover behaviour between the Gaussian chain and self-avoiding chain limits. This renormalisation method does not rely on formal analogies between polymer systems and magnetic systems (de Gennes 1972, Emmery 1975), and it utilises a monodisperse chain length distribution. This aspect of our renormalisation group approach is important because there is no simple polymer-magnet analogy for dynamical problems. However, as is demonstrated in the work of Yamazaki and Ohta (1981) on the effect of elongational flow on a polymer chain, the present methods enable the development of a unified renormalisation group theory of both static and dynamic properties of polymer systems.

   In the preceding papers (Oono *et al* 1981, Ohta *et al* 1981) we consider the end-to-end vector distribution function and the static coherent scattering functions only in the self-avoiding polymer limit. Experiments rarely are performed in this

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idealised limit of fully developed excluded volume, and here we generalise these calculations to describe the dependence of these distribution functions and the second virial coefficient upon the strength of the excluded volume interaction.

The end-to-end vector distribution and the coherent scattering function have never been calculated previously in the crossover region, but the second virial coefficient A_2 has already been evaluated by several authors (Burch and Moore 1976, Elderfield 1978, 1980, Lawrie 1976). The most detailed crossover calculation of A_2 and the mean square end-to-end vector $\langle R^2 \rangle$ have been performed by Elderfield (1980). Lawrie (1976) has also evaluated A_2. Both these workers and Burch and Moore (1976) have attempted to relate the conventional z parameter in the traditional two-parameter theory of polymer excluded volume (e.g. Yamakawa 1971) to the scaling variable which describes the strength of excluded volume interaction in the renormalisation group theory. Since the two-parameter theory for small z shows apparent agreement with experiment, the latter identification is effectively with a renormalised empirical parameter rather than the microscopic z parameter.

The simplest case involves fully developed excluded volume, the self-avoiding walk limit. Here, the renormalised interaction parameter becomes totally insensitive to microscopic parameters such as those of the two-parameter theory. The situation becomes more complicated in the crossover regime where there are two theoretical goals to be distinguished. The first involves the description of long-wavelength observable macroscopic quantities in terms of the macroscopic renormalised interaction parameter, while the second focuses on the calculation of this renormalised interaction parameter in terms of truly microscopic interactions. The former problem is conveniently treated within the renormalisation group by virtue of the fact that these macroscopic relations can be correctly deduced with very simple microscopic models containing only the most essential information concerning the general nature of the interactions. The second problem, on the other hand, requires the treatment of detailed, realistic microscopic interactions, producing a complicated many-body problem that has not been attempted for the polymer excluded volume problem. Thus, while the renormalisation group calculations do provide an expression for the renormalised interaction parameter in terms of the microscopic ones, this part of the calculation pertains only to the simple microscopic model invoked.

Lawrie (1976) attempts to calculate the renormalised interaction parameters by using the characteristic equation of the renormalisation group equation as analogues of differential recursion relations (Nelson and Rudnick 1975) describing how the bare microscopic quantities become converted into the macroscopic interaction parameters during the renormalisation process. However, this analogy is questionable since the homogeneous renormalisation group equations used by Lawrie can be defined only in the macroscopic limit (i.e., only in the critical regime). Elderfield simply identifies z with a complicated quantity which is essentially $vN^\varepsilon/2$ (for $\varepsilon = 4 - d$ with d the spatial dimensionality) when the renormalised interaction parameter v is small and when N is the renormalised chain length. Elderfield's identification of z is in the same spirit as the use of the conventional two-parameter theory expressions to fit to experimental data, where z then effectively takes on the role of the appropriate renormalised quantity. It should be stressed that nobody has yet succeeded in deriving a self-consistent relationship between the microscopic conventional two-parameter theory z parameter and the macroscopic $vN^\varepsilon/2$ quantity.

The renormalisation group equation determines the proper scaling variables describing the excluded volume dependence of macroscopic observable quantities.

When the renormalised perturbation series for A_2, $\langle \boldsymbol{R}^2 \rangle$, etc are rewritten in terms of the scaling variables dictated by the renormalisation group equations, the desired universal functional representation of these macroscopic observables is obtained. This enables us to present the excluded volume parameter dependence of the end-to-end vector distribution function, the coherent scattering function, $\langle \boldsymbol{R}^2 \rangle$, $\langle \boldsymbol{S}^2 \rangle$, A_2 and the penetration function Ψ, defined in 3-space by

$$\Psi = A_2 \mathcal{M}_N^2 / N_A 4 \pi^{3/2} \langle \boldsymbol{S}^2 \rangle^{3/2} \tag{1.1}$$

with N_A Avagadro's constant and $\mathcal{M}_N$ the molecular weight. The value of Ψ in the self-avoiding chain limit has already been evaluated by Witten and Schafër (1978), but the most interesting crossover behaviour is evaluated here.

We impose the stringent requirement that the theory properly reproduces the well known and more simply derived limits of the Gaussian chain and of the self-avoiding walk. Because of this criterion, we explicitly show that the expansion factors,

$$\alpha^2 = \langle \boldsymbol{R}^2 \rangle / \langle \boldsymbol{R}^2 \rangle_0 \qquad \text{and} \qquad \alpha_s^2 = \langle \boldsymbol{S}^2 \rangle / \langle \boldsymbol{S}^2 \rangle_0, \tag{1.2}$$

where the subscript 0 denotes the values for the Gaussian chain limit, are not universal quantities dependent only on the single excluded volume strength parameter. However, it is also demonstrated that they are approximately universal quantities when the renormalised interaction parameter is small and the chain length is sufficiently long. Thus, it is possible to construct an approximate universal plot of Ψ versus α_s^3. Although the crossover behaviour between the Gaussian self-avoiding walk limits is different from the crossover between the Θ-point and the self-avoiding chain limits, the resultant universal plot appears to be in reasonable accord with experiment. Additional experimental and theoretical work is desirable to establish the degree of non-universality and the role of three-body interactions. Our non-universal behaviour for certain quantities contrasts with the universal behaviour given by Elderfield (1980). He essentially assumes their universality and employs a finite renormalisation to ensure this universality. However, this then implies that his crossover formulae do not tend to the proper self-avoiding walk limit. Our desire to reproduce correctly this limiting result then requires the presence of some weak non-universality with apparently no available experimental implications.

The crossover behaviour of the end-to-end vector distribution function is studied in § 2 and the non-universality of the expansion factor $\alpha^2 = \langle \boldsymbol{R}^2 \rangle / \langle \boldsymbol{R}^2 \rangle_0$ is shown. The crossover behaviour of the static scattering function is evaluated in § 3. The second virial coefficient A_2 and the interpenetrating function Ψ are calculated in § 4, and the Ψ against $\alpha_s^2 = \langle \boldsymbol{S}^2 \rangle / \langle \boldsymbol{S}^2 \rangle_0$ relation is compared with experimental results. Section 5 consists of a discussion which contains an explanation of why α^2 or α_s^2 are non-universal quantities when the crossover calculation is required to reproduce the Gaussian and self-avoiding walk limits.

2. $G(R, N)$ as a function of interaction parameter

2.1. 'Microscopic' model

The model is defined through the bare dimensionless Hamiltonian,

$$H_a(\boldsymbol{c}) = \frac{1}{2} \int_0^{N_0} \left(\frac{\mathrm{d}\boldsymbol{c}(\tau)}{\mathrm{d}\tau} \right)^2 \mathrm{d}\tau + \tfrac{1}{2} v_0 \int_{|\tau - \tau'| \geq a} \mathrm{d}\tau \int \mathrm{d}\tau' \, \delta(\boldsymbol{c}(\tau) - \boldsymbol{c}(\tau')), \tag{2.1}$$

where $c(\tau)$ represents the continuous chain conformation with the contour parameter τ in $[0, N_0]$, $v_0(>0)$ is the bare coupling constant, N_0 is the microscopic measure of the chain length, and a is a cut-off contour length to eliminate self-interactions of (monomer) units. The word microscopic is understood in the 'kinetic' sense explained in our previous paper V (Ohta *et al* 1981). If v_0 vanishes, then (2.1) gives Gaussian chain behaviour, while in the $v_0 N_0^{\varepsilon/2} \to \infty$ limit, (2.1) is a good model of the self-avoiding walk (Edwards 1965). Thus, the Hamiltonian (2.1) can be employed to analyse the dependence of quantities on the strength of the excluded volume, i.e., the crossover behaviour between the simple random walk and the self-avoiding random walk limits.

Here it must be stressed that (2.1) cannot describe the region near the Θ-point. As noted in previous papers, (Oono and Oyama 1978, Oono 1976, Oono and Freed 1981, de Gennes 1975) near the Θ-point there is a very subtle cancellation between the attractive effects of the two-body interactions and the repulsive effect due to multiple collision of units. Therefore, a description of the Θ-point region requires the addition to (2.1) of an extra term which describes effective three-body interactions; however, for long chains this region is expected to be rather small.

The microscopic model, defined by (2.1), can be used to evaluate the bare partition function $G_B(\boldsymbol{R}, N_0, v_0; a)$ for a chain of length N_0 with the fixed end-to-end vector $\boldsymbol{R}$. An explicit calculation (Oono *et al* 1981) of G_B by the ε-expansion method demonstrates that singularities appear at $\varepsilon = 0$ in the $a \to 0$ limit. The presence of these singularities implies that G_B depends very strongly on short-wavelength microscopic details.

2.2. Extraction of macroscopic universal picture or renormalisation

It can be shown that the strong dependence of G_B on the microscopic details presents no difficulty if we introduce microscopic–macroscopic relations which are defined to absorb all the singularities. The cut-off length a cannot be estimated from the usual long-wavelength (macroscopic) experiments. Hence, even if the molecular weight is known, the corresponding model parameter N_0 cannot be observed, since the model chain has short-range characteristics which cannot be perceived in long-wavelength experiments. Likewise, the microscopic small-scale excluded volume v_0 is not separately observable in long-wavelength experiments. However, there must be corresponding macroscopic parameters N, which designate the length of the chain, and v which represents the solvent quality. Long-wavelength experiments are characterised by an observational length scale L where $L \gg a$ or a monomer size.

The observable end-to-end distribution function is proportional to the partition function, expressed in terms of N and v, $G(\boldsymbol{R}, N, v, L)$ where L is equivalently representative of the scale of coarse-graining microscopic details to generate the macroscopic description. This $G(\boldsymbol{R}, N, v, L)$ must be proportional to $G_B(\boldsymbol{R}, N_0, v_0, a)$ because when normalised they must both provide the same end-vector distribution function. Thus, we have the set of microscopic–macroscopic relations,

$$N = Z_2 N_0 \tag{2.2}$$

$$v = v(v_0, a/L) \quad \text{with} \quad v(0, a/L) = 0 \tag{2.3}$$

$$G(\boldsymbol{R}, N, v; L) = \lim_{a/L \to 0} Z G_B(\boldsymbol{R}, N_0, v_0; a). \tag{2.4}$$

In (2.2) and (2.4), Z_2 and Z may depend on v_0. Both N and N_0 must be proportional to the molecular weight, so N and N_0 must be proportional to each other. Equation (2.3) must be independent of N (or N_0) because interactions are local occurrences. Introducing the dimensionless interaction parameters,

$$u_0 = v_0 L^{\varepsilon/2} \quad \text{and} \quad u = v L^{\varepsilon/2}, \tag{2.5}$$

for convenience, enables (2.3) to be rewritten as

$$u = u(u_0, a/L).$$

If the limit $a/L \to 0$ is not taken, then (2.2) and (2.3) might be utilised to calculate bare quantities from the renormalised quantities. However, in the $a/L \to 0$ limit, these relations develop singularities in ε and should be handled with caution. This is discussed in the next subsection.

2.3. Renormalisation group equation and its general solution

Since G_B is defined microscopically, it is independent of the macroscopic length scale L which is imposed by the experimental conditions. Hence, it follows that

$$L(\partial/\partial L)G_B(\boldsymbol{R}, N_0, v_0; a)|_{N_0, v_0, a} = 0. \tag{2.6}$$

The seemingly vacuous statement (2.6) is combined with (2.2)–(2.5) to produce the renormalisation group equation,

$$\left(L\frac{\partial}{\partial L} + \beta(u)\frac{\partial}{\partial u} + \gamma_1(u) + \gamma_2(u)N\frac{\partial}{\partial N}\right) G(\boldsymbol{R}, N, u; L) = 0. \tag{2.7}$$

This equation governs the functional form of G. The macroscopically observable G must also satisfy (2.7) in the $a/L \to 0$ limit. The quantities β, γ_1, γ_2 are defined by

$$\beta(u) \equiv L\frac{\partial u}{\partial L}\bigg|_{N_0, v_0, a}, \tag{2.8}$$

$$\gamma_1(u) \equiv L\frac{\partial \ln Z}{\partial L}\bigg|_{N_0, v_0, a}, \tag{2.9}$$

$$\gamma_2(u) \equiv L\frac{\partial \ln Z_2}{\partial L}\bigg|_{N_0, v_0, a}. \tag{2.10}$$

The values of β, γ_1, and γ_2 are already given in paper III (Oono *et al* 1981) in the $a/L \to 0$ limit as

$$\beta(u) = \pi^{-2}u(u^* - u) + O(u^3, \varepsilon u^2), \tag{2.11a}$$

$$\gamma_1(u) = \gamma_2(u) + O(u^2) = (2\pi)^{-2}u + O(u^2), \tag{2.11b}$$

where the non-trivial fixed point u^* is the solution to $\beta(u^*) = 0$,

$$u^* = \tfrac{1}{2}\varepsilon\pi^2 + O(\varepsilon^2). \tag{2.11c}$$

Note that paper V (Ohta *et al* 1981) also presents these results for non-zero a/L in the $a/L \to 0$ limit. The calculation employing renormalisation with $a/L \neq 0$ yields the same final result for macroscopic quantities.

The general solution of (2.7) is

$$G(\boldsymbol{R}, N, u; L) = \exp\left(-\int_{u_1}^{u} \frac{\gamma_1(x)}{\beta(x)}\,dx\right)$$

$$\times F\left(L \exp\left(-\int_{u_1}^{u} \frac{dx}{\beta(x)}\right), N \exp\left(-\int_{u_1}^{u} \frac{\gamma_2(x)}{\beta(x)}\,dx\right), \boldsymbol{R}\right), \qquad (2.12)$$

where F is an arbitrary well behaved function, and u_1 is a constant. The value of u_1 and the function F are interrelated such that (2.12) is satisfied. Since we consider (2.7) in the limit $a/L \to 0$, the solution (2.12) should be independent of a. Hence, u_1 cannot have a microscopic meaning, so (2.7) is applicable only after a sufficient coarse-graining procedure. Then the renormalised interaction parameter u lies between 0 and u^* since u^* corresponds to the full self-avoiding limit. Therefore, u_1 must be chosen in the macroscopically accessible region between 0 and u^*. For simplicity, u_1 is taken as $u^*/2$.

As explained above, we do not consider the renormalisation group equation as providing a connection between microscopic and macroscopic quantities since more microscopic details are required to evaluate, for instance, the macroscopic u. The equation is consequently meaningful only in providing a macroscopic description. Therefore, the characteristic equations of (2.7) cannot be used as *analogues* of the differential recursion relations employed in the Wilson–Kadanoff type renormalisation group theory.

It may seem possible to make connection between u_0 and u by simply inverting the u–u_0 relation, which is determined to absorb some of the divergences appearing in the $a/L \to 0$ limit (Oono *et al* 1981),

$$u = u_0 - (2/\varepsilon\pi^2)u_0^2 + O(u_0^3), \qquad (2.13)$$

to obtain u_0 as a function of u. However, the coefficient of u_0^2 is singular in ε, so that it cannot be used to replace u by u_0 in the ε-expansion series. This difficulty can be seen more easily when the dimensional regularisation method is not used. If the cut-off contour length a is left finite, this relation is found to be (Ohta *et al* 1981)

$$u = u_0 + \pi^{-1}u_0^2 \ln(a/L) + \ldots. \qquad (2.13a)$$

The dependence of u on a/L clearly shows that the u–u_0 relation can only be used to extract macroscopic functional relations, i.e., the dependence of macroscopic quantities such as G on the macroscopic u corresponding to the observational length scale L. Equation (2.13) or (2.13a) implies that macroscopic measurements cannot be utilised to invert the macro–micro relations to provide values of the bare quantities. The macroscopic observables cannot be expressed simply in terms of microscopic quantities in the $a/L \to 0$ limit. Practically, this means that the macroscopic observables are highly involved (highly coarse-grained) functions of microscopic quantities. Lax *et al* (1978) suggested a simple relation between the scaling variable and microscopic quantities in the case of the lattice polymers. However, as is summarised by Tanaka (1980), the situation is not that simple. He calculates the ratio C_z of the conventional z parameter from computer-experiment data and the parameter z' which produces an apparent universal α^3–z' relation ($0 < z' < 15$) where α is the expansion factor. He finds that C_z attains its constant asymptotic value only for walks longer than about 10^2 steps. This demonstrates that (approximate) universal relations involve a large number of monomer units, so the macroscopic variables of the universal plots inevitably

become many-body quantities. Having stressed that macroscopic variables like u are complicated coarse-grained functions of the microscopic system, we return to the consideration of writing (2.12) more explicitly in terms of N, v, and L.

By using (2.11) and defining the variable

$$w = u/(u^* - u), \tag{2.14}$$

(2.12) is found to become

$$G(\boldsymbol{R}, N, u; L) = [2/(1+w)]^{1/4} F(Lw^{-2/\varepsilon}, N[2/(1+w)]^{1/4}, \boldsymbol{R}). \tag{2.15}$$

Combining (2.15) with the scaling invariance relation (i.e. simple dimensional analysis) of G,

$$G(\boldsymbol{R}, N, u; L) = s^{-d/2} G(\boldsymbol{R}s^{-1/2}, Ns^{-1}, u; Ls^{-1}), \tag{2.16}$$

and choosing the arbitrary scaling parameter as

$$s = N[2/(1+w)]^{1/4}, \tag{2.17}$$

equation (2.15) reduces to a function of two variables $\hat{F}$ with

$$G(\boldsymbol{R}, N, u; L) = N^{-2+\varepsilon/2}[2/(1+w)]^{-1/4+\varepsilon/8}$$
$$\times \hat{F}[LN^{-1}[2/(1+w)]^{-1/4} w^{-2/\varepsilon}, \boldsymbol{R}N^{-1/2}[2/(1+w)]^{-1/8}]. \tag{2.18}$$

Note from (2.14) that $w \to 0$ yields the Gaussian limit where G depends only on $\boldsymbol{R}N^{-1/2}$, while in the self-avoiding walk limit, w tends to infinity.

Introducing the scaling variables

$$\zeta = (2\pi N/L)^{\varepsilon/2} w(1+w)^{-\varepsilon/8} \tag{2.19a}$$

$$X = \boldsymbol{R}^2(1+w)^{1/4}/2N \tag{2.19b}$$

converts (2.18) to the form

$$G(\boldsymbol{R}, N, u; L) = N^{-2+\varepsilon/2-\varepsilon\zeta/8(1+\zeta)} L^{\varepsilon\zeta/8(1+\zeta)} F_1(X, \zeta), \tag{2.20}$$

where numerical factors are suitably absorbed in the definition of F_1. Equation (2.19a) can be rearranged to order ε to yield

$$(1+w)^{1/4} = [1 + \zeta(1+\zeta)^{\varepsilon/8}]^{1/4}(2\pi N/L)^{-\varepsilon\zeta/8(1+\zeta)}.$$

w becomes infinite when $u \to u^*$, i.e., in the self-avoiding walk limit. In order that G of (2.20) exists in this limit, F_1 must depend only on the single variable $x = X\zeta^{-(1+\varepsilon/8)/4}$, which is the usual scaling variable in this limit and which is the only combination of X and ζ to be defined in the $w \to \infty$ limit.

2.4. Determination of $F_1(X, \zeta)$

Paper III provides a derivation of G to $O(u, \varepsilon)$ as

$$G(\boldsymbol{R}, N, u; L) = (2\pi N)^{-2+\varepsilon/2} \exp\{-\alpha + [u/(2\pi)^2]$$
$$\times [1 + \alpha + (1-\alpha)(\hat{\gamma} + \ln \alpha) - (1-\alpha) \ln (2\pi N/L)\}, \tag{2.21}$$

where $\hat{\gamma} = 0.577 \ldots$ is Euler's constant and $\alpha = \boldsymbol{R}^2/2N$. To determine F_1, it is merely

necessary to rewrite (2.21) using the scaling variables (2.19). After simple rearrangement and partial discarding of higher order terms than order ε, we get

$$G(\boldsymbol{R}, N, u; L)$$

$$= (2\pi N)^{-2+\varepsilon/2-\varepsilon\zeta/8(1+\zeta)\varepsilon\zeta/8(1+\zeta)}[X(1+\zeta)^{-1/4}]^{\varepsilon\zeta/8(1+\zeta)}$$

$$\times \exp\left\{-[X(1+\zeta(1+\zeta)^{\varepsilon/8})^{-1/4}]^{1+\varepsilon\zeta/8(1+\zeta)}\right.$$

$$\left. +(1-\hat{\gamma})\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}X(1+\zeta)^{-1/4}+\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}(1+\hat{\gamma})\right\}. \tag{2.22}$$

Here we introduce effective exponents which explicitly depend on the crossover parameter. This procedure is used in critical phenomena (Nelson and Dominy 1976). As $\zeta \to 0$, (2.22) can be approximated by

$$G(\boldsymbol{R}, N, u; L)$$

$$\simeq (2\pi N)^{-2+\varepsilon/2-\varepsilon\zeta/8}X^{\varepsilon\zeta/8}$$

$$\times \exp[-X(1+\zeta)^{-1/4-\varepsilon\zeta/32}+(1-\hat{\gamma})\tfrac{1}{8}\varepsilon\zeta X+\tfrac{1}{8}\varepsilon\zeta(1+\hat{\gamma})]. \tag{2.23}$$

If $\zeta = 0$, (2.23) turns out to be the zeroth-order Gaussian distribution. In the opposite $\zeta \to \infty$ limit, equation (2.22) recovers our previous result for the case of self-avoiding polymers (Oono *et al* 1981).

The mean square end-to-end distance is obtained from (2.22) as

$$\langle \boldsymbol{R}^2 \rangle = 4N\left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w}\right)^{1/4}\left(1-\frac{\varepsilon}{4}-\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\right) \tag{2.24}$$

$$= 4N\left(\frac{2\pi N}{L}\right)^{\varepsilon\zeta/8(1+\zeta)}\left(1-\frac{\varepsilon}{4}-\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\right). \tag{2.24a}$$

Using (2.22) and (2.24) enables the density distribution function for $r = \boldsymbol{R}/\sqrt{\langle \boldsymbol{R}^2 \rangle}$ to be obtained as

$$f(r) = \left(\frac{2}{\pi}\right)^{2-\varepsilon/2}2^{\varepsilon\zeta/8(1+\zeta)}\exp\left[\hat{\gamma}\frac{1}{8}\frac{\zeta\varepsilon}{1+\zeta}-\left(\frac{1}{4}\frac{\zeta}{1+\zeta}+\frac{1}{2}\right)\varepsilon\right]|r|^{\varepsilon\zeta/4(1+\zeta)}$$

$$\times \exp\left[-(2r^2)^{1+\frac{1}{8}\varepsilon\zeta/(1+\zeta)}\left(1-\frac{\varepsilon}{4}-\frac{\varepsilon\zeta}{8(1+\zeta)}\right)+\frac{\varepsilon}{4}\frac{\zeta}{1+\zeta}(1-\hat{\gamma})r^2\right]. \tag{2.25}$$

This is a universal function of the scaling variable ζ. It reduces in the $\zeta \to \infty$ limit to our former result† (5.5) of paper III. Figure 1 displays the general features of equation (2.25) as a function of ζ. Substitution of (2.19a) into (2.24) converts the latter to the equivalent form

$$\langle \boldsymbol{R}^2 \rangle = 4N\left(\frac{1+(2\pi N/L)^{\varepsilon/2}w}{1+w}\right)^{1/4}\left(1-\frac{\varepsilon}{4}-\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\right)+O(\varepsilon^2). \tag{2.26}$$

If w is small, equation (2.14) gives $w \propto u$. Then if N is also sufficiently large, equation (2.26) reduces to

$$\langle \boldsymbol{R}^2 \rangle \simeq dN(2\pi N/L)^{\varepsilon/8}u^{1/4}. \tag{2.27}$$

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† Unfortunately, there is a small numerical error in the coefficient of (5.6) in Oono *et al* (1981); 1.5 should read 1.4. However, our semiquantitative conclusions remain intact.
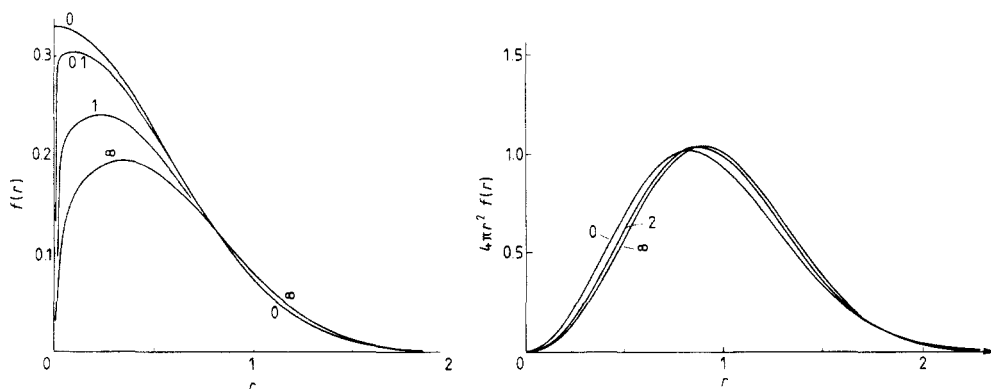
Figure 1. The crossover behaviour of the end-vector distribution function in 3-space. (a), The density distribution function for the normalised end-vector $r = R/\langle R^2 \rangle^{1/2}$. (b), The density distribution functions for $|r|$, i.e. $4\pi r^2 f(r)$. The numbers beside the curves denote ζ. $\zeta = 0$ is the Gaussian case and $\zeta = \infty$ the self-avoiding case.

This is equivalent, to order ε, to the well known result

$$\langle R^2 \rangle \propto N^{6/5} u^{2/5} \qquad (2.28)$$

or to the asymptotic $(z \to \infty)$ result given by Elderfield (1980),

$$\langle R^2 \rangle = N z^{2\rho\omega/\varepsilon} \left[1 - \frac{\varepsilon}{8} \left(\frac{59}{16} - \hat{\gamma} \right) \right] [1 + \mathrm{O}(z^{-2\omega/\varepsilon})], \qquad (2.29)$$

where $\rho\omega = 2\nu - 1$ and $z = wN^{\varepsilon/2}$ to order ε. In our notation (2.29) results essentially by redefining the new chain length as

$$N' \equiv \mathrm{d}N(1 + w)^{-1/4}$$

to absorb the non-universal factor $(1 + w)^{-1/4}$. Elderfield assumes $\langle R^2 \rangle$ to be a universal quantity to obtain (2.29). Hence, he fixes $N' = \langle R^2 \rangle_\theta$, so in our notation and to order ε his results are in the universal form

$$\langle R^2 \rangle = \langle R^2 \rangle_\theta [1 + \zeta'(1 + \zeta')^{\varepsilon/8}]^{1/4} \left(1 - \frac{\varepsilon}{4} - \frac{\varepsilon}{8} \frac{\zeta'}{1 + \zeta'} \right), \qquad (2.29a)$$

where ζ' is given by

$$\zeta' = (2\pi \langle R^2 \rangle_\theta L^{-1})^{\varepsilon/2} w. \qquad (2.29b)$$

When $u \to u^*$ but $\langle R^2 \rangle_\theta$ remains finite, we have $w \to \infty$. Hence, $\zeta' \to \infty$ and $\langle R^2 \rangle$ of $(2.29a)$ becomes infinite *at fixed finite* $\langle R^2 \rangle_\theta$ in contrast to our previous calculation (Oono *et al* 1981) at $u = u^*$,

$$\langle R^2 \rangle_{u=u^*} = 4(1 - \tfrac{3}{8}\varepsilon)(4\pi L^{-1})^{\varepsilon/8} N^{1+\varepsilon/8} < \infty.$$

An infinite value of $\langle R^2 \rangle$ of $(2.29a)$ for $u = u^*$ contradicts the rigorous results of Westwater (1980) concerning the finite value of this quantity. Hence, we must conclude that the choice of N' as the renormalised polymerisation degree is physically inappropriate to describe the full crossover from the Gaussian *to the self-avoiding chain* limits.

On the other hand, equation (2.28) follows from blob arguments (Farnoux *et al* 1978) if u is very small and $uN^{\varepsilon/2}$ is very large. Our result (2.26) reduces to (2.28) for small w (or u), and it also produces the well defined self-avoiding walk limit when w tends to infinity where $\langle R^2 \rangle$ remains finite if N is finite.

2.5. Non-universality of α^2

The non-universal factor $(1+w)^{-1/4}$ in (2.26) is crucial in obtaining the sensible asymptotic behaviour discussed at the end of the previous subsection. Thus, we are forced to conclude that the expansion factor α^2, defined by $\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_{u=0}$, cannot be universal if we require these functions to reproduce correctly both Gaussian and self-avoiding limits. α^2 is represented to $O(\varepsilon)$ in the two equivalent forms:

$$\alpha^2 = \left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w}\right)^{1/4}\left(1-\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\right) \tag{2.30}$$

$$= \left(\frac{2\pi N}{L}\right)^{\frac{1}{8}\varepsilon\zeta/(1+\zeta)}\left(1-\frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\right). \tag{2.30a}$$

α^2 has been believed to be universal, but the existence of an explicit dependence of (2.30a) on L clearly shows its non-universality. This conclusion readily follows from the structure of the scaling variable X in (2.19b). The quantity $R^2/2N$ is not a scaling variable, and the $(1+w)^{1/4}$ factor must appear to produce one. Furthermore, in the language of critical phenomena α corresponds to ζ/ζ_0, where ζ is the correlation length of the ϕ^4-theory and ζ_0 is that for the corresponding Gaussian model. Such a quantity cannot be universal in the theory of critical phenomena. A simple explanation of the non-universality of α^2 is given in § 5.

If w is small and N is sufficiently large, then the definition

$$\hat{z} = (2\pi N/L)^{\varepsilon/2}w \tag{2.31}$$

enables (2.30) to be recast into

$$\alpha^2 = \left(\frac{1+\hat{z}}{1+w}\right)^{1/4}\left(1-\frac{\varepsilon}{8}\frac{\hat{z}}{1+\hat{z}}\right) \simeq (1+\hat{z})^{1/4}\left(1-\frac{\varepsilon}{8}\frac{\hat{z}}{1+\hat{z}}\right), \tag{2.32}$$

so that α^2 is approximately universal, i.e., there is a variable $\hat{z}$ in terms of which α^2 can be expressed without any other polymer dependent parameters. Previous authors (Burch and Moore 1976, Lawrie 1976, Elderfield 1978, 1980) have attempted to connect $\hat{z}$ or some corresponding parameter and a renormalised interpretation of the conventional two-parameter theory parameter z (Yamakawa 1971) which is thought to be proportional to $v_0 N^{\varepsilon/2}$. However, this search for an internally consistent relation between z and $\hat{z}$ has been unsuccessful. As explained in subsection 2.3, the many-body nature of the macroscopically observable excluded volume implies that there cannot be such a relation. No universal relation between z and $\hat{z}$ exists. Moreover, the z of the conventional two-parameter theory is seemingly well defined. However, it cannot be, since the effective unit of the chain is not uniquely defined. It therefore clearly follows that the determination of z by using existing 'theories' (pseudotheories) is simply meaningless. Indeed, Yamakawa (1971) cleverly avoids the estimation of his β (corresponding to the present v_0). However, this is a major retreat from an original aim of the two-parameter theory.

3. Mean square radius of gyration

The coherent scattering function in the self-avoiding limit is calculated by Ohta *et al* in paper V (1981). For the general interaction parameter, the solution of the renormalisation group equation for $S(N, k)$,

$$[L(\partial/\partial L) + \beta(u)(\partial/\partial u) + \gamma_3(u) + \gamma_2(u)N(\partial/\partial N)]S(N, k, u; L) = 0, \quad (3.1)$$

where $\gamma_3(u) = \gamma_2(u) + O(u^2)$, combined with the scaling property of $S(N, k)$ fixes the functional form as

$$S(N, k, u; L) = N^2(1+w)^{-1/4}F(Y, \zeta) \quad (3.2)$$

with the scaling variable

$$Y = \tfrac{1}{2}k^2 N/(w+1)^{1/4}. \quad (3.3)$$

The normalised scattering intensity

$$I(k, N) = S(N, k, u; L)/S(N, 0, u; L) = f(Y, \zeta) \quad (3.4)$$

can be obtained by rewriting the result for (3.4) given to order u and ε in paper V in terms of scaling variables. From this form of f, we finally obtain

$$\langle S^2 \rangle = \frac{d}{6}\left(1 - \frac{13}{96}\varepsilon\frac{\zeta}{1+\zeta}\right)\left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w}\right)^{1/4}N + O(\varepsilon^2). \quad (3.5)$$

The dependence of f on ζ is small in the experimentally accessible region of Y values. The detailed formula is given in appendix 1. This weak dependence on ζ can be expected from the closeness of I for the self-avoiding walk and I_0 for a Gaussian chain shown in paper V. Combining (3.5) and (3.26) produces the universal relation (see appendix 1)

$$\frac{\langle S^2 \rangle}{\langle R^2 \rangle} = \frac{1}{6}\left(1 - \frac{\varepsilon}{96}\frac{\zeta}{1+\zeta}\right) + O(\varepsilon). \quad (3.6)$$

Unfortunately, the ζ dependence of this universal ratio is rather small. The expansion factor for $\langle S^2 \rangle$ defined by $\alpha_s^2 = \langle S^2 \rangle/\langle S^2 \rangle_{u=0}$ is given by

$$\alpha_s^2 = \left(\frac{1+\zeta(1+\zeta)^{\varepsilon/8}}{1+w}\right)^{1/4}\left(1 - \frac{13}{96}\frac{\varepsilon\zeta}{1+\zeta}\right) \quad (3.7)$$

$$= \left(\frac{2\pi N}{L}\right)^{\frac{1}{8}\varepsilon\zeta/(1+\zeta)}\left(1 - \frac{13}{96}\frac{\varepsilon\zeta}{1+\zeta}\right). \quad (3.7a)$$

Again as in the case of α^2 discussed in § 2.5, equation (3.7a) depends on w, so α_s^2 is not a universal ratio. However, if w is small and N is large enough, then an approximate universal form,

$$\alpha_s^2 \approx (1+\hat{z})^{1/4}\left(1 - \frac{13}{96}\varepsilon\frac{\hat{z}}{1+\hat{z}}\right), \quad (3.8)$$

is once more obtained.

4. Osmotic second virial coefficient

Using the McMillan–Mayer theory (McMillan and Mayer 1945) of solutions the second virial coefficient is defined for chains of unequal lengths N_0 and M_0 by

$$A_{2B}(N_0, M_0) = -[(P_2(N_0, M_0) - P_1(N_0)P_1(M_0))/P_1(N_0)P_1(M_0)]N_A/\mathcal{M}_{N_0}\mathcal{M}_{M_0} \tag{4.1}$$

where $P_1(N_0)$ and $P_1(M_0)$ are the partition functions for chains of lengths N_0 and M_0, respectively, and $P_2(N_0, M_0)$ is the partition function for a pair of interacting chains. $\mathcal{M}_x$ is the molecular weight of X. If $N_0 = M_0$, it is necessary to include the symmetry number as

$$A_{2B}^s(N_0) = \tfrac{1}{2}A_{2B}(N_0, N_0). \tag{4.2}$$

The bare second virial coefficient to $O(\varepsilon, u)$ calculated by using the dimensional regularisation is given as

$A_{2B}(N_0, M_0)$

$$
\begin{aligned}
= & \frac{N_0 M_0 N_A}{\mathcal{M}_{N_0}\mathcal{M}_{M_0}} v_0 \Bigg\{ 1 - \frac{2v_0}{(2\pi)^2}\Bigg[\frac{2}{\varepsilon} + \frac{1}{2} + \ln\frac{2\pi N_0 M_0}{L(N_0 + M_0)} \\
& + \frac{1}{2}\frac{N_0}{M_0}\ln\left(\frac{N_0 + M_0}{N_0}\right) + \frac{1}{2}\frac{M_0}{N_0}\ln\left(\frac{N_0 + M_0}{M_0}\right)\Bigg]\Bigg\},
\end{aligned}
\tag{4.3}
$$

where N_A is Avogadro's constant and the calculation is summarised in appendix 2. The renormalised second virial coefficient is defined in the $a/L \to 0$ limit as

$$A_2(N, M, u; L) = A_{2B}(Z_2^{-1}N, Z_2^{-1}M, u_0(u); a), \tag{4.4}$$

and is finite in this limit. Z_2 is already defined in § 2 equation (2.2). Thus, introducing Z_2 and $u_0(u)$ into (4.3) and (4.4) yields

$A_2(N, M, u; L)$

$$
\begin{aligned}
= & \frac{NMN_A}{\mathcal{M}_N\mathcal{M}_M} uL^{-\varepsilon/2}\Bigg\{ 1 - \frac{u}{(2\pi)^2}\Bigg[1 + 2\ln\frac{2\pi NM}{L(M + N)} \\
& + \frac{N}{M}\ln\left(\frac{N}{N + M}\right) + \frac{M}{N}\ln\left(\frac{M}{N + M}\right)\Bigg]\Bigg\},
\end{aligned}
\tag{4.5}
$$

where $\mathcal{M}_N = \mathcal{M}_{N_0}$, $\mathcal{M}_M = \mathcal{M}_{M_0}$, are utilised.

The renormalised group equation for A_2^s is derived from (4.2) and (4.4) as

$$\left(L\frac{\partial}{\partial L} + \beta(u)\frac{\partial}{\partial u} + \gamma_2(u)N\frac{\partial}{\partial N}\right)A_2^s(N, u; L) = 0. \tag{4.6}$$

Combining the general solution of (4.6) and the scaling property of A_2^s,

$$A_2^s = s^{2-\varepsilon/2}F(Ns^{-1}, Ls^{-1}, u) \tag{4.7}$$

the functional form of A_2^s is fixed as

$$A_2^s = [N/(1 + w)^{1/4}]^{2-\varepsilon/2}f(\zeta) \tag{4.8}$$

where f is some well behaved scaling function. Comparing (4.5) and (4.8), the scaling

form is obtained as

$$A_2^s = \frac{N_A N^{2-\varepsilon/2}(1+w)^{-\frac{1}{2}+\varepsilon/8}\zeta\pi^2 \exp[-\frac{1}{2}\varepsilon \ln 2\pi + \frac{1}{8}\varepsilon\zeta(1+4\ln 2)/8(1+\zeta)]}{4\mathcal{M}_N^2[1+\zeta(1+\zeta)^{\varepsilon/8}]^{1/2}}. \quad (4.9)$$

In the self-avoiding polymer limit, (4.9) reduces to

$$A_2^s = \frac{N_A}{4\mathcal{M}_N^2}N^{2-\varepsilon/4}L^{-\frac{1}{4}\varepsilon}(4e)^{\frac{1}{8}\varepsilon}\pi^{-\frac{1}{4}\varepsilon}$$

$$\propto N^{2-\frac{1}{4}\varepsilon}/\mathcal{M}_N^2 = N^{\nu d}/\mathcal{M}_N^2 \propto N^{\nu d-2}. \quad (4.10)$$

Equation (4.5) becomes in the same limit

$$A_2(N, M) \propto (NM)^{\nu d/2}/\mathcal{M}_N\mathcal{M}_M \propto (NM)^{\frac{1}{2}\nu d-1} \qquad \text{if } N \sim M \quad (4.11a)$$

$$\propto (N/M)M^{\nu d}/\mathcal{M}_N\mathcal{M}_M \propto M^{\nu d-2} \qquad \text{if } N \gg M. \quad (4.11b)$$

This result agrees with that generated by de Gennes' blob argument. Elderfield (1980) also obtained a similar result, but unfortunately in his paper the equation corresponding to (4.11b) is given for the case of $N \ll M$. The crossover from (4.11a) to (4.11b) can be represented by the universal ratio

$$\varphi(\xi) = A_2(\xi M, M)/2A_2^s(M) = \exp\{-\tfrac{1}{8}\varepsilon[4 \ln 2 - (\sqrt{\xi} + \sqrt{\xi^{-1}})^2 \ln (1+\xi^{-1})]\}, \quad (4.12)$$

where $\xi = N/M$. This function is shown in figure 2 for a polymer chain in ε-space ($\varepsilon = 1$). φ almost reaches its asymptotic value around $\zeta = 5$. Near $\xi = 1$, φ decreases exponentially. As a function of $x = \xi - 1 = (N - M)/M$, φ behaves as

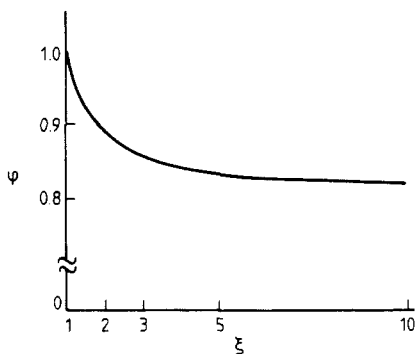$$\varphi(x) \sim \exp\left[-\frac{\varepsilon x}{4}\ln 2\right] = \exp(-0.173x) \qquad (x \sim 0). \quad (4.13)$$

Figure 2. The universal ratio φ defined by (4.12) in 3-space.

The interpenetration function Ψ, defined by (1.1), is readily calculated from (3.5) and (4.9) to be,

$$\Psi = \frac{\varepsilon\xi \exp[-\frac{1}{2}\ln 2 + \frac{1}{8}\varepsilon\zeta(-1+6\ln 2)/(1+\zeta)]}{16[1+\zeta(1+\zeta)^{\varepsilon/8}]^{1-\varepsilon/8}\left[\frac{d}{6}\left(1-\frac{13}{96}\varepsilon\frac{\zeta}{1+\zeta}\right)\right]^{2-\varepsilon/2}}. \quad (4.14)$$

Note that Ψ is a true universal quantity, dependent only on the scaling variable ζ. In

the self-avoiding limit $\zeta \to \infty$, (4.14) reduces to

$$\Psi^* = \frac{\varepsilon \exp(-\frac{1}{8}\varepsilon + \frac{1}{4}\ln 2)}{16[\frac{1}{6}d(1 - 13\varepsilon/96)]^{2-\varepsilon/2}}. \qquad (4.15)$$

When ε is set to 1 and $d = 3$, then $\Psi^* = 0.231$. However, if d times $(1 - 13\varepsilon/96)$ is expanded in ε, the result is different. So this order Ψ^* is somewhat unreliable with regard to the manner in which higher order terms are retained. Witten and Schäfer (1978) obtained $\Psi^* = 0.268 \pm 100\%$. We think that d in (4.15) should be set to 3 and not ε-expanded, so we adopt $\Psi^* = 0.231$ henceforth.

If w is small and N is large enough, then ζ in (4.14) can be simply replaced by $\hat{z}$. Then using Ψ as a function of $\hat{z}$ and equation (3.8), a conventional Ψ against α_s^3 plot can be made as is shown in figure 3. The theoretical model is, strictly speaking, not
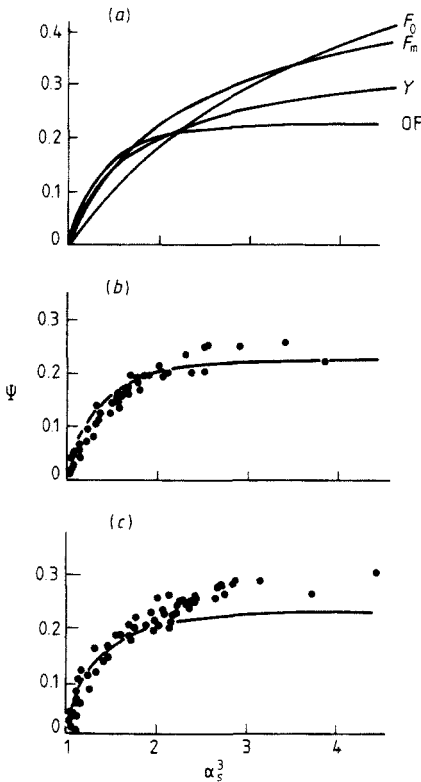

Figure 3. Approximate universal plot of Ψ against α_s^3. As is explained in the text, α_s is not a universal ratio in contrast to the true universal one Ψ. The plot is, strictly speaking, not universal. However, for sufficiently small renormalised interaction parameters, the plot is universal to a good approximation. (a) Compares our result, OF obtained from (3.8) and (4.14), with other curves given in Yamakawa's book (1971). F_0: $\Psi = [\ln(1 + 2.30z/\alpha_s^3)]/2.3$ with $\alpha_s^5 - \alpha_s^3 = 2.60z$, F_m: $\Psi = [\ln(1 + 5.73z/\alpha_s^3)]/5.73$ with $\alpha_s^5 - \alpha_s^3 = 1.276z$ and Y: $\Psi = 0.547[1 - (1 + 3.903z/\alpha_s^3)^{-0.4683}]$ with $\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.46}$. The experimental data involves polychloroprene in (b) (Norisuye *et al* 1968) and polystyrene in (c) (Berry 1966). F_0 and F_m fail to produce the correct finite limit to Ψ, so these results are unsound. Y may seem the best fit to the data. However, this curve has no sound theoretical basis; its derivation involves *ad hoc* assumptions. Note that our theory contains neither adjustable parameters nor *ad hoc* procedures.

capable of describing the situation very near the Θ-point because of the omission of three-body effects, but for long chains this region should be very small.

Figure 3 contains comparisons with experimental data over the full available region of α_s. The agreement with experimental data is encouraging. Figure 3(a) compares our theory with other existing theories. Flory's theories (Flory and Krigbaum 1950, Flory 1949, Orofino and Flory 1957, Stockmayer 1960) fail to give finite values for Ψ in the self-avoiding walk limit. The curve of Yamakawa and co-workers (Kurata *et al* 1964, Yamakawa 1971, Yamakawa and Tanaka 1967) seems best fit to the experimental data. However, the approximation of the theory is questionable. We must stress that our theory represents the first approximation in a well defined scheme; there are no adjustable parameters nor *ad hoc* procedures involved.

5. Discussion

The polymer conformation space renormalisation group method has been used to calculate the crossover behaviour between the Gaussian and self-avoiding polymer limits of the end-to-end vector distribution function, the mean square end-to-end distance, the mean square radius of gyration and osmotic second virial coefficient. The crossover behaviour describes how these properties vary with the strength of the phenomenological excluded volume parameter and it correctly reproduces the Gaussian and self-avoiding limits. Our calculations explicitly show that the expansion factors for the radius of gyration and mean square end-to-end distance cannot be universal, i.e., they are not functions of a single renormalised excluded-volume parameter when required to describe the full crossover behaviour from the Gaussian to the self-avoiding chain limits. These conclusions stand in marked contrast with previous assumptions of the 'two-parameter' theories (Yamakawa 1971) that these quantities are universal (i.e., they have been thought to depend only on the z parameter defining the strength of the excluded-volume perturbation).

The simplest argument to derive this 'two-parameter' picture involves elementary dimensional analysis. Since we are interested in very long polymer chains, the continuous chain model can be exploited. The simplest model is the one given in § 2. It only contains three dimensional parameters N_0, v_0 and a, the minimum possible number. Two independent dimensionless quantities N_0/a and $v_0N_0^{\varepsilon/2}$ can be constructed from these parameters. Dimensional analysis then implies, for example, that

$$\langle S^2 \rangle = N_0 f(v_0 N^{\varepsilon/2}, N_0/a). \tag{5.1}$$

Henceforth, the symbol f is used repeatedly to denote some function appropriate to the context. Since the chain is very long, the microscopic scale a should be unimportant. Or, following the standard argument of dimensional analysis that very large or very small dimensionless quantities should become irrelevant, we have

$$\langle S^2 \rangle = N_0 f(z), \tag{5.2}$$

or

$$\alpha_s^2 = f(z)/f(0), \tag{5.2a}$$

where z is the conventional parameter $z \propto v_0 N^{\varepsilon/2}$.

However, equation (5.1) is not well defined in the $a \to 0$ limit, and this affects properties at the interesting cases of $d = 2$ and 3. Therefore, the crucial step of

ignoring N_0/a from (5.1) to obtain (5.2) is illegitimate. Equation (5.2) does not follow from (5.1). The renormalisation procedure involves the introduction of extra dimensional quantities N, v and L where L represents the observational length scale $L \gg a$. Thus, we have for instance,

$$\langle S^2 \rangle = Nf(u, N/L; N/N_0, v/v_0, a/L), \tag{5.3}$$

where N/N_0 and v/v_0 are so chosen that the singularities introduced in the long-wavelength $a/L \to 0$ limit are cancelled by these choices. Hence in the macroscopic, $a/L \to 0$ limit, we are left with

$$\langle S^2 \rangle = Nf(u, N/L), \tag{5.4}$$

or

$$= Nf(\zeta, u), \tag{5.5}$$

or

$$= Nf(\zeta, N/L), \tag{5.6}$$

where the scaling variable ζ is given by (2.19a) and is analogous to z in having the same $N^{\varepsilon/2}$ dependence. Using (5.5) for example, the expansion factor is obtained in the form

$$\alpha_s^2 = f(\zeta, u)/f(0, 0) \equiv g(\zeta, u). \tag{5.7}$$

Hence, in general, α_s^2 cannot be a universal function of only ζ. However, fortunately if $u \ll 1$ and $N \gg 1$, then we find $g(\zeta, 0) \approx g(\zeta, u)$, and equation (5.7) turns out to be approximately universal,

$$\alpha_s^2 \approx g(\zeta, 0), \qquad u \ll 1, \qquad N \gg 1, \tag{5.8}$$

i.e., for $u \ll 1$ and $N \gg 1$ the separate u-dependence can be ignored.

As is already discussed by Witten and Schäfer (1978) and also explicitly shown in this paper, the penetrating function Ψ is a true universal function of ζ,

$$\Psi = \Psi(\zeta). \tag{5.9}$$

Because ζ (like z of the two-parameter theories) is not directly measurable, it has been customary to eliminate ζ (like z) between a pair of macroscopic variables to obtain interrelations between observables. The α_s^3–Ψ relation has been considered widely because it was believed to be universal. Our derivation, by contrast, demonstrates that it cannot be. The relation takes the functional form of

$$\Psi = f(\alpha_s^3, u). \tag{5.10}$$

However, again if u is small and N is large enough, the u dependence of (5.10) becomes negligible and (5.10) becomes approximately universal,

$$\Psi = f(\alpha_s^3), \qquad u \ll 1, N \gg 1. \tag{5.11}$$

The approximate equation (5.11) obtained to order ε is compared with experimental data and other theories in figure 3. The agreement between our result and experiment is very good. However, the data appear to indicate a polymer dependence of the limiting Ψ^* value at large excluded volume, whereas the theory shows Ψ^* to be a universal constant in the limit of $\zeta \to \infty$. This conclusion remains independent of the approximation involved in passing from (5.10) to (5.11). Hence an experimental revaluation of this point is desirable.

The theoretical analysis is not valid in a small neighbourhood of the Θ-point for long chains as emphasised previously. A correct theoretical description involves the introduction of effective three-body interactions whose physical origins (e.g. Oono and Freed 1981) can lie in the microscopic two-body interactions. Nevertheless, the fit to experimental data in figure 3 does not exhibit any serious deficiency due to the omission of the three-body interactions. This is in accordance with the result of the ϕ^6 field theoretic consideration (Stephen 1975). The precise role of the three-body interactions must await their incorporation into the theory and further experimental studies.

In the meantime it would be worthwhile to neglect cautiously the three-body interactions to consider the following interesting analyses. The universal relation (5.9) can be inverted to give

$$\zeta = \zeta(\Psi), \tag{5.12}$$

enabling ζ to be determined from experimental data on Ψ. Since Ψ attains its asymptotic limit for $\zeta \sim 20$, only a limited part of the interesting range can be covered. (This seems to correspond to conventional empirical $z \sim 7$.) The molecular weight dependence $\zeta \propto N^{1/2}$ should be readily verifiable, and the temperature dependence of this highly renormalised quantity would be of interest. Given the empirical values of ζ, the individual approximate relations for α_s^2 against $\hat{z} \simeq \zeta$ (for w small) in (3.8) and the corresponding approximation for A_2 generated from (4.9) can be tested to determine whether there are additional polymer dependences. If so (and still assuming the negligibility of effective three-body interactions), then the non-universality of A_2 and α_s^2 would be experimentally observable.

Non-universal quantities can be expressed in terms of the variable N/L. It is tempting to interpret N/L as the effective number of segments in the chain given the observational or coarse-graining length scale L. However, just as the individual segment size is never a definable nor measurable quantity for long-wavelength properties, parameters such as u and hence w depend on the value of L such that the macroscopic parameter ζ is independent of this choice of L in the $a/L \to 0$ limit.

The macroscopic excluded volume interaction u represents a cooperative coarse-grained excluded volume interaction over a distance L. Thus, a difficult many-body problem is required to evaluate u in terms of the detailed microscopic interactions. In fact, for the purposes of actually calculating u, the simple model (2.1) is obviously insufficient; more details of the microscopic interactions are necessary. Tanaka (1980) underscores this point by noting that lattice Monte Carlo calculations for polymers yield universal (e.g., lattice structure independent) relations only when represented in terms of the parameter $C_z z$, with $z = v_0 N_0^{\epsilon/2}$ the excluded volume perturbation parameter and C_z lattice dependent. Since Tanaka finds that C_z approaches its asymptotic value for walks of ≥ 100 steps, a true microscopic theory of u would require the treatment of 100 units on the chain.

Our formulation of the Gell-Mann–Low type renormalisation group method essentially gives up hope of calculating u from microscopic quantities, e.g., in terms of u_0. The theory notes the existence of the macroscopic parameter u and calculates the dependence of the macroscopic observables on this u. For these purposes the simple model Hamiltonian (2.1) is perfectly sufficient.

Scaling theories of polymer solutions (de Gennes 1979) have been used only in the random walk and self-avoiding walk limits. However, experiments are generally never performed in these idealised limits. We show how general scaling laws for

polymers may be derived which depend on the excluded volume. These scaling laws thus have an additional scaling variable ζ beyond that for the random or self-avoiding walk limits. This makes it much more difficult to intuit the behaviour of the scaling functions in the crossover region. We show here how the chain conformation space renormalisation group method can be used to derive the scaling laws as well as to calculate explicitly the scaling functions. Some applications of field theoretic renormalisation group methods have been also applied to the description of this crossover behaviour. None have considered the wide variety of properties that are given here.

Acknowledgments

Appendix 1. The scaling form of the normalised scattering intensity (3.4)

From paper V (Ohta *et al* 1981) $S(N, k, u; L)$ is given to $O(u, \varepsilon)$ as

$$S(N, k, u; L) = N^2\{S_0(\beta) - u(2\pi)^{-2}[\ln(2\pi N/L)(\partial S_0(\beta)/\partial \beta) + D(\beta)]\}, \tag{A1.1}$$

$$S_0(\beta) = \beta^{-1} + \beta^{-2}(e^{-\beta} - 1), \tag{A1.2}$$

$$\beta = \tfrac{1}{2}k^2 N = Y(1+w)^{1/4}$$

$$= Y(1 + \zeta(1+\zeta)^{\varepsilon/8})^{1/4}\left[1 - \frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\ln\left(\frac{2\pi N}{L}\right)\right]$$

$$\equiv \hat{\beta}\left[1 - \frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}\ln\left(\frac{2\pi N}{L}\right)\right], \tag{A1.3}$$

$$D(\beta) = 2\int_0^1 dt\left(\frac{e^{-\beta}}{\beta^2}A(\beta - \beta t + \beta t^2) + (\beta^{-1} - \beta^{-2})A(-\beta t + \beta t^2)\right.$$

$$+ \frac{1 - \exp(-\beta t + \beta t^2)}{\beta^2 t(1-t)}\right) + \int_0^1 dt\left(\frac{1}{\beta(1-t)} + \frac{\exp(-\beta t + \beta t^2) - 1}{\beta^2 t(1-t)^2}\right)$$

$$- \beta^{-2}e^{-\beta}A(\beta) + \beta^{-1}e^{-\beta}A(\beta) + \beta^{-1}e^{-\beta}, \tag{A1.4}$$

$$A(x) = \int_0^x dt(e^t - 1)/t.$$

Introducing $\hat{\beta} = Y(1 + \zeta(1+\zeta)^{\varepsilon/8})^{1/4}$ for convenience and combining terms yields to $O(\varepsilon)$

$$S(N, k, u; L) = N^2\left[S_0(\hat{\beta}) - \frac{\varepsilon}{8}\frac{\zeta}{1+\zeta}D(\hat{\beta}) + O(\varepsilon^2)\right]$$

$$\approx N^2 S_0(\hat{\beta})\exp[-\tfrac{1}{8}\varepsilon\zeta(1+\zeta)^{-1}D(\hat{\beta})/S_0(\hat{\beta})]. \tag{A1.5}$$

Since $S_0(0) = \frac{1}{2}$ and $D(0) = \frac{1}{2}$, (3.7) implies that

$$P(N, \mathbf{k}, u; L) = 2S_0(\hat{\beta}) \exp\left[-\frac{\varepsilon}{8} \frac{\zeta}{1+\zeta} \left(\frac{D_0(\hat{\beta})}{S_0(\hat{\beta})} + 1 \right) \right] \tag{A1.6}$$

to $O(\varepsilon)$.

Given the definition of $\langle S^2 \rangle$, the radius of gyration squared, from

$$P(N, \mathbf{k}, u; L) \equiv 1 - d^{-1}\langle S^2 \rangle k^2 + O(k^4), \tag{A1.7}$$

equation (A1.6) can be expanded in powers of k^2 (i.e., in $\hat{\beta}$) to give

$$P(N, \mathbf{k}, u; L) = 1 - \frac{1}{6}\left(1 - \frac{13}{96}\varepsilon\frac{\zeta}{1+\zeta}\right) k^2 N [1 + \zeta(1+\zeta)^{\varepsilon/8}]^{1/4} + O(k^4). \tag{A1.8}$$

Comparing (A1.7) and (A1.8) produces the crossover form

$$\langle S^2 \rangle = \frac{d}{6}\left(1 - \frac{13}{96}\varepsilon\frac{\zeta}{1+\zeta}\right) [1 + \zeta(1+\zeta)^{\varepsilon/8}]^{1/4} N + O(\varepsilon^2). \tag{A1.9}$$

This expression for $\langle S^2 \rangle$ can be combined with that for A_2 derived in § 4 to provide the ζ-dependence of Ψ of (1.1).

Appendix 2. Calculation of osmotic second virial coefficient

The diagrammatic expressions of P_1 and P_2 are given in figure A1. The values of the diagrams are found to be

$$P_1(N_0) = 1 + (u_0/(2\pi)^2)[(2/\varepsilon) + 1 + \ln(2\pi N_0/L) + O(\varepsilon)],$$

$$A = -u_0 N_0 M_0 L^{-\varepsilon/2},$$

$$B = \frac{u_0^2}{(2\pi)^2} N_0 M_0 L^{-\varepsilon/2}\left(\frac{2}{\varepsilon} + \ln\frac{(2\pi)^2 N_0 M_0}{L^2} + \frac{N_0}{2M_0}\ln\frac{N_0}{N_0+M_0}\right.$$
$$\left. + \frac{M_0}{2N_0}\ln\frac{M_0}{N_0+M_0} + \frac{1}{2} - \ln\frac{2\pi(N_0+M_0)}{L} + O(\varepsilon)\right),$$

Figure A1. The diagrammatic expression of P_1 and P_2 necessary to calculate the second virial coefficient. P_{2c} is the connected part of P_2. The full line implies the Gaussian propagator and the broken line the interaction. Compare with figure 11 or table 1 in part I (Oono and Freed 1981) for more detailed definition of the diagrams.

$$C = -\frac{u_0^2}{(2\pi)^2} N_0 M_0 L^{-\varepsilon/2} \left(\frac{2}{\varepsilon} + \ln \frac{2\pi N_0}{L} + \mathrm{O}(\varepsilon) \right),$$

$$D = \frac{u_0^2}{(2\pi)^2} N_0 M_0 L^{-\varepsilon/2} \left(\frac{2}{\varepsilon} - 1 + \ln \frac{2\pi N_0}{L} + \mathrm{O}(\varepsilon) \right).$$

Therefore the bare $A_{2B}(N_0, M_0)$ is given by (4.3).

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