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Coil–globule transition: comparison of field theoretic and conformational space formulations

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Abstract. The description of polymer collapse is presented both in conformational space and field theoretic forms along the same lines as we have provided for treating the theta point (tricritical) region for polymers. This enables the problem to be considered in terms of the same measurable parameters which are used in the theta and good solvent regimes, thereby removing a serious deficiency of some previous treatments where the basic parameters of the theory are not directly measurable. We consider the self-consistency and range of validity of various mean field approaches and demonstrate the need for reinterpretation of some previous works. We generalise prior descriptions of the coil–globule transition to include contributions from fluctuations and to determine the excitations of the globule. In addition, criteria are derived giving the limits of stability of the globular phase. Our analysis underlies the profound role played by the effective three-body interaction upon the nature of the transition, explaining the source of previously suggested ‘non-universality’ of this transition.

1. Introduction

The collapsed globular state of polymers is the normal state of most biological macromolecules such as proteins. DNA in living cells is densely packed and is effectively in the collapsed state (Tanaka 1983). In addition, many interesting phases of block copolymers involve collapsed states of one of the blocks. Hence, the study of the collapsed polymer as well as the coil–globule transition poses an important scientific problem. It is natural to first attack this problem for simple uncharged flexible homopolymers before considering the more complicated biopolymers with specific monomer sequences, local interactions, and charged groups.

According to Flory (1953) a single flexible polymer chain, immersed in a solvent, can exist in either a swollen or collapsed state depending on the solvent quality which, in turn, is determined by a delicate balance between the polymer–polymer and polymer–solvent interactions. The net effects of these interactions are represented in terms of effective two- and three-body interactions as described below. In good solvents it is found experimentally that the magnitude of the two-body interactions is directly related to the second virial coefficient. The polymer chain is defined to be ideal (Gaussian) at the theta temperature Θ where the second virial coefficient vanishes. This theta

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temperature serves as the borderline between the good solvent (somewhat above Θ) and the poor solvent (below Θ) regimes. (For convenience, we consider Θ to be an upper Θ -temperature for the purposes of this discussion as the treatment of a lower Θ -temperature follows simply.) As the temperature T is raised above Θ , the polymer swells, while below Θ it dramatically shrinks in size. The two- and three-body interactions in the theta and poor solvent domains are used to represent the counteracting attractive and repulsive portions of the actual interactions, so in good solvents, where polymer-polymer interactions are primarily repulsive, the three-body terms are unnecessary.

The importance of the collapsed state of polymers has led to its recent study by numerical simulations (Baumgärtner 1982, Kremer *et al* 1981) and experimental methods (Pritchard and Caroline 1980, Nishio *et al* 1982). It is still necessary, however, to understand the connection between the theoretical parameters in the description of the collapsed state and those used empirically and theoretically for polymers in the theta region (Kholodenko and Freed 1984a, b, Douglas and Freed 1984) and in good solutions, in order to develop a predictive theory of the coil-globule transition. For instance, the extensive work of Lifshitz *et al* (1978) uses a set of parameters which are not experimental measurables, making many predictions difficult, if not impossible, to verify. Despite the theoretical advances in treating the collapsed polymer, a number of fundamental problems remain unsolved; these are described below after briefly discussing the status of some of the available theory.

Average polymer properties, such as the mean square end-to-end vector $\langle R^2 \rangle$, the coherent scattering function $S(\mathbf{k})$, etc, are believed (de Gennes 1975, 1978) to be described by a single crossover scaling function. For $\langle R^2 \rangle$ this is written as

$$\langle R^2 \rangle^{1/2} = N^\nu f(gN^\phi), \quad (1.1)$$

where N is the chain length, g the effective two-body interaction strength (proportional to $1 - (\Theta/T)$ with T the absolute temperature), ν is the size exponent in the theta solvent regime, ϕ is a crossover exponent and f is a scaling function. Our previous chain space renormalisation group calculation (Kholodenko and Freed 1984a) derives an explicit form like (1.1) in the theta point ('tricritical') region and provides an estimate of the collapse transition temperature. These calculations show that the scaling form (1.1) is rigorously valid only in the theta point regime. It is somehow necessary to match the theta regime results with those valid in the good solvent limit for $T > \Theta$ and with those for collapsed polymers ($T < \Theta$) in order to achieve a smooth crossover and a comprehensive theory of the possible states of a flexible polymer in terms of a small set of measurable phenomenological parameters.

The coil-globule crossover has been the subject of Monte Carlo calculations using a finite scaling analysis (Baumgärtner 1982). Baumgärtner (1982) and Kremer *et al* (1981) show that the scaling form (1.1) is valid in the theta and good solvent regimes, but below the theta point the data are rather inconclusive and 'distinct and systematic deviations from the expected scaling laws are apparent' (Kremer *et al* 1981). Technical difficulties are very serious in applying numerical simulations to polymers with large N in the coil-globule transition region, so these highly useful methods cannot yet adequately treat the transition.

Hence, it is necessary to study the coil-globule transition by purely theoretical means. Kremer *et al* (1981) summarises the large body of theoretical work to date.

All these previous theories are of the mean field variety and are inconclusive in many respects. Arguments still exist as to the order of the transition with some claiming that it is a second-order transition (Moore 1977) while others find that it is sometimes first or second order (Lifshitz *et al* 1978). Baumgärtner (1982) quotes de Gennes as believing that the collapse transition should be associated with the 'tricritical' region and therefore be first order, although he states that 'no evidence for tricriticality of the collapse has been demonstrated so far, neither by experiment nor by computer simulation'. Earlier computer simulations by Domb (1974) suggest a first-order transition.

Here we extend previous mean field descriptions to include *fluctuations* about the mean field, an analysis of the stability of the globular state, and an approximate calculation of the thermal excitations of the globule. The treatment of fluctuations is shown to be crucial in determining the stability of the globular state. In the transition region the fluctuations become comparable to the mean field, so purely mean field methods are insufficient to determine the order of the coil-globule transition. Mean field theories are only useful for describing the *final* collapsed state; they must be modified to treat the transition. The order of the collapse transition may only be approximated with mean field theories in terms of differences between the coil before transition and the globule after it.

In order to permit us to include the effects of fluctuations, it is necessary to considerably extend and generalise previous mean field descriptions of the coil-globule transition. We consider this transition using *the same microscopic model* as in our treatment of the theta point region (Kholodenko and Freed 1984a, b) in order to permit the development of a unified description of the states of a flexible polymer as a function of temperature using the same phenomenological parameters for the coil, globule and swollen states. Besides reproducing old results and adding contributions from the important fluctuations, our work clarifies and reinterprets the physical meaning and determines the range of validity of some of these previous results.

Section 2 introduces the model within the same conformational space functional integral formalism that has been used to describe the theta point and good solvent regimes. Self-consistent field theory and the equivalent renormalised perturbation expansions are introduced. Approximations are established which are necessary to reduce these equations to those postulated previously, as 'mean field theories' of polymer collapse. Deficiencies of these approximations are indicated. The inability of treating the fluctuations systematically by these methods and the necessity to correctly define the stability criteria lead us to introduce an equivalent field theory formulation in § 3 in which the mean field and fluctuation contributions can clearly be separated. Exact solutions for the spherical globule are obtained in one dimension and are used to construct reasonable approximations in d dimensions when the globule radius is large compared with the thickness of the surface layer. Calculations are provided for the free energy and coil radius which are shown in § 5 to be unaffected by the contributions from fluctuations, except in the region of the coil-globule transition. Two stability conditions are derived for the transition temperature, depending on the magnitude of the three-body interaction parameter, and the thermal excitations of the globule are approximately calculated. The computed transition temperature and coil and globule free energies are used in § 6 to evaluate the specific heat of the collapse transition. The crucial role of the three-body interaction parameter (as well as other non-universal terms in the free energy that have previously been neglected) in determining the order of the transition is manifested by the calculated heat of transition.

2. Description of the model

The same model is used here as for the theta point domain (Kholodenko and Freed 1984a, b). The dimensionless ‘Hamiltonian’ is taken to be

$$H[c(\tau)] = \frac{1}{2} \int_0^N d\tau |\dot{c}(\tau)|^2 + (2!)^{-1} g_0 \int_0^N d\tau \int_0^N d\tau' \delta[c(\tau) - c(\tau')] + (3!)^{-1} w_0 \int_0^N d\tau \int_0^N d\tau' \int_0^N d\tau'' \delta[c(\tau) - c(\tau')] \delta[c(\tau) - c(\tau'')], \quad (2.1)$$

where $c(\tau)$ represents a continuous chain conformation in d -dimensional space, τ is the contour variable, $\tau \in [0, N]$, $\dot{c} \equiv dc/d\tau$ and g_0 and w_0 are two- and three-body coupling constants, respectively. The system of units is defined by the relation $c(\tau) = (d/l)^{1/2} r(\tau)$ where l is the effective step length, and $r(\tau)$ is the spatial position of the polymer segment located at the contour position τ . The model (2.1) is of a polymer without a detailed specific structure in the collapsed state, so it is insufficient for describing different globule phases and the transitions between them.

Dimensional analysis of the model (2.1) is straightforward and was given previously (Oono *et al* 1981, Kholodenko and Freed 1983a). If L is some, as yet arbitrary, length scale and $[\tau]$ designates the dimensions of τ then $[\tau] = [l] = [N] = L$, $[c] = L^{1/2}$, $[g] = L^{(d-4)/2}$ and $[w] = L^{d-3}$.

The fixed end-vector partition function is defined as

$$G(\mathbf{R}, N; g, w) = \int_{c(0)=0}^{c(N)=(d/l)^{1/2} \mathbf{R}} \mathcal{D}[c(\tau)] \exp\{-H[c(\tau)]\}. \quad (2.2)$$

A perturbation treatment of (2.2) is generated by expanding the second and third terms of (2.1) from the exponent of (2.2). This expansion is conveniently represented diagrammatically using the rules described in Kholodenko and Freed (1983a, 1984a). The lowest-order expansion in g_0 and w_0 is depicted in figure 1.

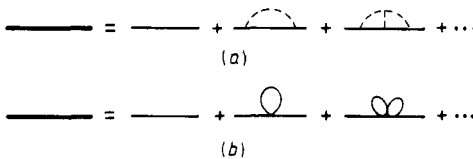


Figure 1. Lowest-order terms in the perturbation expansion for the fixed end-vector partition function (2.2) in (a) the ‘time’ representation and (b) the ‘space’ representation. The diagram rules are given in Kholodenko and Freed (1984a).

2.1. Self-consistent field or renormalised perturbation approximation

When the dimensionless Hamiltonian (2.1) is taken in the limit of a vanishing cut-off, the perturbation calculations encounter singularities which must be removed in a consistent way by a renormalisation procedure. If the *renormalised* expansion parameters are *not* small in some sense, then the perturbation expansion is of no use. However, the diagrammatic analysis allows, in principle, the investigation of arbitrary orders of perturbation theory. Following Dyson (1949) we may introduce the ‘renormalised’ Dyson equation, depicted in figure 2 where the box with the letter M inside

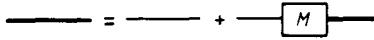


Figure 2. Dyson's equation for the fixed end-vector partition function (2.2). The heavy line is the full G , the light one is G_0 , while the box designates the 'mass' operator.

defines the 'mass' operator. Dyson's equation for the fixed end-vector partition function (2.2) is given analytically as

$$G(\mathbf{R}, N) = G_0(\mathbf{R}, N) + \int_0^N d\tau \int_0^\tau d\tau' \int d\mathbf{r}' \int d\mathbf{r}'' G_0(\mathbf{R}, \mathbf{r}'; N - \tau) \times M(\mathbf{r}', \mathbf{r}''; \tau - \tau') G(\mathbf{r}'', \tau). \tag{2.3}$$

Here M is the full mass operator, i.e. the sum of all compact irreducible diagrams, and g_0 and w_0 need not be small. (The explicit dependence of M on coupling constants g_0 and w_0 is omitted for simplicity.) The free propagator G_0 satisfies the differential equation (Freed 1972)

$$(\partial/\partial N - \frac{1}{2}\nabla^2)G_0(\mathbf{R}, N) = \delta(\mathbf{R})\delta(N) \tag{2.4}$$

in the chosen system of units. Applying the operator $(\partial/\partial N - \frac{1}{2}\nabla^2)$ to both sides of (2.3) produces the equivalent integro-differential equation

$$(\partial/\partial N - \frac{1}{2}\nabla^2)G(\mathbf{R}, N) = \delta(\mathbf{R})\delta(N) + \int_0^N d\tau \int d\mathbf{r} M(\mathbf{R}, \mathbf{r}; N - \tau)G(\mathbf{r}, \tau). \tag{2.5}$$

When $\mathbf{R} \neq 0$ and $N \neq 0$ the delta functions in (2.5) may be neglected, but in the final analysis the delta functions and the Green function character of $G(\mathbf{R}, N)$ must be taken into account.

Equation (2.5) is of no use unless the mass operator is specified. This can only be done within some approximation scheme. An example of the first-order renormalised approximation to M has been considered by us (Kholodenko and Freed 1983b) in the description of the strong coupling limit of Feynman's polaron problem. By analogy with that work, the leading approximation to M is depicted in figure 3. Comparison between figure 1 and figure 3 shows that we have simply replaced the internal zeroth-order propagators in the second and third diagrams on the right-hand side of figure 1(a) by the full propagators. Within this approximation (2.5) is reduced to the simpler nonlinear form

$$\begin{aligned} (\partial/\partial N - \frac{1}{2}\nabla^2)G(\mathbf{R}, N) - g \int_0^N d\tau G(\mathbf{R}, \mathbf{R}; N - \tau)G(\mathbf{R}, \tau) \\ + w \int_0^N d\tau \int_0^\tau d\tau' G(\mathbf{R}, \mathbf{R}; N - \tau')G(\mathbf{R}, \mathbf{R}; \tau' - \tau)G(\mathbf{R}, \tau) \\ = \delta(N)\delta(\mathbf{R}) \end{aligned} \tag{2.6}$$

and g and w are interpreted as some sort of renormalised interaction parameters. Since

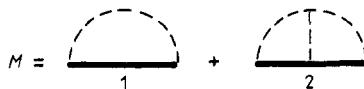


Figure 3. First-order renormalised perturbation theory (same as self-consistent field) equation for the mass operator.

our interest lies in attractive two-body interactions, a minus sign is introduced and for attractive interactions g is defined as $g > 0$. The approximation (2.6) also follows upon introduction of a Markovian self-consistent field formulation to (2.2) as given (Freed 1972) for the case where $w \equiv 0$.

2.2. Previous assumptions of ground state dominance

Lifshitz *et al* (1978) assume that the approximate Green function G in (2.6) can further be approximated by the so-called approximation of ground state dominance,

$$G(\mathbf{R}, \mathbf{R}'; \tau) \doteq \Psi(\mathbf{R})\Psi(\mathbf{R}') \exp(\tau E) \quad (2.7)$$

with E a ground state energy per unit length of polymer. This approximation is motivated by the belief that the spectrum of G has a low-lying discrete portion, so the lowest (largest) eigenvalue must dominate. These previous works do not test the self-consistency of the assumption (2.7). This important question is addressed below, where it is shown that much of this previous work must be reinterpreted. The use of (2.7) in (2.6) reduces the latter to

$$(E - \frac{1}{2}\nabla^2)\Psi(\mathbf{R}) - gN\Psi^3(\mathbf{R}) + \frac{1}{2}wN^2\Psi^5(\mathbf{R}) = 0, \quad \mathbf{R} \neq 0. \quad (2.8)$$

If we redefine the function Ψ by

$$\Psi \Rightarrow N^{-1/2}\Psi \quad (2.9)$$

and assume that $\Psi(\mathbf{R})$ is real, then equation (2.8) is converted to that *postulated ad hoc* by Moore (1977)

$$(E - \frac{1}{2}\nabla^2)\Psi(\mathbf{R}) - g\Psi^3(\mathbf{R}) + \frac{1}{2}w\Psi^5(\mathbf{R}) = 0, \quad \mathbf{R} \neq 0. \quad (2.10)$$

Unlike Lifshitz *et al* (1978) our derivation of (2.10) does not invoke any thermodynamic analogies or assumptions like the 'polymer chain is replaced by a set of broken monomers' etc. The ansatz (2.7) is valid only in the limit $\tau \rightarrow \infty$, but (2.6) contains integrals over all τ , so the validity of the assumption (2.7) must be tested.

2.3. The full self-consistent Green function

Alternatively, define the Laplace transform of a general function $f(N)$ by

$$F(s) = \int_0^\infty dN \exp(-sN)f(N) \quad (2.11)$$

and its inverse by

$$f(N) = (2\pi i)^{-1} \int_C ds \exp(sN)F(s), \quad (2.11a)$$

with C the usual Laplace contour. Then, by applying the Laplace transform to (2.6) we obtain

$$(s - \frac{1}{2}\nabla^2)G(\mathbf{R}; s) - gG(\mathbf{R}, \mathbf{R}; s)G(\mathbf{R}; s) + w[G(\mathbf{R}, \mathbf{R}; s)]^2G(\mathbf{R}, s) = 0, \quad \mathbf{R} \neq 0. \quad (2.12)$$

Equation (2.12) can be made to resemble (2.10) by expressing the Green function in

the form

$$G(\mathbf{R}, \mathbf{R}'; s) = \Psi_{>}(\mathbf{R}_{>}, s) \Psi_{<}(\mathbf{R}_{<}, s) \quad (2.13)$$

where $\mathbf{R}_{>}$ is the greater of \mathbf{R} and \mathbf{R}' , $\Psi_{>}$ and $\Psi_{<}$ satisfy the appropriate boundary conditions for large and small $|\mathbf{R}|$ separately, and the Wronskian is defined to be unity. In contrast to the ansatz (2.7) where τ is assumed large, equation (2.12) combined with (2.13) is an *exact* representation of the first-order renormalised perturbation theory.

In general, the Green function has a spectral expansion

$$G(\mathbf{R}, \mathbf{R}'; \tau) = \sum_n \Psi_n(\mathbf{R}) \Psi_n^*(\mathbf{R}') \exp(\tau E_n) \quad (2.14)$$

which when Laplace transformed is converted into

$$G(\mathbf{R}, \mathbf{R}'; s) = \sum_n (E_n - s)^{-1} \Psi_n(\mathbf{R}) \Psi_n^*(\mathbf{R}'). \quad (2.15)$$

In contrast, the assumption (2.7) just gives

$$G(\mathbf{R}, \mathbf{R}'; s) = (E - s)^{-1} \Psi(\mathbf{R}) \Psi^*(\mathbf{R}'), \quad (2.16)$$

where the subscript $n=0$ is dropped. The assumption (2.7) is invalid if the solutions to (2.12) and (2.13) cannot be represented in the simple form of (2.16). In § 4 we provide an exact solution for $G(\mathbf{R}, \mathbf{R}, s)$ in one dimension and an approximate three-dimensional one which demonstrates the invalidity of the simple model (2.7) used as the basis of previous mean field theories because the solutions display a *continuous* spectrum as a function of s . A difficulty with the assumption (2.16) is readily apparent by rescaling the function $\Psi \rightarrow (E - s)^{1/2} \Psi$ whereupon (2.16) and (2.12) reduce to (2.10) with the substitution $E \rightarrow s$. Hence, Ψ depends in a rather non-trivial fashion (see § 4) on s in contrast to the assumption in (2.16).

Equations (2.12) and (2.13) are free of unwarranted assumptions and can be used as the basis for our discussion. However, this mean field or renormalised perturbation approach suffers from a number of serious deficiencies. Firstly, it is unclear as to how corrections are to be incorporated apart from just evaluating successive orders of diagrams and investigating the conditions under which the corrections are small. A full theory requires the calculation of the contributions from fluctuations in the globule shape. The validity of the description of the globular state is dependent on having the fluctuations small enough and on explicitly satisfying conditions for the stability of the globule state. The dominant fluctuation terms are not readily apparent to us using this renormalised perturbation formulation. In addition, it is unclear to us how to use the self-consistent field method to determine the conditions for the stability of the globular state and thereby to locate the coil-globule transition.

These important questions are addressed in the following sections by employing a field theoretic formulation which is fully equivalent to the use of (2.1) and (2.2) but which permits us systematically to determine the mean field results, the contributions from fluctuations, and the conditions for stability of a globular phase. The mean field equations are like (2.10) with $E \rightarrow s$ and slightly different coefficients. The solutions do not, however, conform with the previous assumption (2.16).

3. Field theoretic description for the case of coil-globule transition

In our treatment of the theta point ('tricritical') region for polymers (Kholodenko 1984a, b) we show that the Laplace transform of the distribution function (2.2) can be associated with the $n \rightarrow 0$ limit of the $O(n)$ component $\phi^4 - \phi^6$ field theory as follows:

$$G(\mathbf{R}, \mathbf{0}; s) = \lim_{n \rightarrow 0} \sum_{i=1}^n n^{-1} \mathcal{N}^{-1} \int \mathcal{D}[\Phi] \Phi_i(\mathbf{R}) \Phi_i(\mathbf{0}) \exp(-S[\Phi]) \tag{3.1}$$

where the action S is given in d -dimensional space as

$$S[\Phi] = \frac{1}{2} \int d^d x \left[\frac{1}{2} (\nabla \Phi)^2 + s \Phi^2 + (g/4) (\Phi^2)^2 + (w/24) (\Phi^2)^3 \right] \tag{3.2}$$

and

$$\Phi^2 \equiv \sum_{i=1}^n \Phi_i^2, \quad (\nabla \Phi)^2 = \sum_{i=1}^n (\nabla \Phi_i)^2, \quad \mathcal{N} = \int \mathcal{D}[\Phi] \exp(-S[\Phi]). \tag{3.1a}$$

The limiting procedure $n \rightarrow 0$ is to be taken at the very end of the calculations. The coefficients of the $(\Phi^2)^2$ and $(\Phi^2)^3$ terms in (3.2) are chosen to provide identical results as from the conformation space functional integral (2.2).

Our previous theta point region calculations take w to be positive and g small, while the collapse transition occurs for g larger and negative. Small g enables the use of perturbation expansions, but when g exceeds a certain value (Kholodenko and Freed 1984a) the perturbation expansion is invalid. Then an alternative non-perturbative method is required to describe the globular state. It is not self-evident *a priori* that the coil-globule transition must take place *within or at the edge* of the theta point domain because of the finite size of the system under consideration. It is only when the polymer length N tends to infinity that a standard first-order transition could possibly appear. In the spirit of our previous works we treat the case of *finite* N directly. The asymptotic limit of $N \rightarrow \infty$ is *only* considered at the end of the calculations.

When g or w or both are not small and a perturbation expansion is inapplicable, two types of non-perturbative approaches are available as follows.

(a) Analyse the higher-order terms by use of the Schwinger-Dyson equation in analogy with the analysis in § 2.

(b) Use the saddle point approximation to evaluate the functional integral (3.1). It is instructive to discuss both approaches to determine the approximations required to produce a mean field theory similar to (2.12).

3.1. General theory

Following Brézin *et al* (1976) let $J(\mathbf{x})$ be an arbitrary function; then use of the identity

$$\begin{aligned} 0 &= \int \mathcal{D}[\Phi] \frac{\delta}{\delta \Phi} \exp\left(-S[\Phi] + \int \mathbf{J} \cdot \Phi\right) \\ &= \int \mathcal{D}[\Phi] \left[\frac{\delta S}{\delta \Phi} - \mathbf{J} \right] \exp\left(-S[\Phi] + \int \mathbf{J} \cdot \Phi\right) \end{aligned} \tag{3.3}$$

produces the equation

$$[\mathcal{L}(\delta/\delta \mathbf{J}(\mathbf{x})) - \mathbf{J}(\mathbf{x})]Z(\mathbf{J}) = 0 \tag{3.4}$$

where the generating functional $Z(J)$ as defined as

$$Z(J) = \mathcal{N}^{-1} \int \mathcal{D}[\Phi] \exp\left(-S[\Phi] + \int d^d x J(x) \cdot \Phi(x)\right) \quad (3.5)$$

and $\mathcal{L}[\Phi]$ is defined from the relation $S[\Phi] = \int d^d x \mathcal{L}[\Phi(x)]$.

The normalisation factor \mathcal{N} is defined from the condition

$$Z(J=0) = 1. \quad (3.5a)$$

Equation (3.4) gives rise to the Dyson-Schwinger hierarchy of equations which are obtained by subsequent functional differentiation of (3.4). Introducing the $n \rightarrow 0$ procedure into (3.4) produces the equation of motion for the longitudinal Green function as

$$(s - \frac{1}{2}\nabla^2)G_{ii}^{(1)}(\mathbf{x}, \mathbf{y}; s) - (g/2)G_{iiii}^{(2)}(\mathbf{x}, \mathbf{x}, \mathbf{x}, \mathbf{y}; s) + (w/8)G_{iiiiii}^{(3)}(\mathbf{x}, \mathbf{x}, \mathbf{x}, \mathbf{x}, \mathbf{x}, \mathbf{y}; s) = \delta(\mathbf{x} - \mathbf{y}) \quad (3.6)$$

where equation (3.5a) is used and, by definition,

$$G_{ii}^{(1)}(\mathbf{x}, \mathbf{y}; s) = [(\delta/\delta J_i(\mathbf{x})) (\delta/\delta J_i(\mathbf{y})) Z(J)]_{J=0}$$

etc, for the higher Green functions setting $J=0$ in (3.6). It is found that equation (2.12) (*not* (2.10)) can be obtained from (3.6) if we introduce the Markovian decoupling (Freed 1972) of the $G^{(2)}$ and $G^{(3)}$ propagators, sum over i indices, and formally define the $n \rightarrow 0$ limit. Use of standard field theory, therefore, permits us to study the mean field and higher-order terms in a systematic fashion.

3.2. Saddle point approximation and fluctuations

Since our prime interest lies in determining the mean field and the contribution from fluctuations about the mean field, it suffices to evaluate the functional integral (3.1) by the saddle point method with subsequent expansions about the saddle point. The saddle point solution is determined from the equation

$$\delta S[\Phi] / \delta \Phi|_{\Phi=\Phi_c} = 0. \quad (3.7)$$

The stability of this solution is determined from the requirement that the operator

$$M(\Phi_c) = \delta^2 S / \delta \Phi_i \delta \Phi_j |_{\Phi=\Phi_c} \quad (3.8)$$

has a spectrum of only positive eigenvalues. Because of the $n \rightarrow 0$ limit, we only need to calculate the longitudinal part of the operator (3.8) associated with the 'symmetry breaking' direction of Φ_c in $O(n)$ space.

Introducing the definition $\Phi = \Phi_c + \delta\Phi$ into both the numerator and denominator of (3.1) and (3.1a), expansion in powers of $\delta\Phi$ and retention of only terms through $(\delta\Phi)^2$ in the usual fashion yields

$$G(\mathbf{R}, \mathbf{0}, s) = \Phi_c(\mathbf{R}, s)\Phi_c(\mathbf{0}, s) + G_c(\mathbf{R}, \mathbf{0}; s) + \dots \quad (3.9)$$

where $G_c(\mathbf{R}, \mathbf{0}; s)$, the contribution from Gaussian fluctuations, is the Green function of the operator $M(\Phi_c)$ and $\Phi_c = n\Phi_c$ where n is a unit vector such that $n^2 = 1$. Hence, Φ_c is just the 'classical' solution to (3.7) for the one-component case as explained in § 4. The quantity Φ_c represents a 'broken symmetry' phase which is effectively the

mean field solution for the collapsed state. The finite size of the polymer implies that this mean field solution is of necessity inhomogeneous as explicitly demonstrated by the calculation of Φ_c and G_c in § 4.

4. Saddle point calculations

Brézin *et al* (1977) and Zinn-Justin (1981) show in other contexts that the saddle point solution for $O(n)$ theory can be obtained in terms of that for a one-component field theory with the action (3.2). The one-component field saddle point equation (3.7) gives

$$(s - \frac{1}{2}\nabla^2)\Phi_c - (g/2)\Phi_c^3 + (w/8)\Phi_c^5 = 0. \quad (4.1)$$

Once Φ_c is determined from (4.1), then the saddle point for the n -component case is

$$\Phi_c = n\Phi_c \quad (4.2)$$

where $n^2 = 1$.

Equation (4.1) is virtually identical to the ground state dominance mean field equations (2.10) with $E \leftrightarrow s$ and some minor changes in numerical coefficients. The change $E \leftrightarrow s$ with s a Laplace variable, however, has important implications. Ignoring differences between $\Psi_>$ and $\Psi_<$ also makes (4.1) the same form as (2.12). This correspondence between the field theory and chain space formulations is expected from our previous work on the good solvent (Kholodenko and Freed 1983a) and theta point (Kholodenko and Freed 1984a) regions.

4.1. Solution of mean field equations

We consider only the spherically symmetric solution to (4.1) for Φ_c . When the globule is in its ground state, surface tension prevents the formation of mean field configurations departing from spherical. The spherical solution to (4.1) satisfies the equation

$$\frac{1}{2} \left(\frac{d^2}{dr^2} + \frac{d-1}{r} \frac{d}{dr} \right) \Phi_c = \Phi_c V(\Phi_c) \quad (4.3)$$

where d is the dimension of space and

$$V(\Phi_c) = s - (g/2)\Phi_c^2 + (w/8)\Phi_c^4. \quad (4.3a)$$

The dimensional analysis of § 2 enables us to introduce the dimensionless quantity $x = s^{1/2}r$. Defining $\Phi_c = (2s/g)^{1/2}\chi(2^{1/2}x)$ converts (4.3) to

$$\left(\frac{d^2}{dx^2} + \frac{d-1}{x} \frac{d}{dx} \right) \chi(x) = \chi(x)(1 - \chi^2 + \alpha\chi^4) \quad (4.4)$$

where $\alpha = sw/2g^2$.

We specialise to $d = 3$ and note that as $x \rightarrow \infty$ the solution $\chi(x) \rightarrow 0$ because the globule is a finite system. For large globules the outer regions of x can be studied by neglecting the d/dx term provided that the solution $\chi(x)$ dies off for large x faster than some power of x . In fact, the action (3.2) is finite only if $\chi^2 x^{3+\varepsilon} \rightarrow 0$ as $x \rightarrow 0$ for any $\varepsilon \rightarrow 0^+$. Straightforward analysis of (4.4) in the $x \rightarrow \infty$ limit precludes a power law type solution, so the neglect of the $x^{-1}d/dx$ term here is justified. Hence, for $x \rightarrow \infty$

the solution to (4.4) is the same as that of the one-dimensional problem

$$(d^2/dx^2)\chi(x) = \chi(x)(1 - \chi^2 + \alpha\chi^4), \quad x \rightarrow \infty. \quad (4.5)$$

When $\chi \rightarrow 0$, an analysis of (4.4) shows that the only consistent solution is one for which χ is a constant. This homogeneous solution follows from (4.4) as

$$\chi^2 = A^2 \equiv (2\alpha)^{-1}[1 \pm (1 - 4\alpha)^{1/2}], \quad x \leq x_0. \quad (4.6)$$

Both signs provide possible solutions to (4.5), but in § 4.4 the lower sign is shown to correspond to a globular state. When the globule is large, i.e. N is large, and when the inhomogeneous surface thickness is much smaller than the globule radius $r_0 = s^{-1/2}x_0$, our approximate three-dimensional solution is then obtained by matching (4.6) at $x = x_0$ onto the solution to (4.5) of

$$\chi^2(x) = a[(\frac{1}{4} + \frac{1}{2}a)^2 - \frac{1}{3}\alpha]^{-1}, \quad x > x_0, \quad (4.7)$$

where

$$a = |B| \exp[(x - x_0)/2^{1/2}], \quad B = A^{-2}\{2 + 2[(\alpha A^4/3) - (A^2/2) + 1]^{1/2} - A^2/2\},$$

and x_0 is an integration constant related to the globule radius. The matching condition is that χ^2 or (4.7) satisfies $\chi^2(x_0) = A^2$. As $\chi \rightarrow \infty$ the solution (4.7) indeed satisfies the condition $\chi^2 x^{3+2\epsilon} \rightarrow 0$. When the surface layer thickness ξ becomes comparable to the globule radius r_0 , the $(2/x)(d/dx)$ term in (4.4) should be retained and an improved solution determined. Since this procedure probably requires numerical analysis, we continue to use (4.6)–(4.7) in this transition zone as a zeroth-order approximation.

It is instructive to compare our solution (4.6) and (4.7) with that of previous workers. First of all, the condition of ground state dominance (Lifshitz *et al* 1978, Moore 1977) has not been invoked. Consequently the solution (4.6) and (4.7) is formally valid for *any* s . The spectrum is continuous without a discrete bound state. Unlike the variational ansatz of Moore (1977) under the assumption of ground state dominance, our solution is *exact* in one dimension and requires the knowledge of only one parameter x_0 in three dimensions. (Moore introduces four parameters for $d = 3$.)

Our solution (4.6)–(4.7) alone does not provide any indication of how x_0 is to be determined. However, in § 4.4 below it is shown that both x_0 and the sign in (4.6) are uniquely specified by the imposition of additional physical constraints. It turns out that x_0 depends upon the Laplace parameter s (for given values of g and w). Physical quantities after inverse Laplace transformation must be real, but in s space it is not absolutely necessary for quantities to be real. However, if A^2 in (4.6) is required to be real, restrictions are imposed on the allowed range of s with a bound coinciding with the ‘ground state energy’ of Moore (1977). In summary, we conclude unlike Moore (1977) and Lifshitz *et al* (1978) that the mean field solution (4.6) and (4.7) is *not a dominant ground state contribution* coming from the *discrete* spectrum of the self-consistent mean field equation. In fact, the solution (4.6)–(4.7) determines a *unique* ground state for the globule as is demonstrated in §§ 5.1, 5.2 where we show that it is the surface fluctuations which contribute to a discrete spectrum of thermal excitations of the globule.

4.2. Globule free energy and density

The parameter x_0 is found by considering the calculation of the polymer free energy and density. Using the functional integral formulation of § 2 it follows that the

Helmholtz free energy F for the polymer chain is represented in terms of $G(\mathbf{r}_1, \mathbf{r}_2, s)$ as

$$-\frac{F}{kT} = \ln \left[\mathcal{L}^{-1} \left(\int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{r}_2; s) \right) \right] \quad (4.8)$$

where T is the absolute temperature, k is Boltzmann's constant and \mathcal{L}^{-1} is the inverse Laplace transform operator as defined in (2.11a).

In critical phenomena with $n \neq 0$ the classical term $S[\Phi_c]$ dominates the free energy, so the polymer case displays an essential difference in this respect. The monomer density at the point \mathbf{R} is given in a Hartree (self-consistent field (Freed 1972)) approximation in terms of G as

$$\rho(\mathbf{R}) = \frac{\int_0^N d\tau \int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{R}; N - \tau) G(\mathbf{R}, \mathbf{r}_2; \tau)}{\int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{r}_2; N)} \quad (4.9)$$

with G the full Green function (3.8). By construction of (4.9) the density has the normalisation

$$\int d^d \mathbf{R} \rho(\mathbf{R}) = N. \quad (4.10)$$

It is this normalisation constraint which is used in § 4.4 to determine the globule 'radius' x_0 . Combining (4.9) and (4.10) and taking Laplace transforms of both sides of the equation

$$\int_0^N d\tau \int d^d \mathbf{R} \int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{R}; N - \tau) G(\mathbf{R}, \mathbf{r}_2; \tau) = N \int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{r}_2; N) \quad (4.11)$$

we obtain the s -space normalisation condition

$$\int d^d \mathbf{R} \int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{R}; s) G(\mathbf{R}, \mathbf{r}_2; s) = -\frac{\partial}{\partial s} \int d^d r_1 \int d^d r_2 G(\mathbf{r}_1, \mathbf{r}_2; s). \quad (4.12)$$

The Green functions in (4.8), (4.9) and (4.11) are presumed to be exact and to have an expansion in terms of spherical harmonics $Y_{lm}(\Omega)$. Introduction of this expansion yields

$$\begin{aligned} \int d^3 r_1 \int d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s) &= \int d r_1 r_1^2 d\Omega_1 \int d r_2 r_2^2 d\Omega_2 \sum_{lm;l'm'} G_{lm'l'm'}(\mathbf{r}_1, \mathbf{r}_2; s) \\ &\times Y_{lm}(\Omega_1) Y_{l'm'}^*(\Omega_2) \equiv (4\pi)^2 \int r_1^2 d r_1 \int d r_2 r_2^2 G_{0000}(\mathbf{r}_1, \mathbf{r}_2; s), \end{aligned} \quad (4.13)$$

so only the spherically symmetric portion of G is required to compute the free energy in (4.8). In general, the normalisation condition (4.10) has contributions from the non-spherical parts of $G(\mathbf{r}_1, \mathbf{r}_2; s)$, but here we retain the leading spherical portions.

4.3. Steepest descents Laplace inversion

It is convenient to express the free energy in the form

$$\exp(-F/kT) = (2\pi i)^{-1} \int_C \exp\left(sN + \ln \int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s)\right). \quad (4.14)$$

The complexity of the actual form of G precludes the analytic evaluation of (4.14). However, when N is sufficiently large, but finite, it should be possible to approximate (4.14) by steepest descents. First of all, it is necessary to calculate the saddle point s^* which is determined from the solution of the equation

$$N = -\left(\frac{\partial}{\partial s} \int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s)\right) \bigg/ \left(\int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s)\right) \bigg|_{s=s^*}. \quad (4.15)$$

Inversion of (4.15) produces a solution for s^* in the form $s^* = f(N, g, w)$. Combining (4.12) with (4.15) produces the equation

$$N = \left(\int d^3 R \int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{R}; s) G(\mathbf{R}, \mathbf{r}_2; s)\right) \bigg/ \left(\int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s)\right) \bigg|_{s=s^*}. \quad (4.16)$$

It is instructive to evaluate (4.15) and (4.16) using approximations to G of increasing accuracy. First we consider the leading mean field part of (3.8), and later the fluctuations are included. Insertion of $G(\mathbf{r}_1, \mathbf{r}_2; s) = \Phi_c(\mathbf{r}_1)\Phi_c(\mathbf{r}_2)$ into (4.16) simply yields

$$N = \int d^3 R \Phi_c^2(\mathbf{R}, s) \big|_{s=s^*}, \quad (4.17)$$

where $\Phi_c^2(\mathbf{R}, s)$ is given by (4.6)–(4.7). Inversion of this equation gives x_0 as a function of s^* and, of course, N , g and w .

Moore (1977) has postulated equation (4.17) for s^* , the ‘ground state energy’. The approximations inherent in obtaining (4.17) are clear in our analysis. In order to further reduce (4.17) to the result of Moore, the tail part of χ^2 given by (4.7) is dropped, and only (4.6) is retained. For the special case $\alpha_m = \frac{1}{4}$, related to Moore’s ‘ground state energy’, A^2 in (4.6) is unique, and the evaluation of (4.17) readily yields

$$N \doteq (4\pi/3)r_0^3(2g/w), \quad \alpha_m = \frac{1}{4}, \quad (4.18)$$

where r_0 is the globule radius. Converting back to ordinary units, (4.18) is equivalent to

$$r_0 \doteq (3wN/8\pi g)^{1/3}(1/3)^{1/2} \equiv (3N/4\pi\rho_G)^{1/3}(1/3)^{1/2}, \quad \alpha_m = \frac{1}{4}, \quad (4.18a)$$

where the globular ‘density’ of Lifshitz *et al* (1978) is defined as $\rho_G = 2g/w$. The variable ρ_G and a chemical potential with respect to the addition of monomers to a polymer are the basic parameters of the theory of Lifshitz *et al* (1978). Since these quantities are not directly physically measurable, there is no way of testing their theory. Our approach, by contrast, uses the traditional parameters g and w whose values and temperature dependence can, at least in principle, be determined in the theta point and good solvent regions. When $g \rightarrow 0$, the globule radius tends towards the unphysical limit $r_0 \rightarrow \infty$. Equation (4.18a) is clearly invalid for $g \rightarrow 0$ because the globule-coil transition must intervene before g gets too small in order that r_0 remain finite for N finite.

Now we consider the full solution for $\Phi_c(\mathbf{R}, s)$ along with steepest descents Laplace inversion to exhibit how similar results with somewhat different physical interpretation are obtained with the more rigorous approach. These methods are then used in § 5 to include the effects of fluctuations. Let $s_0 = g^2/2w$, so that Φ_c^2 is written for $0 \leq x \leq x_0$ as $\Phi_c^2 = (2g/w)\{1 \pm [1 - (s/s_0)]^{1/2}\}$. In order that Φ_c^2 be real it is necessary that $0 \leq s \leq s_0$. The saddle point is written in the form $s^* = s_0 - \delta s$, defining δs . A full analysis shows

δs to be much smaller than s_0 . Before providing the details, it is instructive to analyse the implications of the result (4.18) upon the full solution (4.7).

In terms of r and r_0 the parameter a in (4.7) is

$$a = |B|[(g^2/4w)(s_0/s)(r-r_0)] \equiv |B| \exp[(r-r_0)/\xi],$$

where the screening length ξ is defined in ordinary units as

$$\xi^2 = (s/s_0)(4w/g^2)l/3 \xrightarrow{s=s_0} 8l/3g\rho_G. \quad (4.19)$$

This screening length for $s = s_0$ coincides with that introduced by Edwards (1966) (see also de Gennes 1979 and Freed 1983) for semidilute solutions. The definition (4.19) has the screening length ξ diverge when $g \rightarrow 0$. The solution (4.7) associates this screening length with the thickness of the globule surface layer, so our approximation is well defined only when the ratio of the globule surface thickness ξ to its radius,

$$(\xi/r_0)^2 \propto w^{1/3} g^{-4/3} N^{2/3}, \quad s \approx s_0, \quad (4.20)$$

is much smaller than unity. Hence, equation (4.18) is a good approximation when

$$g \gg w^{1/4} N^{-1/2}, \quad s \approx s_0. \quad (4.21)$$

When $\xi \sim r_0$, we expect to have the polymer in or near the coil-globule transition region. Corrections from the $(2/r)(d/dr)$ term in (4.3a) are then necessary, but we use (4.6)–(4.7) as a zeroth-order approximation because improved solutions require numerical analysis.

4.4. Determination of saddle point s^*

Assume that (4.21) is satisfied and approximate the integral in (4.15) by the homogeneous portion of Φ_c for $r < r_0$ to give

$$\begin{aligned} -N &= (\partial/\partial s) \ln\{(4\pi r_0^3/3)^2(2g/w)[1 \pm (1 - (s/s_0))^{1/2}]\}_{s=s^*} \\ &= 6 \frac{d \ln r_0(s^*)}{ds^*} \mp \frac{1}{2s_0} \frac{1}{[1 - (s^*/s_0)]^{1/2}} \frac{1}{\{1 \pm [1 - (s^*/s_0)]^{1/2}\}} \end{aligned} \quad (4.22)$$

where the previously noted dependence of r_0 on s^* is explicitly included. Within the same approximation the normalisation condition (4.12) produces

$$\begin{aligned} 6 d \ln r_0(s^*)/ds^* &= -(4\pi r_0^3/3)(2g/w)\{1 \pm [1 - (s^*/s_0)]^{1/2}\} \\ &\quad \pm \{2s_0[1 - (s^*/s_0)]^{1/2}[1 \pm (1 - (s^*/s_0))^{1/2}]\}^{-1}. \end{aligned} \quad (4.23)$$

Combining (4.22) and (4.23) to eliminate $d \ln r_0(s^*)/ds^*$ leads to

$$N = (4\pi/3)r_0^3(2g/w)\{1 \pm [1 - (s^*/s_0)]^{1/2}\}. \quad (4.24)$$

Applying d/ds^* to both sides of (4.24) generates after some algebra

$$d \ln r_0(s^*)/ds^* = \pm \{6s_0[1 - (s^*/s_0)]^{1/2}[1 \pm (1 - (s^*/s_0))^{1/2}]\}^{-1}. \quad (4.25)$$

Substituting (4.25) back into (4.22) finally gives an equation for s^* in terms of N and s_0 only as

$$-N = \pm \{2s_0[1 - (s^*/s_0)]^{1/2}[1 \pm (1 - (s^*/s_0))^{1/2}]\}^{-1}. \quad (4.26)$$

Given that N is non-negative, the only possibility in (4.26) involves the lower sign, corresponding to the solution in (4.6) with the negative sign. In addition, s^* is required to be real and less than or equal to s_0 . These considerations imply that (4.26) becomes

$$2Ns_0 = [1 - (s^*/s_0)]^{-1/2} \{1 - [1 - (s^*/s_0)]^{1/2}\}^{-1}. \quad (4.27)$$

The solution of (4.27) for large N produces the leading terms

$$s^* = s_0 [1 - (16N^2 s_0^2)^{-1} + \dots], \quad (4.28)$$

verifying our statement that $\delta s \ll s_0$ and that the condition (4.21) holds for a globule with a narrow surface layer. Insertion of (4.28) into (4.24) and use of the minus sign enables the determination of r_0 as

$$r_0(s^*) = (3Nw/8\pi g)^{1/3} (1 + w/6Ng^2 + \dots). \quad (4.28a)$$

Equation (4.28), condition (4.21) and the homogeneous portion of Φ_c^2 produce our initial estimate of the globule free energy as

$$-F/kT \approx s_0 N + O(\ln N) \approx g^2 N/2w. \quad (4.29)$$

This agrees with the final conclusion of Moore and Lifshitz *et al*, but for somewhat different physical reasons.

The remainder of the steepest descents calculation requires a demonstration that the function $\exp\{\ln[\int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s)] + sN\}$ has a maximum at $s = s^*$, so we now show that

$$\left[\frac{\partial^2}{\partial s^2} \ln \left(\int \int d^3 r_1 d^3 r_2 G(\mathbf{r}_1, \mathbf{r}_2; s) \right) \right]_{s=s^*} < 0. \quad (4.30)$$

Using (4.22), (4.25) and (4.27) it is found that

$$\begin{aligned} & \frac{\partial^2}{\partial s^2} \ln \left(\int \int G(\mathbf{r}_1, \mathbf{r}_2; s) \right) \Big|_{s=s^*} \\ &= -\{ (s_0/\delta s)^{1/2} - [1 - (\delta s/s_0)^{1/2}]^{-1} \} / 4 (s_0 \delta s)^{1/2} [1 - (\delta s/s_0)]^{1/2} \end{aligned} \quad (4.30a)$$

with $\delta s = s_0 - s^* > 0$ given in (4.28), thereby satisfying the requirement of (4.30) of a minimum. The contribution of (4.30a) to the free energy from a steepest descents integration is of the order of $\ln N$ and can be ignored with respect to (4.29).

Substitution of s^* from (4.28) into (4.7) and neglect of the $O(N^{-2})$ correction term converts the tail of Φ_c into the form

$$\chi^2 = \frac{(4/3)(1+2/\sqrt{3}) \exp[(r-r_0)/\xi]}{\{1 + (1+2/\sqrt{3}) \exp[(r-r_0)/\xi]\}^2 - \frac{4}{3}}, \quad r \geq r_0, \quad (4.31)$$

where $\alpha \rightarrow \frac{1}{4}$ in the definition of A^2 in (4.6). When $|r-r_0|/\xi \gg 1$, equation (4.31) reduces to

$$\chi^2 = 4\{1 + \exp[(r-\hat{r}_0)/\xi]\}^{-1} = 2\{1 - \tanh[(r-\hat{r}_0)/2\xi]\}, \quad (4.32)$$

where \hat{r}_0 differs from r_0 by an additive constant. The last form in (4.32) is identical to the interfacial profile of the van der Waals theory of liquid-vapour phase transitions (Widom 1981) which indicates the close relationship between the coil-globule and liquid-vapour phase transitions, an analogy we consider further in § 6 where the order of the transition is discussed.

Our analysis of the mean field solution and steepest descents integration establishes only *necessary but not sufficient* conditions for the existence of a saddle point (i.e. mean field) solution of (3.6). Sufficient conditions emerge from a treatment of the contributions of the fluctuations to the free energy.

5. Stability of globule and thermal excitations

Globule stability is determined, in part, by the condition that the operator $M(\Phi_c)$ in (3.7) be non-negative, i.e. that its eigenvalues all be positive. The solution for Φ_c now enables this question to be studied in detail along with the determination of contributions from the fluctuation term G_c in (3.8) to the globule free energy (4.8).

Because of the $n \rightarrow 0$ limiting procedure, it is only necessary to consider the longitudinal part of the operator M which follows from (3.2) and (3.7) as

$$M(\Phi_c) = [-\frac{1}{2}\nabla^2 + s - \frac{3}{2}g\Phi_c^2(\mathbf{r}) + \frac{5}{8}w\Phi_c^4(\mathbf{r})]\delta(\mathbf{r} - \mathbf{r}'). \tag{5.1}$$

This follows upon writing M in terms of the longitudinal M_L and transverse M_T parts as $M_{ij} = n_i n_j M_L + (\delta_{ij} - n_i n_j) M_T$. The Gaussian fluctuations give M_L^{-1} and M_T^{-1} contributions to $\langle \delta\Phi \delta\Phi \rangle$, and only the former survives in the $n \rightarrow 0$ limit.

The mean field Φ_c^2 is given in (4.6) and (4.7) with $x_0 = s^{1/2}r_0$ and r_0 the globule radius to be determined from the saddle point equation (4.15) and normalisation (4.11). When the globule is stable, it is to be anticipated that fluctuations provide small contributions, and $r_0(s^*)$ with fluctuations should depart little from (4.28a). Hence, one of the purposes of this section is the determination of the conditions under which Φ_c and s^* of § 4 are qualitatively unchanged by the fluctuations.

In the traditional theory of phase transitions, the eigenvalues of $M(\Phi_c)$ describe the possible excitations of the system, whereas here s is a Laplace variable, so this simple interpretation must be applied with some caution. It is only for values of s contributing to physical observables that $M(\Phi_c)$ be required to be a non-negative operator. For large N it is only necessary to consider $s \approx s^*$, greatly simplifying the analysis.

We begin by assuming that the globule has a surface thickness ξ , which from (4.7) is generally represented as

$$\xi^2 = 2/s \equiv (s/s_0)(4w/g^2), \tag{5.2}$$

and is small compared with the square of the radius r_0 . Taking r_0 from (4.24) with s^* replaced by s and combining it with (5.2) leads to the condition $(\xi/r_0)^2 \ll 1$ for a narrow surface layer of

$$gN^{1/2} \gg w^{1/2}(64\pi/3)(s_0/s)^{3/4}\{1 - [1 - (s/s_0)]^{1/2}\}^{1/2}. \tag{5.2a}$$

When $s \approx s^* \approx s_0$, then (5.2a) reduces to the inequality (4.21) apart from numerical factors. Our restriction $\xi^2/r_0^2 \ll 1$ in (5.2a) is imposed in order that (4.6) and (4.7) be a good approximation. If $\xi \sim r_0$, the same general methods can be pursued, but the approximate solution (4.6)–(4.7) becomes inadequate, and other more accurate solutions for Φ_c are required, probably necessitating numerical methods. The spectrum of $M(\Phi_c)$ and the contribution from fluctuations are, therefore, accurately studied under the conditions of (5.2a) with $s \approx s_0$, while when $\xi \sim r_0$ in the transition region, our calculations represent only a qualitative description.

For $s \approx s^*$ the substitution of (4.6) and (4.32) into (5.1) for the fluctuation kernel produces an operator similar to that used in the liquid drop model of the atomic nucleus (Bohr and Mottelson 1974). This analogy between nuclear physics and the present problem is somewhat useful. Potentials of this form are known as Saxon-Woods type potentials, and they have both discrete and continuum spectra which are often approximated either by a square well potential or by a harmonic oscillator potential if only the lowest excitations are of interest. In general, the lowest eigenvalue of $M(\Phi_c)$ can also be determined variationally.

5.1. Stability criterion

Given the condition $\xi^2/r_0^2 \ll 1$, it is permissible to introduce a 'square well' approximation to Φ_c , taking it to be equal to (4.6) for $x \leq x_0$ and zero for $x > x_0$. This assumption leads to the vanishing of (4.3a) for $x \geq x_0$ and implies

$$(w/8)\Phi_c^4 = (g/2)\Phi_c^2 - s, \quad x \leq x_0, \quad (5.3)$$

so we can define the quantity

$$\begin{aligned} K(s) &\equiv -2[s - (3g/2)\Phi_c^2 + (5w/8)\Phi_c^4] \\ &= 8s_0[1 - (s/s_0)]^{1/2}\{1 - [1 - (s/s_0)]^{1/2}\}, \quad x \leq x_0. \end{aligned} \quad (5.4)$$

A full analysis with (5.4) shows that $\delta s = s_0 - s \ll s_0$, for s in the vicinity of s^* , but it is much simpler to invoke this as an assumption, showing that the final results are consistent. When $\delta s \ll s_0$ we find

$$K(s) \approx 8(s_0 \delta s)^{1/2}. \quad (5.5)$$

The spectrum of the operator $M(\Phi_c)$ then follows from

$$[-\frac{1}{2}\nabla^2 - \frac{1}{2}K(s)]\lambda_n(\mathbf{r}) = E_n\lambda_n(\mathbf{r}), \quad 0 \leq r \leq r_0, \quad (5.6)$$

$$[-\frac{1}{2}\nabla^2 + s]\lambda_n(\mathbf{r}) = E_n\lambda_n(\mathbf{r}), \quad r_0 \leq r < \infty. \quad (5.7)$$

By analogy with the liquid drop model of the nucleus (Bohr and Mottelson 1974) the spherically symmetric ($l=0$) solutions describe contractions or expansions of the globule, and the $l=1$ terms represent a uniform translation of the globule as a whole. Only terms with $l \geq 2$ describe surface oscillations. Arbitrary l could be treated easily, but they naturally yield higher E_n than for $l=0$, so the evaluation of the spherical case is all that is required to ensure $E_n > 0$ for all n . In the present problem equation (4.13) implies that only the consideration of $l=0$ is required.

Equations (5.6)–(5.7) are supplemented by the boundary conditions that G_c is finite when $r \rightarrow 0$ and $G_c \rightarrow 0$ when $r \rightarrow \infty$. It is clear that (5.6) and (5.7) possess a continuous spectrum of eigenvalues for $E > s$, but we seek to determine when lower discrete eigenvalues may violate the stability condition $E_n(s) > 0$ for $s \approx s^*$. Standard methods for this square well problem can be used to generate the transcendental s -dependent eigenvalue equation

$$[2E + K(s)]^{1/2} \cot\{r_0[2E + K(s)]^{1/2}\} = -[2(s - E)]^{1/2}. \quad (5.8)$$

Note from (5.4) that $K > 0$ for $s < s_0$, but it becomes complex for $s > s_0$. Since our saddle point s^* is real and satisfies $s^* \leq s_0$, only the real eigenvalues of (5.8) are considered. It is obvious from (5.6) and (5.7) that possible real eigenvalues for $K(s) > 0$ may arise for $E > -K(s)/2$, so stability is not automatically assured.

Define $x = r_0(2E + K)^{1/2} > 0$ and $y = r_0[2(s - E)]^{1/2} > 0$, so (5.8) can be converted to the pair of equations

$$x^2 + y^2 = r_0^2[2s + K(s)], \quad y = -x \cot x. \tag{5.9a, b}$$

Specialising to $s = s_0 - \delta s$ with $\delta s \ll s_0$ converts (5.9a) into

$$x^2 + y^2 = 2s_0r_0^2[1 + 4(\delta s/s_0)^{1/2}]. \tag{5.10}$$

Equations (5.9b) and (5.10) may be solved graphically, as depicted in figure 4, to yield discrete values of E for given g, w and N . By definition x and y are non-negative, so solutions to (5.9b) and (5.10) exist only for $x \geq \pi/2$. We now consider the conditions under which (5.9b) and (5.10) yield $E < 0$, since this leads also to the stability condition $E > 0$. When $E < 0$, the definition of y implies $y^2 > 2r_0^2s_0$ for $\delta s \ll s_0$. Hence (5.10) and $x \geq \pi/2$ produce the inequalities

$$(\pi/2)^2 \leq x^2 = 2s_0r_0^2[1 + 4(\delta s/s_0)^{1/2}] - y^2 < 8s_0r_0^2(\delta s/s_0)^{1/2}. \tag{5.11}$$

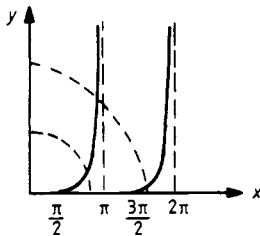


Figure 4. Graphical solution of (5.9)–(5.10).

Stability requires the absence of roots for $E < 0$, and consequently the reversal of signs in (5.11). Use of δs from (4.28) then yields the stability condition

$$r_0^2 \leq \pi^2 N/8. \tag{5.11a}$$

Then the value of r_0 in (4.28a) converts (5.11a) into

$$gN^{1/2} \geq w(2)^{3/2}(3/\pi). \tag{5.12}$$

If $\xi \sim r_0$, then only a single inequality appears in (5.2a). Simple Flory-type mean field calculations (Ptitsyn *et al* 1968) show a perceptible coil–globule transition with a sharp drop in coil radius only when w is small, $w < 1$. When w is small, our condition (5.2a) (even with a single inequality) for $\xi < r_0$ is stronger than the stability criterion (5.12).

Assuming the condition (5.11a) is obeyed, then equations (5.9b) and (5.10) can be graphically solved for the real roots E_n , whose number increases as $2s_0r_0^2$ increases. When $(2s_0)^{1/2}r_0$ lies between $[n\pi/2]$ and $[(n + 1)\pi/2]$ for some integer n , there are exactly n possible roots. Since $\frac{1}{2}(\xi/r_0)_{s=s_0} = [(2s_0)^{1/2}r_0]^{-1}$, the occurrence of more discrete levels in the spectrum of $M(\Phi_c)$ implies a narrower boundary layer for the globule.

5.2. Fluctuations and thermal excitations of the globule

Given the discrete and continuous eigenfunctions of $M(\Phi_c)$, it is possible to evaluate G_c of (3.8) from its spectral decomposition. In order to prove that the fluctuations do

not appreciably alter s^* and measurable properties given the stability conditions, it is necessary to determine G_c as a function of s , so that s^* and r_0 can be computed from (4.15) and (4.16) with the full G of (3.8). Using the square well approximation as above, it is straightforward to determine the $l=0$ Green function of $M(\Phi_c)$ as

$$G_c(\mathbf{r}, \mathbf{r}'; s)|_{l=0} = 2(r_{>}r_{<}K^{1/2})^{-1} \sin(r_{<}K^{1/2}) \cos(r_{>}K^{1/2}) [1 + \gamma(s) \tan(r_{>}K^{1/2})], \quad (5.13)$$

$$r, r' \leq r_0$$

and

$$\gamma(s) = [(\frac{K}{2s})^{1/2} \sin(r_0 K^{1/2}) - \cos(r_0 K^{1/2})] / [\sin(r_0 K^{1/2}) + (\frac{K}{2s})^{1/2} \cos(r_0 K^{1/2})], \quad (5.14)$$

where $r_{>} = \max(r, r')$, $r_{<} = \min(r, r')$, the s dependence of K is not explicitly represented, and we drop the tail portion with r or $r' > r_0$ since we expect its contribution to the free energy (4.14) to be small for $\xi/r_0 \ll 1$.

Integration of G_c over $d^3 r d^3 r'$ and inverse Laplace transformation provide contributions to the globule partition function of the form $e^{s_i N}$ if G_c of (5.14) has poles at $s = s_i$. Such contributions from poles physically correspond to the thermal excitations of the whole globule from its ground state with $N(s^* - s_i)$ the excitation free energies. The square well provides some approximation to these excitations coming from the poles of equation (5.14) given by

$$(2s)^{1/2} = -[K(s)]^{1/2} \cot\{r_0[K(s)]^{1/2}\}. \quad (5.15)$$

Equation (5.15) has a structure similar to (5.8). The graphical solution of (5.15) is facilitated by defining $h = K^{1/2}(s)/2s_0^{1/2}$ and then inverting to find $s = s_0 \Lambda(h)$. It is readily determined that h lies in the range $0 \leq h \leq \frac{1}{2}$ as s ranges between zero and s_0 and that Λ has two branches $\Lambda_{>}$ and $\Lambda_{<}$ for s in this range. Let $\eta = 2s_0^{1/2} r_0$ ($\eta \gg 1$ gives a narrow boundary layer) so the roots of (5.15) follow from

$$\Lambda(h) = -\sqrt{2} h \cot(\eta h), \quad 0 \leq h \leq \frac{1}{2}, \quad (5.16)$$

$$s_{>}/s_0 \equiv \Lambda_{>}(h) = \frac{1}{2} + h^2 + (\frac{1}{2})(1 - 4h)^{1/2}, \quad (5.16a)$$

$$s_{<}/s_0 \equiv \Lambda_{<}(h) = \frac{1}{2} + h^2 - (\frac{1}{2})(1 - 4h)^{1/2}. \quad (5.16b)$$

The threshold for roots is at about $\eta = 4.9$, which gives $\xi/r_0|_{s_0} \approx 0.57$, while for $\eta > (2n+1)\pi$ or $\xi/r_{0s_0} \approx 2^{3/2}/(2n+1)\pi$ there can be up to n roots coming from both (5.16a) and (5.16b) when they are combined with (5.16). An increase in the number of solutions of (5.15) now directly corresponds to increasing the number of globule excitations as well as the narrowness of its boundary layer. Note that $K(s)$ is real only for $s < s_0$, so possible real roots lie in the range $0 \leq s_i \leq s_0$. The range of h implies $0 \leq \Lambda_{<} \leq \frac{3}{4}$ and $\frac{3}{4} \leq \Lambda_{>} \leq 1$. Hence, (5.16a) may yield low-lying excitations (assuming, as verified below, that $s^* \approx s_0$ emerges from the full treatment with G_c) when roots are obtained from (5.16) and (5.16b) for $s_{>} = s_0$. However, solution $(s_{>})_i = s_0$ cannot occur because (5.16b) implies that $\Lambda_{>} > 1$ only for $h = 0$. Taking this limit in (5.16) would require $\eta = -(2)^{-1/2}$ which is physically forbidden. Hence, equation (5.16) has solutions only for $s_i < s_0$.

When $N \rightarrow \infty$, a contribution to the partition function from $\mathcal{L}^{-1} \iint \Phi_c(\mathbf{r}_1, s) \Phi_c(\mathbf{r}_2, s)$, involving $\exp(s^* N)$ with $s^* \rightarrow s_0$ as $N \rightarrow \infty$, dominates over the contributions from the globule excitations with $s_i < s_0$. It remains, however, to consider the additional portion

of G_c , other than the contributions from the poles s_i , in the saddle point and normalisation equations (4.15) and (4.16). Integration of (5.13) over the globule of radius $r_0(s)$ reduces to

$$\iint d^3r_1 d^3r_2 G_c(\mathbf{r}_1, \mathbf{r}_2; s) = 4(4\pi)^2 [K(s)]^{-5/2} \int_0^{[K(s)]^{1/2} r_0} dy y (\sin y - y \cos y) \times (\cos y + \gamma(s) \sin y). \quad (5.17)$$

It is possible to evaluate the integral in (5.17) and proceed with solution of (4.15) and (4.16) using (5.17) with the contribution of $\Phi_c \Phi_c$, but the algebra is very involved, and the final results yield $s^* = s_0$ again when (5.2a) is satisfied. It is much simpler, however, to demonstrate that (5.17) gives a negligible contribution to the free energy in the saddle point approximation of § 4.

We simplify the analysis by writing $s^* = s_0 - \delta s$ with $\delta s < s_0$, so that in this region $[K(s)]^{1/2} r_0|_{s^*} = N^{-1/6} (2)^{1/2} (3w/8\pi g)^{1/3}$ which tends to zero for fixed g and w as $N \rightarrow \infty$. The globule stability condition (5.12) converts this to an inequality

$$[K(s)]^{1/2} r_0|_{s^*} < w^{1/6}/2 \quad (5.18)$$

which for small w (Ptitsyn *et al* 1968) permits us to take $[K(s)]^{1/2} r_0 \ll 1$ to simplify (5.17) to

$$\iint G_c \approx [2(4\pi)^2 r_0^5/45][1 + O(Kr_0^2)], \quad (5.19)$$

where $\gamma(s)$ from (5.19) is taken as non-singular to treat these contributions from G_c not involving the excited states of the globule.

Combining (5.19) with our previous mean field portion in braces in the first line of (4.22) leads to

$$\iint d^3r_1 d^3r_2 [\Phi_c(\mathbf{r}_1, s) \Phi_c(\mathbf{r}_2, s) + G_c(\mathbf{r}_1, \mathbf{r}_2; s)] \approx \left(\frac{4\pi r_0^3}{3} \right)^2 \left\{ \frac{2g}{w} \left[1 - \left(\frac{\delta s}{s_0} \right)^{1/2} \right] + \frac{2}{45r_0} \right\}. \quad (5.20)$$

The estimate of the added term from G_c is reduced to the calculation of the ratio of its contribution to that involving the $(\delta s/s_0)^{1/2}$. This ratio of $(\delta s/s_0)^{1/2}/(w/45gr_0)$ is approximated by use of our previously evaluated s^* in (4.28) to give

$$\left(\frac{\delta s}{s_0} \right)^{1/2} \left(\frac{45gr_0}{w} \right) \Big|_{s=s^*} = \frac{45w^{1/3}}{4(N^{1/2}g)^{4/3}} \left(\frac{3}{\pi} \right)^{1/3} \ll \frac{(3^3)(5)}{4^5\pi} = 0.003, \quad (5.21)$$

where the last inequality follows from the condition (5.2a) of a narrow globule surface region compared with r_0 . Hence, when $\xi^2 \ll r_0^2$, the fluctuation part from G_c makes a negligible contribution to the globule free energy, so its alteration of s^* is ignored. At the limit of stability (5.12), the ratio on the left-hand side of (5.21) becomes of the order of unity, and fluctuations provide a non-negligible contribution, as expected in the coil-globule transition region.

Our calculations employ the approximation throughout that the surface thickness ξ be much smaller than the homogeneous density inner globule radius r_0 . The theory can be applied for ξ comparable to r_0 , but in this case an improved approximation to (4.6) and (4.7) must be invoked, perhaps using a variational approximation based on

(3.6) in order to include corrections from the $[(d-1)/r](d/dr)$ term of (4.3). Tail portions of Φ_c would then also be required in evaluating $\iint d^3r_1 d^3r_2 \Phi_c(r_1, s)\Phi_c(r_2, s)$, a task which is possible, but tedious, analytically with (4.6) but which probably becomes prohibitive with an improved solution. In addition, the above estimate of the fluctuation part $\iint d^3r_1 d^3r_2 G_c(r_1, r_2; s)$ indicates that it is not negligible at the limits of globule stability. It is possible that at this stability limit poles in G_c lead to a quasi continuum of low-lying excitations which ultimately destroy the globule stability in the transition region. Hence, the treatment of the transition region, where $\xi \sim r_0$, follows by the methods developed here, but the analysis is much more involved.

6. Thermodynamics of the coil-globule transition

Finite polymers, i.e. finite N , cannot have a true phase transition, a situation already well understood for the helix-coil transition which only becomes a first-order phase transition when $N \rightarrow \infty$. Hence, the 'transition' is a smeared one over a range ΔT . Inside this transition zone, we have $\xi \sim r_0$ and some rather complicated algebra. However, for N large the size of the transition zone ΔT must narrow, and it is meaningful to estimate the properties of the transition by comparing the coil and globule at either end of the transition zone. This procedure departs from the traditional approach of comparing the two phases at the same temperature where their chemical potentials are equal. However, we can adopt the reasonable assumption that the free energy of the metastable coil or globule phases vary little over the temperature range ΔT of the transition zone. Consequently, we compare the coil free energy at $T_c + \Delta T$ with that of the globule at $T_c - \Delta T$, where T_c is the centre of the transition zone, in order to describe the thermodynamics of the coil-globule transition.

We estimate T_c as the temperature at which $\xi \sim r_0$, since for w small, as anticipated from experiments, this gives a stronger constraint than the stability condition. Assuming w to be weakly temperature dependent, the coupling constant g_c at T_c is obtained from using an equality in (5.2a) along with $s^* \sim 0(s_0)$ to yield

$$g_c N^{1/2} \approx w^{1/2} (64\pi/3). \quad (6.1)$$

The coil radius at T_c is approximated by substitution of (6.1) into (4.28a) as

$$r_{0|g=g_c} = (3/\pi)^{1/3} \frac{1}{8} N^{1/2} w^{1/6} (\frac{1}{3}J)^{1/2} \quad (6.1a)$$

which is proportional to the free coil $N^{1/2}$ dependence with a w -dependent coefficient that is both difficult to separate experimentally and difficult to calculate accurately with the approximation (4.6) and (4.7). Hence, the transition begins in the region where the polymer is nearly ideal, so the coil state before onset of collapse is well described as a perturbed coil with weakly attractive two-body interactions and repulsive three-body ones.

We have previously analysed the theta point ('tricritical') region for polymers (Kholodenko and Freed 1984a) using renormalisation group methods with both two-body and three-body interactions. The renormalisation group treatment in this region provides a description of physically observable quantities in terms of an effective coupling constant g_{eff} . Under the conditions that $22w \ln(N/L) \gg 1$ with L a phenomenological scaling length of the theory, the effective coupling constant contains logarithmic corrections, $g_{\text{eff}} = \delta g [22w \ln(N/L)]^{4/11}$ where δg is chosen to vanish at the same point as the second virial coefficient. Since the precise magnitude of w is not

yet known (nor has L yet been related to experiment in the theta point region), we prefer to use g_{eff} as the renormalised two-body interaction parameter without further specifying its dependence on w and N/L . Given these considerations, the theta domain is defined as

$$|g_{\text{eff}}|N^{1/2} \ll 1, \quad (6.1b)$$

providing the conditions under which the renormalised expansions in g_{eff} are valid.

Calculation of the coil-globule equilibrium requires the evaluation of the coil free energy within the theta domain. It is known (des Cloizeaux 1981, Elderfield 1981) that both the free energy and entropy for the coil state are in general, *non-universal* functions and display a strong sensitivity to microscopic parameters describing the polymers. The same sensitivity is exhibited by lattice calculations on avoiding walks. A lattice with coordination number z yields $C_n = z^n$ different random walks with n steps, giving a free energy of $F = -kTn \ln z$ or a free energy per step of $F = -kT \ln z$. Self-avoiding walks have a renormalised connectivity constant of $\mu < z - 1$, because immediate self-reversals are forbidden. The total free energy is $F = -kTn \ln \mu - kT(\gamma - 1) \ln n$ where γ is the usual 'critical exponent', and the term in $\ln n$ is the universal portion of the free energy which for $n \rightarrow \infty$ is *negligible* in comparison with the leading ($\propto n$) non-universal portion. In general, this non-universal free energy varies with the coupling constant, and its additivity implies proportionality to chain length N which must have a form like $Nf(g^{1/2})$ with l a microscopic length scale and $g \rightarrow g_{\text{eff}}$. When computed perturbatively, it must have a form like $Nf(g^{1/2}) = N[A + g_{\text{eff}}\Delta_c + O(g_{\text{eff}}^2)]$ with A and Δ_c some microscopic parameters appropriate to the coil state.

The calculations of Kholodenko and Freed (1984a) give under the condition (6.1b)

$$\int d^3r G(r, N) = 1 + 2g_{\text{eff}}(2N/\pi)^{1/2} + O(g_{\text{eff}}^2). \quad (6.2)$$

Combining the definition (4.8) of the free energy with the non-universal contributions described above yields the coil free energy as

$$-F_c/kT = N(A + g_{\text{eff}}\Delta_c) + 2g_{\text{eff}}(2N/\pi)^{1/2} + O(g_{\text{eff}}^2). \quad (6.3)$$

The reference free energy is chosen as that for the theta point. Then the free energy above the theta point must be positive, while below the theta point it must be negative to ensure that the globular state has free energy lower than that for the coil state. Taking $g_{\text{eff}} \equiv -g/2\pi$ (since our convention in this paper is $g > 0$ for attractive interactions, while $g_{\text{eff}} \geq 0$ for repulsive ones above the theta point and since our previous work absorbs a factor of 2π into the coupling constant) these conditions imply that (6.3) becomes in the coil-globule transition region

$$F_c/kT = g\Delta_c N + g(2N/\pi^3)^{1/2} + O(g^2) \quad (6.3a)$$

where Δ_c is negative.

The globule free energy likewise has a non-universal portion which is written as $kTg\Delta_g N$ analogous to (6.3a). Adding this to the calculated universal terms in § 5 gives the full globule free energy as

$$-F_g/kT = \ln \left(c_0 \exp(s^* N) + \sum_i c_i \exp(s_i N) + \text{fluctuation part} \right) + Ng\Delta_g, \quad (6.4)$$

where Δ_g is, in general, different from Δ_c , and c_0 and c_i are constants which are unnecessary here. The s_i from (5.16) lie in the range of $0 < s_i < s_0$, so that as $N \rightarrow \infty$, $s^* \rightarrow s_0$, and the terms in s_i can be neglected, leaving the globule free energy as

$$F_g/kT = -N[(g^2/2w) + g\Delta_g]. \quad (6.4a)$$

The condition of phase equilibrium at T_c implies $F_g = F_c$. Assuming that w is negligibly temperature dependent, we let $g_c = g(T_c)$. Equating (6.3a) and (6.4a) at T_c and rearranging yields

$$g_c = 2w(\Delta_c - \Delta_g) - 2w(2/\pi^3 N)^{1/2}. \quad (6.5)$$

We have already obtained two other estimates of g_c . One is provided by the limit of stability from (5.12) with an equality sign of

$$g_c = N^{-1/2} w(2)^{3/2} (3/\pi) \quad (6.6)$$

while the other arises from the condition $\xi_0(s^*) = r_0(s^*)$ from (5.2a) with the equality sign and $s \rightarrow s_0$, which is reduced then to an estimate (6.1). Beginning at low temperatures in the globule state, it is necessary to determine which condition (6.6) or (6.1a) is first attained as the temperature is raised. We continue the empirical form (Berry 1966)

$$g = \lambda[(\Theta/T) - 1] \quad (6.7)$$

from above the theta point with λ a constant and Θ the theta temperature. Comparison of (6.6) and (6.1a) shows that estimate (6.1) provides the lower temperature when

$$w < 2^9(\pi/3)^4 \approx 615, \quad (6.8)$$

whereas for $w > 615$, g_c given by (6.6) determines the transition temperature. As w is expected to be small (Ptitsyn *et al* 1968), the case of (6.8) is treated first, but then the opposite limit is analysed because experimental values of w for real polymer systems are not yet available.

Equating (6.5) with (6.1) and rearranging leads to

$$(\Delta_c - \Delta_g)|_{T_c} = (32\pi/3 + (2/\pi^3)^{1/2})w^{-1/2}N^{-1/2}. \quad (6.9)$$

Writing the heat of transition as

$$Q = T_c(S_c - S_g)|_{T_c} \quad (6.10)$$

where $S_c = -(\partial F_c/\partial T)_v$, etc for the globule, using (6.9), (6.3a), (6.4a) and (6.7) gives (per monomer)

$$Q/N = \lambda k\Theta N^{-1/2}[(\frac{32}{3}\pi - (2/\pi^3)^{1/2})w^{-1/2} + (2/\pi^3)^{1/2}] \quad (6.11)$$

where $O(1/N)$ differences between T_c and Θ are dropped except in terms containing g_c where they are relevant. Equation (6.11) implies that in the limit $N \rightarrow \infty$, the specific heat of transition vanishes for any finite w . The total heat for the system is non-zero and behaves as $N^{1/2}$. This dependence is indicative of the fact that polymers are unusual 'critical' systems since for large N they always possess long-range correlations. Equation (6.11) for finite w suggests a coil-globule transition that is closer to being second order (when $N \rightarrow \infty$) in agreement with the conclusion of Moore (1977). However, if the combination $\lambda(wN)^{-1/2} \rightarrow \text{constant}$ for $w \rightarrow 0$, $N \rightarrow \infty$, the specific heat

of (6.11) stays non-zero, and the coil-globule transition becomes first order. Kholodenko and Freed (1984a) show that the effective three-body interaction $w \rightarrow 0$ as $N \rightarrow \infty$, and therefore, depending on the empirical behaviour of λ , (6.11) could establish the long sought 'tricriticality' of the coil-globule transition in this special limit. This strong dependence of the order of the coil-globule transition on the magnitude of the three-body interaction parameter w is in accord with the $O(n)$ model renormalisation group treatment of Blankschtein and Aharony (1983) of the tricritical region. They show that the magnitude of the ϕ^6 coupling constant as well as additional marginal and irrelevant terms can alter the order of the transition. The sensitivity of (6.11), and hence the order of the coil-globule transition, to the value of w and perhaps other marginal and irrelevant operators associated with unaccounted microscopic variables may explain the suggested non-universality of this transition.

For $w > 615$ we equate (6.5) to (6.6) to find

$$(\Delta_c - \Delta_g)|_{T_c} = \left(\frac{2}{\pi^3 N} \right)^{1/2} (1 + 3\pi^{1/2}). \quad (6.12)$$

The specific heat of transition is then obtained as

$$Q/N = \lambda k \Theta N^{-1/2} (2/\pi^3)^{1/2} (1 + 9\pi^{1/2}) \quad (6.13)$$

corresponding to a second-order-like transition for $N \rightarrow \infty$. Hence, (6.13) is consistent with (6.11) for non-zero w , merely indicating that for large enough w , the specific heat becomes independent of w .

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