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Theory of the polymer coil-globule transition

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Abstract. The change of a polymer from an extended coil form above the θ point to a dense globular form below the θ point is investigated in a self-consistent field approximation and found to be a second-order phase transition in the limit of an infinitely long polymer. Other theories of the transition are reviewed and further information obtained as to the dimensionality dependence of the transition by means of the analogy between the θ point and a tricritical point.

1. Introduction

The change of a flexible polymer chain from an extended coil in a good solvent to a collapsed dense globule in a poor solvent has attracted a great deal of attention both theoretical and experimental, possibly because of its connection with the denaturation and renaturation of globular proteins (Ptitsyn *et al* 1968). In this paper we shall review some of the existing theories of this change and present a description of it based on a self-consistent field approach.

The change from good-solvent behaviour to poor-solvent behaviour may be produced by altering the temperature or composition of the solvent. Good-solvent behaviour occurs when polymer segment-solvent contacts are more favoured than segment-segment contacts. If the attraction between the segments becomes sufficiently large the polymer will collapse to a globule whose density is close to that of dry polymer (Cuniberti and Bianchi 1974). The temperature at which this occurs is close to the θ temperature—the temperature at which the attractive forces just balance the excluded volume forces. A more precise definition of the θ temperature is the temperature at which the second virial coefficient of the osmotic pressure, A_2 , vanishes (Flory 1953). It is commonly supposed that at the θ point the polymer has its random coil dimensions.

For a given solution below its θ temperature, where the attractive forces between polymer segments predominate, polymer-polymer contacts can increase by two different mechanisms: the contraction of the individual chains or the interpenetration of different chains. If only one chain were present in the solution, it would collapse to a globule; in a solution of finite concentration of polymer, chain contraction and aggregation will be competitive processes and phase separation could occur either by coalescence of globules or the aggregates made up of interpenetrating chains.

It has been known for a long time (Debye *et al* 1960a, b) that at the critical concentration for phase separation, extensive order sets in before reaching the critical temperature and that the coil size is much reduced with respect to its θ point dimensions. This rapid change of dimensions with temperature below the θ point has

been recently confirmed by Mazur and McIntyre (1975), who worked with polystyrene of molecular weight $M_w = 4.4 \times 10^7$ in cyclohexane.

In dilute solutions where the polymers may be presumed not to overlap each other to a first approximation, the lowering of the temperature below the θ point gives rise at first to a shrinkage of coil dimensions, followed by precipitation (Flory 1953). The precipitation mechanism which prevails is determined by the detailed chemistry of the solute and solvent. Poly (acrylic) acid in dioxane assumes a compact globular form before precipitating from solution, while polystyrene in cyclohexane gives rise to progressively growing clusters before precipitating (Cuniberti and Bianchi 1974).

In this paper only isolated chains in solution will be considered. We believe that in the limit of infinite molecular weight the coil-globule change can be regarded as a phase transition occurring at the θ temperature. (In § 3 we shall discuss what will happen for general dimension d and argue that for $d > 4$ there will be no phase transition at the θ temperature.) We believe that this phase transition is second order (continuous). There seems to be evidence from numerical studies on lattices that there may also exist another transition, possibly first order, at a temperature much lower than the θ temperature (Finsy *et al* 1975). We shall comment further on this possible transition in § 3, and return here to our main topic, the coil-globule transition.

There have been several attempts at a theory of the coil-globule transition. The approaches and the conclusion as to the order of the transition have varied widely. Edwards (1970), in a calculation he characterized as a 'crude approximation to a crude approximation', found the transition to be first order. Lifshitz (1969) and Lifshitz and Grosberg (1974) obtained under various circumstances both first- and second-order transitions. However, this aspect of their work is completely incorrect, since their transitions occur at finite N , where N is the number of segments in the polymer. This is, of course, impossible as a phase transition can only take place in the limit of infinite N . Domb (1974) reviewed the numerical work on self-avoiding walks in which attractive forces between nearest-neighbour segments had been included and suggested that the transition was first order. In our opinion, the numerical evidence, such as it is, supports the opposite hypothesis; namely, that the transition at the θ point is second order.

There are two main theoretical approaches to polymer solutions. For non-dilute solutions, the Flory-Huggins theory and variations on it are employed. (Physicists will recognize it as a mean-field approximation.) As in the globule the density of monomers is high, we constructed a Flory-Huggins-type theory of the coil-globule transition (Massih and Moore 1975). It was done by solving exactly for the partition function for walks on a triangle cactus Bethe lattice, in which no lattice bond could be used more than once during the walk. This restriction on the walks is to be thought of as a consequence of the short-range excluded-volume forces. Attractive forces were incorporated in the model by interactions which occurred only at sites at which the polymer touched or crossed itself. It was found that the entropy was continuous at the transition, but that the monomer density changed abruptly from zero to its maximum close-packing value at the transition. Subsequent work suggests that this transition may not be related to the coil-globule transition at the θ point, but instead may be related to the transition of Finsy *et al* (1975), which occurs well below their earlier estimated value for the θ temperature. We shall return to this point in § 3.

The other main approach to polymers in solution is based on Flory self-consistent field ideas which are used mainly for dilute solutions or single polymer molecules. A theory of the coil-globule transition based on the Flory approach has been given by Ptitsyn and Eizner (1965) and by Kron (1965) (see also de Gennes 1975). For certain

ranges of the parameters in the problem, their calculation predicts a second-order transition, but outside this range it fails to make sense, in that it predicts a transition even for polymers of finite length. However, the formalism on which this approach is based is now known to be without foundation (see des Cloizeaux 1976).

In § 2, we give a treatment of the coil-globule transition based on a variation of the Edwards (1965) self-consistent field idea. We are able to show in the large- N limit that this treatment is consistent with the use of perturbation theory and give an approximate solution of the equations. Outside the large- N limit we are unable to provide an analytic solution—a feature common to nearly all polymer self-consistent field calculations—but in this region, perturbative calculations are possible as an alternative. The calculation predicts that the transition takes place at the θ point and is second order.

In § 3 we shall discuss what can be learnt from the analogy of the coil-globule transition at the θ point with a tricritical transition (de Gennes 1975). Simple renormalization group arguments (given elsewhere) predict that in three dimensions there should be a logarithmically divergent specific heat per monomer at the transition (Burch and Moore 1976). What happens in other than three dimensions is also described and the question of whether there is a θ point or θ region is discussed.

2. Self-consistent field calculations

The self-consistent field (SCF) approach in good solvents has been reviewed by Freed (1972), whose procedure we shall follow here. We shall begin by finding SCF equations for worse than θ solvents.

The model used is a Gaussian random-flight equivalent chain of contour length L , composed of N effective bonds, each of length l . Let us suppose initially that there exist non-bonded pairwise interactions between them. The distribution function for \mathbf{R} , the end-to-end distance, is

$$P(\mathbf{R}) = Z^{-1} \int \dots d\mathbf{r}_0 d\mathbf{R}_1 \dots d\mathbf{R}_N \delta(\mathbf{r}_0) \delta\left(\mathbf{R} - \sum_i \mathbf{R}_i\right) \exp\left(-\beta/2 \sum_{i \neq j} U_{ij}\right) \prod_{i=1}^N \tau_i(\mathbf{R}_i) \quad (1)$$

$$\equiv Z^{-1} G(\mathbf{R}, N). \quad (2)$$

\mathbf{r}_0 is the position of the first segment which will be taken to be the origin of coordinates. $\mathbf{R}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$ is the bond vector between segments i and $i-1$. $\mathbf{R} \equiv \mathbf{r}_N = \sum_i \mathbf{R}_i$ is the end separation vector. U_{ij} is the non-bonded interaction between segments i and j . We shall suppose initially that $U_{ij} = v\delta(\mathbf{r}_i - \mathbf{r}_j) \equiv l^2 V(\mathbf{r}_i - \mathbf{r}_j)$ where v is the binary cluster integral for a pair of segments. Its temperature dependence near the θ point is as

$$v = v_0(1 - \theta/T). \quad (3)$$

For $T > \theta$, the net binary force between the segments is repulsive; for $T < \theta$ the force is attractive ($v < 0$). $\tau_i(\mathbf{R}_i)$ is a Gaussian with $\langle \mathbf{R}_i^2 \rangle^{1/2} = l$. Z is the total configurational integral; for large N it is expected to vary as

$$Z_N \sim N^{\gamma-1} \mu^N(v), \quad (4)$$

where μ is the 'connectivity constant' of lattice enumeration studies. The free energy of the polymer is

$$F/kT = -\ln Z_N \rightarrow -N \ln \mu(v) \quad \text{as } N \rightarrow \infty. \quad (5)$$

We shall usually study the continuum version, i.e. the Wiener integral of $G(\mathbf{R}, N)$, $G(\mathbf{R}\mathbf{0}; L\mathbf{0})$.

Turning off the interaction U_{ij} leads to the usual Gaussian form for $G(\mathbf{R}\mathbf{0}; L\mathbf{0})$, which can be found by solving the differential equation

$$\left(\frac{\partial}{\partial L} - \frac{l}{6}\nabla_{\mathbf{R}}^2\right)G(\mathbf{R}\mathbf{R}'; Ls) = \delta(\mathbf{R} - \mathbf{R}')\delta(L - s). \quad (6)$$

To discuss the effect of interactions it is useful to introduce the probability distribution that a polymer of contour length L and end-to-end vector \mathbf{R} have its segment at contour length L' (measured from the initial segment at $s = 0$), located at the point \mathbf{R}' . It is given by

$$P(\mathbf{R}'L'|\mathbf{R}L) = \frac{G_3(\mathbf{R}\mathbf{R}'\mathbf{0}; LL'\mathbf{0})}{G(\mathbf{R}\mathbf{0}; L\mathbf{0})}, \quad (7)$$

where $G_3(\mathbf{R}\mathbf{R}'\mathbf{0}; LL'\mathbf{0})$ is the Green function for a polymer starting at the origin, of length L , terminating at \mathbf{R} and where L' th segment passes through \mathbf{R}' . In terms of G_3 , the equation for G is

$$\left(\frac{\partial}{\partial L} - \frac{l}{6}\nabla_{\mathbf{R}}^2\right)G(\mathbf{R}\mathbf{0}; L\mathbf{0}) + \int d\mathbf{R}' V(\mathbf{R} - \mathbf{R}') \int_0^L ds G_3(\mathbf{R}\mathbf{R}'\mathbf{0}; Ls\mathbf{0}) = \delta(\mathbf{R})\delta(L). \quad (8)$$

There is an analogous equation for G_3 in terms of a four-point function G_4 , etc. For a continuous chain the hierarchy never terminates. The Edwards approximation results from introducing a Markovian approximation to the lowest member of the hierarchy:

$$G_3(\mathbf{R}\mathbf{R}'\mathbf{0}; Ls\mathbf{0}) \approx G_{\text{SCF}}(\mathbf{R}\mathbf{R}'; Ls[\mathbf{R}L])G_{\text{SCF}}(\mathbf{R}'\mathbf{0}; s\mathbf{0}[\mathbf{R}L]), \quad (9)$$

where

$$\left(\frac{\partial}{\partial s} - \frac{l}{6}\nabla_{\mathbf{R}'}^2 + V_{\text{SCF}}(\mathbf{R}'[\mathbf{R}L])\right)G_{\text{SCF}}(\mathbf{R}'\mathbf{R}''; ss'[\mathbf{R}L]) = \delta(\mathbf{R}' - \mathbf{R}'')\delta(s - s'') \quad (10)$$

and

$$V_{\text{SCF}}(\mathbf{R}'[\mathbf{R}L]) = \int d\mathbf{r} \int_0^L ds V(\mathbf{R}' - \mathbf{r})P_{\text{SCF}}(\mathbf{r}; s|\mathbf{R}L). \quad (11)$$

The potential of (11) when substituted in (10) generates SCFs, which depend only on the chain segment position with respect to the fixed end points of the chain—hence the notation $[\mathbf{R}L]$. There is another way of writing (11) in terms of the local segment density

$$\rho(\mathbf{R}'|\mathbf{R}L) = l^{-1} \int_0^L ds P(\mathbf{R}'; s|\mathbf{R}L); \quad (12)$$

i.e.

$$V_{\text{SCF}}(\mathbf{R}'[\mathbf{R}L]) = l \int d\mathbf{r} V(\mathbf{R}' - \mathbf{r})\rho(\mathbf{R}'|\mathbf{R}L). \quad (13)$$

Now up to this point we have supposed $V(\mathbf{R}' - \mathbf{r})$ to be of the form $l^{-2}v\delta(\mathbf{R}' - \mathbf{r})$, and below the θ point $v < 0$. However, if one simply takes $v < 0$ and do not alter (13) in any way one finds that the polymer collapses to unphysically high densities. It is necessary to introduce terms which simulate the stabilizing effects of the hard-core repulsive forces

between the segments. A convenient way of doing this is to replace (13) by

$$V_{\text{SCF}}(\mathbf{R}'[\mathbf{RL}]) = l^{-1}(v\rho(\mathbf{R}'|\mathbf{RL}) + \beta\rho^2(\mathbf{R}'|\mathbf{RL})) \quad (14)$$

where $\beta > 0$. The parameter β is related to the ternary cluster integral which appears in the third virial coefficient of the osmotic pressure.

We now have a complete set of equations (8, 9, 10, 12, 14) for an approximate calculation of G (we shall drop the SCF label from now on). The equations are quite intractable analytically. However, there is one region, which corresponds to working in the large- L limit for any $v < 0$ (i.e. below the θ point) where a simplifying approximation based on the following argument is possible. Imagine that V_{SCF} is given in (10). For concreteness, one might take it to be a square-well potential. Below the θ point one expects that V_{SCF} is strong and deep enough to split off at least one bound state from the continuum. The approximation consists of supposing that there is only one bound state, with eigenvalue λ , and that it dominates G ; i.e.

$$G(\mathbf{R}\mathbf{0}; L\mathbf{0}) \approx e^{\lambda L}\psi(\mathbf{R})\psi(\mathbf{0}), \quad (15)$$

where

$$\left(\lambda - \frac{l}{6}\nabla_{\mathbf{R}}^2 + l^{-1}(v\rho(\mathbf{R}) + \beta\rho^2(\mathbf{R})) \right) \psi(\mathbf{R}) = 0 \quad (16)$$

and

$$\rho(\mathbf{R}) = L\psi^2(\mathbf{R})/l = \chi^2(\mathbf{R}). \quad (17)$$

is the segment density.

Equation (16) can be viewed as the Euler-Lagrange equation which derives from minimizing the free-energy expression

$$F/kT = \int d\mathbf{R} \left[\frac{1}{6}l^2(\nabla\chi)^2 + \frac{1}{2}v\chi^4 + \frac{1}{3}\beta\chi^6 \right], \quad (18)$$

subject to the constraint

$$\int d\mathbf{R} \chi^2(\mathbf{R}) = L/l \quad (19)$$

(i.e. the integral over space of the segment density is just the total number of segments $N = L/l$ in the polymer). λ now can be regarded as a Lagrangian multiplier for handling the constraint of (19).

Equations (18) and (19) are similar to the equations derived by Lifshitz (1969) and can be regarded as the Ginzberg-Landau equations of the coil-globule transition. The 'order parameter' is $\sqrt{\rho(\mathbf{R})} = \chi(\mathbf{R})$; the gradient term in (18) represents the energy which arises if the density of segments varies spatially; the other two terms in (18) are energies of interactions between the segments arising from binary and ternary interactions.

Even the approximate SCF equation (16) cannot be solved analytically. However, it is easy to understand the form the solution takes well below the θ points, where the polymer has collapsed to a dense globule. A simple variational *ansatz* for (18) then suggests itself; if

$$\begin{aligned} |\mathbf{R}| \leq |R_g|, & \quad \chi^2 = L/l\Omega, \\ |\mathbf{R}| > |R_g|, & \quad \chi^2 = 0, \end{aligned} \quad (20)$$

where the volume of the globule $\Omega = \frac{4}{3}\pi R_g^3$, and the free energy

$$\frac{F}{kT} = \frac{1}{2} \left(\frac{L}{l}\right)^2 \frac{v}{\Omega} + \frac{1}{3} \left(\frac{L}{l}\right)^3 \frac{\beta}{\Omega^2}. \quad (21)$$

Varying the volume of the globule, there is a minimum of F when

$$\rho = \chi^2 = \frac{L}{l\Omega} = \frac{-3v}{4\beta} \equiv \rho_g \quad (22)$$

and

$$\frac{F}{kT} = -\frac{3}{16} \frac{L}{l} \frac{v^2}{\beta}, \quad (23)$$

$$\lambda l = \frac{3}{16} \frac{v^2}{\beta}. \quad (24)$$

Notice that $F/kT = -\lambda L$ in agreement with equation (5). Equation (23) implies that the transition is second order, with the classical mean-field exponents, if equation (3) is used for v .

A more refined *ansatz* is to take for χ a Fermi function

$$\chi(\mathbf{R}) = \frac{a}{\exp[b(\mathbf{R} - R_g)] + c}$$

where a , b , R_g and c are variational parameters. The detailed calculations with particular variational functions are not worth recording, but certain common features do emerge: (i) the 'radius' of the globule is always of order R_g , where $\frac{4}{3}\pi R_g^3 = -(L/l)4\beta/3v$; (ii) the density does not fall abruptly to zero at the radius R_g , as in the extreme *ansatz* of (20), but heals over a distance ξ_E around R_g , where

$$\xi_E^2 \sim \beta l^2 / v^2 \sim l^2 / |v| \rho_g. \quad (25)$$

ξ_E in (25) is of the form which Edwards (1966) gives for the screening length in bulk semi-dilute poor solvents when the segment density is ρ_g . It is easy to see why the density varies on a length scale set by ξ_E . Consider what happens far from the origin, where $\chi(\mathbf{R})$ is small; then (16) reduces to

$$-\frac{1}{6} l \nabla_{\mathbf{R}}^2 \chi(\mathbf{R}) = -\lambda \chi(\mathbf{R})$$

and so as $R \rightarrow 0$, $\chi(R) \sim \exp(-\sqrt{6\lambda}lR)/R$. Substituting (24) for λ , one sees that the length scale for density variations is indeed ξ_E ; (iii) the free energy can be expanded in the form

$$\frac{F}{kT} = -\frac{3}{16} \frac{L}{l} \frac{v^2}{\beta} \left[1 - \lambda_1 \left(\frac{\xi_E}{R_g}\right) + \lambda_2 \left(\frac{\xi_E}{R_g}\right)^2 + \dots \right], \quad (26)$$

if $R_g \gg \xi_E$. The first term represents the bulk energy of the globule. The second term is a surface energy term and the third term a line energy term, etc; λ_1 and λ_2 are numerical constants; (iv) equation (16) is rather like the time-independent version of Schrödinger's equation for a particle moving in a potential well. In three dimensions a bound state is formed if the product of the depth of the well and its (radius)² exceeds a

certain value. In this instance, the depth is about $v^2/\beta l$ and the radius is of the order of R_g , so for a bound state

$$\frac{v^2}{\beta} \frac{R_g^2}{l} \approx R_g^2/\xi_E^2 > \lambda_0^2, \quad (27)$$

where λ_0 is a numerical constant. If $R_g < \lambda_0 \xi_E$, no bound state is formed. Another way of writing (27) is

$$v^4 L^2 / \beta l^8 \sim \lambda_0^6 \quad (28)$$

as the condition for just forming a bound state. One sees that at given v and β , the polymer has to be longer than a certain critical length before it becomes self-bound.

However, is the use of (16) and (18) valid where (27) holds, i.e. when a bound state just forms? One condition in the validity of (16) and (18) is that the bound state eigenvalue dominates the Green function; this is equivalent to having

$$\lambda L \gg 1. \quad (29)$$

At the point where the bound state disappears, $\lambda = 0$, so a treatment based on (16) or (18) cannot be used to describe the *formation* of a bound state. In fact, such a treatment leads to the incorrect result that a phase transition occurs at finite L when the bound state forms. This is the mechanism by which Lifshitz (1969) and Lifshitz and Grosberg (1974) obtain transitions at finite N . The appearance of a bound state in the Laplace transform of $G(\mathbf{R}\mathbf{0}; L\mathbf{0})$ does not imply any transition. The fact that we are working in the continuum limit (i.e. with L rather than with a definite number of segments N) does not alter the basic requirement that a phase transition can only take place in the limit $L \rightarrow \infty$. It might happen that use of (16) or (18) is permissible nearly up to the point of disappearance of the bound state; one expects in the vicinity of the bound state that

$$\lambda L \sim (v^2 L / l \beta) (1 - \lambda_0 \xi_E / R_g). \quad (30)$$

As $R_g \rightarrow \lambda_0 \xi_E$, $\lambda L \rightarrow 0$. The coefficient $(v^2 L / l \beta)$ is of order $\lambda_0^6 l^7 / v^2 L \sim \lambda_0^4 l^3 / \beta^{1/2}$ and if this is large, i.e. $\beta \ll l^6$, then (16) and (18) will be good approximations nearly up to the point at which the bound state disappears.

Between the θ point and the region of formation of the bound state in (16) one will have to return to the full scf equations. Alternatively, one might span this region by ordinary Fixman (1955) type expansions in v and β . An interesting question which we cannot answer is whether the full scf equations predict a phase transition at finite L as does their approximate form (16) or (18). A question we can answer is whether the scf is consistent with perturbation theory well below the point of globule formation. Despite being set up as a self-consistent calculation, it is strictly only valid within perturbation theory and, as such, is satisfactory if

$$|v| / (l/L + 2|v|\rho)^{1/2} \ll l^3 \quad (31)$$

(Moore 1977). When $2|v|\rho \ll l/L$, this reduces to the condition $|v|L^{1/2} \ll l^{7/2}$ —the usual requirement for a Fixman-type expansion to be valid (Fixman 1955). For $2|v|\rho \gg l/L$, we require $|v| \ll 2\rho l^6$ (which in the globule case implies $\beta \ll l^6$) for the validity of the scf treatment. Hence, provided β is sufficiently small the scf should provide an adequate description of the coil-globule transition. One might wonder, however, to what extent a description which results in classical critical exponents is correct. This is the subject of § 3.

3. Tricritical-point analogies

De Gennes (1975) has already discussed the analogy between the coil-globule transition at the θ point and tricritical behaviour. In this section we shall derive further information by use of this analogy. One aspect of the analogy is the relation of the 'connectivity constant' $\mu(v, \beta)$, which is related by (5) to the free energy per segment, and the transition temperature $T_c(v, \beta)$ in the tricritical spin system

$$\mu(v, \beta) \sim 1/T_c(v, \beta). \quad (32)$$

Now renormalization group studies (Burch and Moore 1976, Riedel and Wegner 1974), show that $1/T_c(v, \beta)$ has a regular power series development in v and β and also non-analytic terms of the form $v^{2/\epsilon}$, $\epsilon > 0$. When $\epsilon = 1$, i.e. for three dimensions (as $\epsilon = 4 - d$), the non-analytic term takes the form $v^2 \ln(v/l^3)$. The free energy per segment must therefore have a term for $d = 3$

$$F/NkT \sim (1 - \theta/T)^2 \ln|1 - \theta/T|$$

so the specific heat at the transition diverges logarithmically. Numerical work by Rapaport (1974) supports this result and incidentally provides numerical evidence against Domb's (1974) assertion that the transition is first order according to numerical studies.

For $d > 4$, we believe that $T_c(v, \beta)$ is probably analytic in v and β and that there is no phase transition in the limit of infinite N at the θ point. We would cite, as evidence for this belief, the calculation of Massih (1975) on the triangle cactus Bethe lattice in which no phase transition occurred at the θ point, defined as the temperature at which the second virial coefficient A_2 is zero. Bethe lattices are essentially infinite dimensional and so by our argument would not be expected to have a phase transition associated with the θ point. The phase transition which is found on this lattice is probably similar to the transition discovered in numerical work by Finsy *et al* (1975). Domb (1974) suggested that the coil-globule transition was related to the gas-liquid transition in segments of the polymer chain. We suspect that the transition of Finsy *et al* and that on the Bethe lattice is related to a liquid-solid transition of the segments. It would be useful to have further numerical work on this transition in order to elucidate its order parameter, etc. It must also be admitted that what we are postulating, namely that the coil-globule transition at the θ point disappears in greater than four dimensions is unusual, in that $d = 4$ is not commonly a boundary between the existence or non-existence of a phase transition.

For $d < 3$ the tricritical behaviour is non-trivial and we shall not comment further here on what might happen at $d = 2$. Right at $d = 3$, tricritical behaviour is essentially that of mean-field theory, but modified by logarithmic corrections (Wegner and Riedel 1973). In other words, the work of § 2 is valid up to logarithmic factors (which will be hard to observe experimentally). An interesting question is whether there is a θ region for $d = 3$ or a θ point. By a θ region we mean that the temperature at which A_2 vanishes is not the same as the temperature at which $\langle R^2 \rangle \sim N$, $N \rightarrow \infty$. If there were a θ point, the two temperatures would coincide. (For finite N there is certainly a θ region. Also, one expects for $d = 3$ logarithmic corrections to the random-walk result $\langle R^2 \rangle \sim N$.) We believe that for $d = 3$ there is a θ point, but that in certain quantities one may have to take N enormously large before this becomes apparent. An example is the third virial coefficient A_3 . It should also fall to zero at the θ point, but will miss being zero at finite N by terms of order $\beta/\ln N$. (Technically, this is because β is essentially a marginal

operator in three dimensions and under renormalization group transformation vanishes logarithmically. It is analogous in its behaviour to the coefficient of the ϕ^6 term in an $O(n)$ symmetric field theory (Massih 1975).) Hence, in the limit of infinite N , A_2 and A_3 would go to zero at the same temperature. In practice, A_3 will be non-zero at the temperature at which A_2 is zero.

4. Conclusions

Our chief result is that the coil-globule phase transition takes place in the infinite- N limit at the θ temperature and that the transition is second order. The behaviour at finite N can be handled within the framework of the SCF formalism of § 2 for temperatures well below the θ point, when the globule is well formed, and, if desired, by ordinary Fixman expansions for temperatures just below the θ point, when the coil's dimensions have hardly fallen below the random coil value.

Further work is needed in several directions; experimentally it would be useful if the light-scattering experiments on polystyrene in cyclohexane (Mazur and McIntyre 1975) could be pushed to the limit, when

$$\alpha^2 \equiv \langle R^2 \rangle / \langle R^2 \rangle_\theta \sim N^{2/3} / N \sim N^{-1/3},$$

i.e. to where the collapse has taken place, so that the density of segments is of order $-v/\beta$ rather than of the random coil value $N/l^3 N^{3/2} \sim 1/l^3 N^{1/2}$. It would then be of interest to probe the density profile of the globule and check whether the density does fall to near zero from its bulk value over the length scale ξ_E , and that the radius of the globule is of order R_g . Theoretically, an outstanding problem is the question of whether the transition of Finsky *et al* (1975) really exists or whether it is just an artefact of numerical work.

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References

- Burch D J and Moore M A 1976 *J. Phys. A: Math. Gen.* **9** 435
 des Cloizeaux J 1976 *J. Physique* to be published
 Cuniberti C and Bianchi U 1974 *Polymer* **15** 346
 Debye *et al* 1960a *J. Chem. Phys.* **32** 993
 — 1960b *J. Chem. Phys.* **33** 1746
 Domb C 1974 *Polymer* **15** 259
 Edwards S F 1965 *Proc. Phys. Soc.* **85** 613
 — 1966, *Proc. Phys. Soc.* **88** 265
 — 1970 *J. Non-Cryst. Solids* **4** 417
 Finsky R, Janssens M and Bellemans A 1975 *J. Phys. A: Math. Gen.* **8** L106
 Fixman M 1955 *J. Chem. Phys.* **23** 1656
 Flory P 1953 *Principles of Polymer Chemistry* (Ithaca: Cornell University Press)
 Freed K F 1972 *Adv. Chem. Phys.* **22** 1
 de Gennes 1975 *J. Physique Lett.* **36** L55

- Kron A K 1965 *Vysokomolek. Soedin.* **7** 1228
Lifshitz I M 1969 *Sov. Phys.-JETP* **28** 1280
Lifshitz I M and Grosberg I M 1974 *Sov. Phys.-JETP* **38** 1198
Massih A R 1975 *PhD Thesis* University of Sussex
Massih A R and Moore M A 1975 *J. Phys. A: Math. Gen.* **8** 237
Mazur J and McIntyre D 1975 *Macromolecules* **8** 464
Moore M A 1977 *J. Physique* to be published
Ptitsyn O B and Eizner Y Y 1965 *Biophysika* **10** 3
Ptitsyn O B, Kron A K and Eizner Y Y 1968 *J Polymer Sci. C* **16** 3509
Rapaport D C 1974 *Phys. Lett.* **48A** 339
Riedel E K and Wegner F J 1974 *Phys. Rev.* **B 9** 294
Wegner F J and Riedel E K 1973 *Phys. Rev.* **B 7** 248