Crossover between random and self-avoiding behaviour in a ring polymer

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Abstract. The crossover between the random walk and the self-avoiding walk limits of a large ring polymer is described using a direct renormalisation theory. The methods of field theory renormalisation are applied directly to the ring polymer system to calculate the mean square radius of gyration $\langle R_G^2 \rangle_{\text{ring}}$ through first order in $\varepsilon = 4 - $ (dimension of space). The expansion factor α^2 for $\langle R_G^2 \rangle_{\text{ring}}$ is not a universal function of the natural scaling variable x that characterises the strength of the self-repelling (excluded volume) interaction. The crossover exhibited by the radius of gyration ratio $R(x) = \langle R_G^2 \rangle_{\text{ring}} / \langle R_G^2 \rangle_{\text{line}}$ is described by a universal scaling function of x and has a range space $\{\frac{1}{2} \leq R(x) \leq \frac{1}{2}(1 + \frac{13}{96}\varepsilon)\}$ that is bounded below and above by finite universal numbers representing the random and self-avoiding limits, respectively.

1. Introduction

The discovery (de Gennes 1972) that a large linear chain molecule has the same renormalisation symmetry as a certain class of critical phenomena enabled the renormalisation group to be incorporated into the language of polymer physics. The renormalisation group theory has provided a detailed understanding of the linear polymer system from first principles. It is unfortunate that a similar understanding does not exist for the ring polymer system. A large ring polymer has the same renormalisation symmetry as the linear polymer and thus is susceptible to the methods of the renormalisation group theory (Prentis 1982).

Ring polymers exist in nature as circular DNA molecules (Vinograd and Lebowitz 1966). The circularity constraint, which characterises the ring polymer, is known to have a profound effect on the function of circular DNA in biological systems (Bauer *et al* 1980). This realisation of ring polymers in nature, together with the recent synthesis of rings in the laboratory (Higgins *et al* 1979, Geiser and Hocker 1980) and in the computer (Chen 1981, Baumgärtner 1982), make a theoretical study of the ring polymer system more than a mathematical exercise.

Previous work in the statistical mechanics of the ring polymer system has been confined to the ideal (random walk) or nearly ideal behaviour using the conventional many body cluster expansion (Casassa 1965). This cluster expansion is meaningless if one wants to understand the effects of the self-repelling (excluded volume) interaction in the self-avoiding limit. The renormalisation group theory has the capability to transcend the perturbation theory and provide an understanding of the self-avoiding behaviour from first principles. In spite of this capability, there exists little work (Lipkin *et al* 1981, Prentis 1982) utilising the renormalisation group ideas in the ring

polymer system. Perhaps this neglect can be attributed to a mathematical complexity that is introduced into the ring polymer perturbation theory due to the circularity constraint. Each order in the ring polymer expansion contains an additional (Feynman) loop integration when compared with the corresponding order in the linear polymer expansion.

In a previous paper (Prentis 1982), we have used a direct renormalisation theory (Witten and Schäfer 1981) to understand the spatial correlations in a large ring polymer in the self-avoiding limit. This direct renormalisation formalism incorporates the concepts and methods of field theory renormalisation directly into the polymer problem. This formalism avoids the Lagrangian field theory isomorphism, thereby providing a unified, self-contained and more natural framework for understanding the polymer system from first principles.

In the present paper, this direct renormalisation theory is used to calculate the size (radius of gyration) of a large ring polymer as a function of the self-repelling interaction. The results are correct through first order in $\varepsilon \equiv 4 -$ (dimension of space). For three-dimensional space, experience in critical phenomena indicates that the ε-expansion is an asymptotic series which provides reliable results in first order (Wallace 1976). The size of a ring polymer is determined by the mean square radius of gyration $\langle R_G^2 \rangle$. The natural scaling variable for describing the crossover behaviour is determined by the renormalisation group equation and is found to have the form

$$x = (g/g^*)(1 - g/g^*)^{-\varepsilon/2\nu\omega} N^{\varepsilon/2}. \tag{1.1}$$

In this expression, the renormalised 'coupling constant' g is a measure of the strength of the self-repelling interaction and the renormalised variable N is proportional to the number of monomers. The quantities ν and ω are the conventional 'critical' exponents for the polymer problem and $g^* \sim O(\varepsilon)$ is the self-avoiding fixed point coupling. The random walk limit corresponds to $x = 0$. The self-avoiding limit is defined by $x = \infty$. We are interested in the behaviour exhibited by the ring polymer system in the more realistic crossover regime corresponding to finite x. The crossover in a large polymer system is realised experimentally by changing the temperature and/or solvent quality.

We find that the crossover from $x = 0$ to $x = \infty$ exhibited in the radius of gyration expansion factor α^2 is not universal. That is, the crossover cannot be described by a function only of the natural scaling variable x. In particular, $\alpha^2 = \alpha^2(x, g)$. The form of this non-universal dependence on g is made explicit in the calculation. However, in the limit $g \ll 1$, this dependence on g becomes weak and we recover an approximate universal function $\alpha^2(x, g) \approx \alpha^2(x)$ of $x \sim gN^{\varepsilon/2}$. Thus, in the limit $N \gg 1$, $g \ll 1$, the renormalisation group prediction behaves in the same way that characterises the conventional two-parameter theory (Yamakawa 1971) of the polymer excluded volume problem. In the two-parameter theory, the polymer observables (in three-dimensional space) are assumed to be functions of a single variable $z \sim vn^{1/2}$ where v is a microscopic measure of the excluded volume interaction and n is the number of monomers. This two-parameter approximation is known to be valid if $n \gg 1$, $v \ll 1$ and $vn^{1/2}$ is finite (Lax *et al* 1978 and Tanaka 1980).

However, in spite of these similarities, the precise connection between the renormalised scaling variable x and the two-parameter variable z is not well established. The reason for this is that the renormalised interaction parameter g is a coarse grained interaction parameter that represents an effective excluded volume interaction on a macroscopic scale much greater than the monomer length. More specifically, g is

obtained from the renormalised four-point vertex function $\Gamma^{(4)}$ of the polymer field theory which is an infinite sum of all the irreducible diagrams representing the interaction between two polymer chains. In the language of polymers, g is proportional to the partition function of two polymer chains which is in turn related to the second virial coefficient. Thus g represents a macroscopic many body object that is a complicated function of the microscopic interaction characterised by z in the two-parameter theory.

Indeed, previous attempts (Burch and Moore 1976, Lawrie 1976, Elderfield 1980) to relate x and z have been unsuccessful. The basic idea was first to assume x and z are simply related and then to fix the scale between x and z by forcing the small x expansion to fit the corresponding small z expansion in three-dimensional space. The results indicate that a consistent scale does not exist.

Recently, des Cloizeaux (1981) has developed a direct renormalisation theory for polymers based on the explicit relationship between g and the two-chain partition function. In this renormalisation scheme, the relationship to the two-parameter theory characterised by z is well defined. Indeed, the renormalisation group prediction for the end-to-end distance expansion factor $\alpha^2(z)$ of a linear polymer assumes a similar form and compares favourably with some of the two-parameter theory predictions. In addition, Oono and Freed (1982) present a detailed discussion of the validity of the two-parameter approximation in the language of scaling and the renormalisation group. They also discuss the many body nature of g and the futility in calculating the effective macroscopic interaction parameter x in terms of the microscopic parameter z.

Crossover phenomena in the ring polymer system has not been studied previously using the renormalisation group theory. This paper represents the first to understand this crossover. We focus attention on a physical observable which is more interesting than α^2 from a theoretical (Zimm and Stockmayer 1949, Prentis 1982), experimental (Higgins *et al* 1979) and numerical (Chen 1981, 1983) point of view. This observable is defined as the ratio R of the mean-square radius of gyration of a ring polymer to that of a linear polymer having the same number of monomers:

$$R \equiv \langle R_G^2 \rangle_{\text{ring}} / \langle R_G^2 \rangle_{\text{line}}. \tag{1.2}$$

This ratio is known to be bounded below by a universal random walk limit (Zimm and Stockmayer 1949) and bounded above by a universal self-avoiding limit (Prentis 1982) having the values:

$$R(0) = \tfrac{1}{2} \qquad R(\infty) = \tfrac{1}{2}(1 + \tfrac{13}{96}\varepsilon + \mathrm{O}(\varepsilon^2)). \tag{1.3}$$

We find that the complete crossover between these two scaling limits is characterised by a universal function $R(x)$ for $N \gg 1$. If, in addition, $g \ll 1$, then one may change variables from x to α^2 and transform $R(x)$ into a function $R(\alpha^2)$ of another well defined experimental observable α^2. This is a consistent and well defined calculation containing no adjustable parameters and yields a result that can be directly tested in an experiment. Parametrising the crossover in terms of the observable α^2 completely avoids, and does not require any understanding of, the connection between the renormalised interaction parameter x and the conventional parameter z, neither of which can be directly measured.

Section 2 contains a brief review of the renormalisation group results describing the self-avoiding limit behaviour of the ring polymer system. In § 3, the general solution to the renormalisation group equation is given which provides a description of the crossover behaviour. Further discussion is presented in § 4.

2. The self-avoiding limit

In this section, a brief summary of our previous renormalisation group theory of the ring polymer system in the self-avoiding limit will be presented. For details on the model, the perturbation theory and the renormalisation, the reader is referred to the original paper (Prentis 1982).

The model used to represent the ring polymer is a self-repelling random polygon on a lattice. The lattice is taken to be a d-dimensional cubic lattice with a lattice spacing l. A random n-gon in d dimensions is defined by a sequence of points r_i, $i = 0, 1, \ldots, n$, on the lattice from r_0 to r_n subject to the ring and connectivity constraints $r_0 = r_n$ and $|r_{i+1} - r_i| = l$, respectively. The self-repelling condition is represented by a short-ranged repulsive potential $v(r_i - r_j)$ between every pair of monomers.

The spatial correlations in the ring are determined by the correlation function $\langle \rho(x)\rho(y)\rangle$, where $\rho(x)$ is the local density of monomers at x. For a ring with n monomers, these correlations are measured in a scattering experiment at wavevector q via the structure factor $S(q, n)$. Mathematically, $S(q, n)$ is the Fourier transform of $\langle \rho(x)\rho(y)\rangle$. The radius of gyration of the ring is the correlation length (second moment) of $S(q, n)$:

$$\langle R_G^2\rangle_{\text{ring}} = -d\,\partial\ln S(q, n)/\partial q^2|_{q=0}. \tag{2.1}$$

Our previous study utilised a renormalised perturbation theory to understand the behaviour of $\langle R_G^2\rangle_{\text{ring}}$ in the self-avoiding limit. The renormalisation of the ring polymer perturbation theory is a process which converts the ill behaved perturbation expansion into a renormalised expansion which makes sense in the self-avoiding limit and can be used to extract non-perturbative information. It is a process whereby the irrelevant short distance (ultraviolet) details of the theory (which manifest themselves as poles in $\varepsilon = 4 - d$ in this formalism) are subtracted out of the perturbation theory and absorbed into a redefinition (rescaling) of the polymer variables. We merely state the final result for the radius of gyration of a large ring polymer obtained from the two-loop order diagrammatic polymer perturbation theory using the direct renormalisation scheme. For details, see Prentis (1982). The perturbation theory for $\langle R_G^2\rangle_{\text{ring}}$ is an expansion in the renormalised coupling constant g and also is a function of the renormalised monomer number N and momentum scale κ:

$$\langle R_G^2\rangle_{\text{ring}} = \tfrac{1}{6}d\kappa^{-2}(1 + \tfrac{1}{2}g(1 - c))N(1 - \tfrac{1}{2}g\ln N) + O(g^2, \varepsilon^2, g\varepsilon) \tag{2.2}$$

where

$$g = \frac{\Omega_d\kappa^{-\varepsilon}\tau_c^2}{(2\pi)^d z_3}\int d^d x\, v(x)$$

$$N = (z_2\kappa^2/\tau_c)n. \tag{2.3}$$

In this expression, $c = 0.577$ is the Euler constant, z_2 and z_3 are the chain length and coupling constant renormalisation factors and depend only on g, $\tau_c = e^{s_c}/l^2$ where s_c is the critical chemical potential for which $\langle n\rangle \to \infty$ and Ω_d is the surface area of a unit sphere in d dimensions. In the original renormalisation scheme, we employed the Laplace (grand canonical) representation of the ring polymer perturbation theory. This representation transforms the perturbation theory into an expansion which is mathematically identical to a Feynman graph expansion. The utility of this representation is that the perturbation theory is susceptible to the well developed methods of

field theory renormalisation. These include a well defined prescription for the calculation of Feynman integrals (dimensional regularisation) and for the renormalisation of the perturbation theory (minimal subtraction) (Amit 1978). The result stated in equation (2.2) is obtained from a simple inverse Laplace transformation of this grand canonical perturbation theory.

A vital property that emerges from the renormalisation group machinery is that in the self-avoiding limit, the renormalised coupling constant g takes on the well defined fixed point value given by Prentis (1982)

$$g^* = -\tfrac{1}{4}\varepsilon + O(\varepsilon^2). \tag{2.4}$$

In this limit, the expression for the radius of gyration in equation (2.2) is the perturbative representation of a scaling law characterised by the power law behaviour:

$$\langle R_G^2 \rangle_{\text{ring}} \sim N^{2\nu} \tag{2.5}$$

with the 'critical' exponent

$$\nu = \tfrac{1}{2}(1 + \tfrac{1}{8}\varepsilon + O(\varepsilon^2)). \tag{2.6}$$

A similar calculation for the linear polymer system yields

$$\langle R_G^2 \rangle_{\text{line}} = \tfrac{1}{3}d\kappa^{-2}(1 + \tfrac{1}{2}g(\tfrac{25}{12} - c))N(1 - \tfrac{1}{2}g \ln N) + O(g^2, \varepsilon^2, \varepsilon g). \tag{2.7}$$

This result, together with the equation (2.2), allows one to construct the radius of gyration ratio:

$$R = \langle R_G^2 \rangle_{\text{ring}} / \langle R_G^2 \rangle_{\text{line}} = \tfrac{1}{2}(1 - \tfrac{13}{24}g) + O(g^2, \varepsilon^2, g\varepsilon). \tag{2.8}$$

In the self-avoiding limit, $g = g^* = -\tfrac{1}{4}\varepsilon + O(\varepsilon^2)$, and we obtain the universal ratio:

$$R = \tfrac{1}{2}[1 + \tfrac{13}{96}\varepsilon + O(\varepsilon^2)] = 0.568 \qquad (d = 3). \tag{2.9}$$

It would be incorrect to use equation (2.8) as a representation of the crossover behaviour from $R = \tfrac{1}{2}$ to $R = \tfrac{1}{2}(1 + \tfrac{13}{96}\varepsilon)$ as g varies from $g = 0$ to $g = g^*$. It must be emphasised that equation (2.8) is only a perturbative representation of R and by itself cannot be used to extract the complete scaling behaviour. A more detailed analysis of the non-perturbative structure of the polymer theory using the renormalisation group equation is necessary in order to extract information on the non-perturbative scaling behaviour of R. This analysis, which follows in § 3, will demonstrate that g is not the correct scaling variable to use for a description of crossover phenomena.

3. The crossover

A complete understanding of the crossover behaviour in the ring polymer system emerges upon solving the field theoretic renormalisation group equation for all values of the coupling g. To find this general solution, we utilise the original approach of Bruce and Wallace (1976) for critical phenomena as adapted to the polymer problem by Elderfield (1980). However, our method is distinguished from these previous approaches in that we use the renormalisation group equation describing the renormalised theory rather than the bare theory. We also emphasise that our direct renormalisation theory provides a self contained and thus a simpler and more natural framework for understanding crossover phenomena in the polymer system. It should

be noted that there also exists an alternative direct renormalisation group calculation of the crossover behaviour in the linear polymer system by Oono and Freed (1982).

The renormalisation group equation is a statement of the renormalisation symmetry of the polymer system. It is a consequence of the renormalisability of the polymer theory. It transcends the perturbation theory so as to enable one to understand the non-perturbative structure of the scaling behaviour of the theory. The renormalisation group equation for the grand canonical radius of gyration (Prentis 1982) is easily Laplace transformed into the following renormalisation group equation describing the scaling behaviour of the radius of gyration of a large ring (or linear) polymer with n monomers:

$$[\kappa \, \partial/\partial \kappa + \beta(g) \, \partial/\partial g + \gamma(g) n \, \partial/\partial n] \langle R_G^2 \rangle = 0. \tag{3.1}$$

In our direct renormalisation scheme (Prentis 1982), the Wilson functions $\beta(g)$ and $\gamma(g)$ for the ring (or linear) polymer system assume the form:

$$\beta(g) = -\varepsilon g - 4g^2 + O(g^3) \qquad \gamma(g) = g + O(g^2). \tag{3.2}$$

This homogeneous equation is conveniently solved by the method of characteristics (Amit 1978). If one defines the following set of functions (renormalisation group recursion relations) of an arbitrary scale parameter b

$$(b/n(b)) \, \mathrm{d}n(b)/\mathrm{d}b = \gamma(g(b)), \qquad n(1) = n$$

$$b \, \mathrm{d}g(b)/\mathrm{d}b = \beta(g(b)), \qquad g(1) = g \tag{3.3}$$

$$\kappa(b) = b\kappa,$$

then the solution to the renormalisation group (equation (3.1)) satisfies the simple relation

$$\langle R_G^2 \rangle(n, g, \kappa) = \langle R_G^2 \rangle(n(b), g(b), \kappa(b)). \tag{3.4}$$

This relation is a realisation of the fundamental idea underlying the theory of renormalisation. That is, to provide a relation which exhibits the structure of the theory at different length (momentum) scales.

The integration of equations (3.3), using the expansions of $\beta(g)$ and $\gamma(g)$ in equation (3.2), result in the following relations, correct through first order in ε

$$\frac{g}{g(b)} \left(\frac{g(b) - g}{g - g^*} \right)^{\varepsilon/\omega} = b^\varepsilon \qquad n(b) = n \left(\frac{g(b) - g}{g - g^*} \right)^{(1-2\nu)/\omega\nu}. \tag{3.5}$$

The fixed point coupling g^*, the correction to scaling exponent ω and the polymer size exponent ν are given by the identities (Prentis 1982):

$$\beta(g^*) = 0 \Rightarrow g^* = -\tfrac{1}{4}\varepsilon + O(\varepsilon^2)$$

$$\omega = \mathrm{d}\beta(g)/\mathrm{d}g|_{g^*} = \varepsilon + O(\varepsilon^2) \tag{3.6}$$

$$\nu = (\gamma(g^*) + 2)^{-1} = \tfrac{1}{2}(1 + \tfrac{1}{8}\varepsilon + O(\varepsilon^2)).$$

With this solution of the renormalisation group equation, the complete scaling behaviour of $\langle R_G^2 \rangle_{\mathrm{ring}}$ can now be understood through order ε. Using the perturbative representation of $\langle R_G^2 \rangle_{\mathrm{ring}}$ (equation (2.2)) in conjunction with the non-perturbative renormalisation group relation (equation (3.4)), one may write

$$\langle R_G^2 \rangle_{\mathrm{ring}} = \tfrac{1}{6}d(\kappa b)^{-2}(1 + \tfrac{1}{2}g(b)(1-c))b^2 N(b)(1 - \tfrac{1}{2}g(b) \ln b^2 N(b)). \tag{3.7}$$

Note that for $N \gg 1$, the polymer perturbation theory is meaningless. However, if one makes the natural choice $b^2 N(b) = 1$, then the dangerous $\ln N$ terms are suppressed and effectively summed into exponentiation by the renormalisation group. With this choice, the crossover behaviour of a large ring polymer to order ε is described by the following scaling law:

$$\langle R_G^2 \rangle_{\text{ring}} = N\kappa^{-2}(1 - g/g^*)^{(2\nu-1)/\omega\nu} f(x) \tag{3.8}$$

where the scaling function $f(x)$ is given parametrically as

$$f(x) = \tfrac{1}{6}d(1 - p(x))^{(1-2\nu)/\omega\nu}[1 + \tfrac{1}{2}g^*(1 - c)p(x)] \tag{3.9}$$

and

$$p(x)(1 - p(x))^{-\varepsilon/2\omega\nu} = x = (g/g^*)(1 - g/g^*)^{-\varepsilon/2\omega\nu} N^{\varepsilon/2}. \tag{3.10}$$

The complete crossover is described in terms of the natural scaling variable x, in addition to a non-universal prefactor dependence on g. Note that $p(x)$ is a bounded function from $p(0) = 0$ to $p(\infty) = 1$. As a special case, in the random walk ($x \ll 1$) and the self-avoiding ($x \gg 1$) limits, we obtain the following familiar power law behaviour (with corrections):

$$\langle R_G^2 \rangle_{\text{ring}} \sim \begin{cases} N(1 + O(x)), & x \ll 1 \\ N^{2\nu}(1 + O(x^{-2\omega\nu/\varepsilon})), & x \gg 1. \end{cases} \tag{3.11}$$

An alternative non-parametric representation of the crossover behaviour is obtained by using the ε-expansion of the exponents ν and ω, together with g^*, and rearranging terms consistently to first order in ε. The result must be expressed in terms of the natural scaling variable x (and the non-universal factor $1 - g/g^*$) as dictated by the renormalisation group equation. We find

$$\langle R_G^2 \rangle_{\text{ring}} = N\kappa^{-2}(1 - g/g^*)^{1/4} f(x) \tag{3.12}$$

where

$$f(x) = \tfrac{1}{6}d[1 + x(1 + x)^{\varepsilon/8}]^{1/4}[1 - \tfrac{1}{8}\varepsilon(1 - c)x/(1 + x)] \tag{3.13}$$

and x is given in equation (3.10). This compact and convenient representation of the crossover behaviour is equivalent to that utilised by Oono and Freed (1982) to study the crossover in the linear polymer system. However, for numerical accuracy and comparison with experiment in three-dimensional space, it is advantageous to retain the parametric representation of the crossover. This enables one to use the accurate pure number values $\nu = 0.588 \pm 0.0015$ and $\omega\nu = 0.470 \pm 0.025$ as determined by the resummation of their ε-expansions for $d = 3$ (Le Guillou and Zinn-Justin 1980). These values for ν and ω represent a significant improvement over their first-order ε-expansions, especially for the exponent ω which has a particularly poorly behaved ε-expansion.

A more useful physical observable is the radius of gyration expansion factor α^2 defined by

$$\alpha^2 \equiv \langle R_G^2 \rangle / \langle R_G^2 \rangle|_{g=0}. \tag{3.14}$$

From equations (3.8) and (3.9), we find to order ε

$$\alpha^2(x, g) = \left(\frac{1 - p(x)}{1 - g/g^*}\right)^{(1-2\nu)/\omega\nu} [1 - \tfrac{1}{8}\varepsilon(1 - c)p(x)] \tag{3.15}$$

where $p(x)$ is given in equation (3.10). It is significant that $\alpha^2(x, g)$ is not a universal function of the scaling variable x only. This non-universality is a contradiction to the conventional 'two-parameter' theory (Yamakawa 1971) of the polymer excluded volume problem. This same non-universality has also been observed and discussed in the context of the linear polymer system (Oono and Freed 1982). For small g, the expansion factor $\alpha^2(x, g) \cong \alpha^2(x)$ is approximately a universal function of $x \cong (g/g^*)N^{\varepsilon/2}$. A plot of $\alpha^2(x)$ for $d = 3$ appears in figure 1.
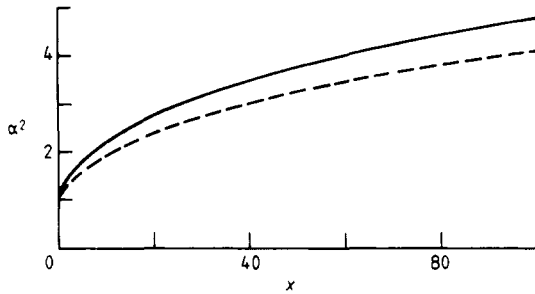

Figure 1. The radius of gyration expansion factor α^2 for a ring (full curve) and a linear (broken curve) polymer as a universal (for $g \ll 1$) function of the natural scaling variable x.

A very useful and interesting theoretical and experimental quantity is the radius of gyration ratio of a ring to that of a linear polymer having the same number of monomers. To calculate this ratio, we need the crossover scaling function for the radius of gyration of the linear polymer system. Although this function has been calculated previously (Oono and Freed 1982, Elderfield 1980), we require the form it assumes in the renormalisation formalism used here. The generality of the renormalisation group analysis of this section allows this function to be constructed simply and immediately from the perturbation expansion given in equation (2.7). To order ε, we find

$$\langle R_G^2 \rangle_{\text{line}} = N\kappa^{-2}(1 - g/g^*)^{(2\nu-1)/\omega\nu}f_{\text{line}}(x) \tag{3.16}$$

where

$$f_{\text{line}}(x) = \tfrac{1}{3}d(1 - p(x))^{(1-2\nu)/\omega\nu}[1 + \tfrac{1}{2}g^*(\tfrac{25}{12} - c)p(x)] \tag{3.17}$$

$p(x)$ is given in equation (3.10) and the exponents ν and ω are identical to those in the ring system. A graph of the expansion factor $\alpha_{\text{line}}^2(x)$ for the linear polymer system appears in figure 1. Using equations (3.9) and (3.17), the radius of gyration ratio can be written to first order in ε as

$$R(x) \equiv \langle R_G^2 \rangle_{\text{ring}} / \langle R_G^2 \rangle_{\text{line}} = \tfrac{1}{2}[1 + \tfrac{13}{96}\varepsilon p(x)] \tag{3.18}$$

with $0 \le p(x) \le 1$ determined by equation (3.10). Thus, unlike the individual radii of gyrations of a ring and a linear polymer, the crossover of their ratio $R(x)$ is described by a universal function of the scaling variable x. The range space of $R(x)$ is bounded by the finite limits characterising the universal random walk ratio $R(0) = 0.5$ and the universal self-avoiding ratio $R(\infty) = 0.568(d = 3)$.

It is convenient to re-express the polymer observables that depend on the experimentally unknown scaling variable x in terms of a more directly measurable quantity,

namely the expansion factor $\alpha^2(x, g)$ given in equation (3.15). If $g \ll 1$, then $\alpha^2(x, g) \cong \alpha^2(x)$, and the radius of gyration ratio $R(x)$ can be transformed into a universal function of α^2. There is experimental evidence that the approximation $\alpha^2(x, g) \cong \alpha^2(x)$ is valid (Oono and Freed 1982) for the large polymer system and thus $R(\alpha^2)$ provides a realistic candidate for experimental observations. A graph of $R(\alpha^2)$ for $d = 3$ appears in figure 2. As mentioned previously, an alternative non-parametric representation of $R(\alpha^2)$ can be obtained upon expanding the exponents ν, ω and all expressions consistently to order ε. The result is:

$$R(\alpha^2) = \tfrac{1}{2}[1 + \tfrac{13}{96}\varepsilon((\alpha^8 - 1)/\alpha^8)]. \tag{3.19}$$
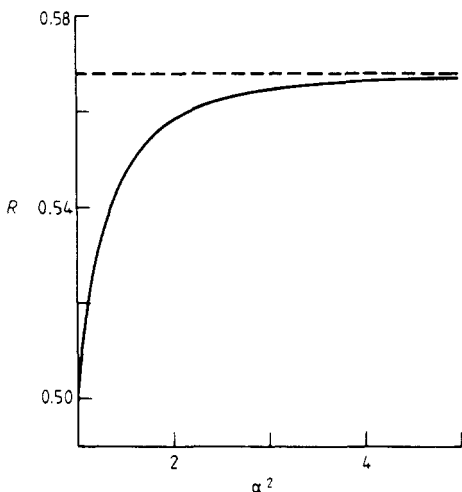

Figure 2. The radius of gyration ratio $R = \langle R_G^2 \rangle_{\mathrm{ring}}/\langle R_G^2 \rangle_{\mathrm{line}}$ as a universal (for $g \ll 1$) function of the ring polymer expansion factor.

4. Discussion

We have calculated the crossover between the random and the self-avoiding behaviour of the radius of gyration of a large ring polymer. The results, correct through first order in ε, have been obtained from first principles using a direct field theoretic realisation of the renormalisation group ideas. The expansion factor for the mean square radius of gyration is not a universal function of the natural scaling variable x. The non-universality appears via a dependence on g which becomes weak for $g \ll 1$. In contrast, the radius of gyration ratio $R(x)$ of a ring to a linear polymer is a universal function of x. Furthermore, $R(x)$ is bounded above by the finite self-avoiding limit $R(\infty) = \tfrac{1}{2}(1 + \tfrac{13}{96}\varepsilon)$ and below by the random walk limit $R(0) = \tfrac{1}{2}$. The convergence of $R(x)$ to well defined and universal finite limits is a distinct advantage in experimental observations. An important prediction of this convergence is that the polymer system should be within one percent of the self-avoiding limit $R(\infty)$ if the ring expansion factor $\alpha \geq 1.6$.

For the linear polymer system, there exists a similar and often studied ratio which does not exhibit a useful crossover behaviour. This is the ratio $A(x)$ of the radius of gyration to the end-to-end distance of a large linear polymer. In the random and

self-avoiding limits (Witten and Schäfer 1978), $A(x)$ is known to assume the universal values:

$$A(x) = \frac{\langle R_G^2 \rangle_{\text{line}}}{\langle R_e^2 \rangle_{\text{line}}} = \begin{cases} \frac{1}{6}, & x = 0 \\ \frac{1}{6}(1 - \frac{1}{96}\varepsilon + O(\varepsilon^2)), & x = \infty. \end{cases} \tag{4.1}$$

The complete crossover behaviour of this ratio, to order ε, follows simply from the renormalisation group analysis presented here. The generality of this analysis allows the immediate construction of the crossover function:

$$A(x) = \frac{1}{6}(1 - \frac{1}{96}\varepsilon p(x)). \tag{4.2}$$

Here $0 \leq p(x) \leq 1$ is given in equation (3.10). This example illustrates the common structure of any given universal observable and the simplicity to obtain this form given the asymptotic (fixed point) limit.

Unfortunately, in this example, the predicted range of $A(x)$ is too small for experimental resolvability. This property is in contrast to the much larger range space of the ratio $R(x)$ involving the ring polymer (equation (3.18)). This is a manifestation of the greater sensitivity to the excluded volume interaction that exists in the ring system when compared with the linear polymer system. This sensitivity is to be expected due to the more compact structure assumed by the ring polymer molecule. It is this sensitivity that endows the ring polymer system with properties, such as $R(x)$, that render it more susceptible to experimental observation.

There exists a controversy regarding the upper bound $R(\infty)$ characterising the self-avoiding limit of the radius of gyration ratio $R(x)$. The recent series (Chen 1981, 1983) of computer experiments to simulate the statistics of large ring and linear polymers predict that $R(\infty) = 0.568$. This result is remarkably identical to our renormalisation group prediction of $R(\infty) = 0.568$ for $d = 3$ (equation (3.18)). The phenomenological 'swollen gaussian' models of the polymer system lead to results that are inconsistent with one another and with the computer study of rings and chains (Chen 1983, Baumgärtner 1982).

Although there exist large ring polymers in biological systems, such as circular DNA, the synthesis of large ring molecules in the laboratory appears to be very difficult (Geiser and Hocker 1980, Higgins *et al* 1979). The neutron scattering experiment (Higgins *et al* 1979) using synthetic cyclic and linear poly (dimethylsiloxane) predicts a radius of gyration ratio of 0.526 ± 0.05. Although consistent with our renormalisation group prediction, it is uncertain whether the conditions of the experiment (solvent, polymer length, polydispersity) are sufficient to realise the asymptotic limit $x = \infty$ (Edwards *et al* 1983). In addition, the existence of knotted structures in the ring polymer system presents a very complex and interesting topological constraint whose effect on the ring behaviour is difficult to ascertain (Elderfield 1982).

The present work describing the crossover from the random to the self-avoiding behaviour in the ring polymer system provides additional data that is more realisable in laboratory experiments. We hope that this work will stimulate further investigation into understanding the behaviour of the ring polymer system.

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