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COLLAPSE OF A POLYMER CHAIN IN POOR SOLVENTS

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Résumé. — Le comportement d'une chaîne flexible unique, près de la température Θ de Flory, est analysé à partir d'une analogie avec un problème magnétique. La transition vers un état globulaire compact est relié aux propriétés d'un *point tricritique* dans le problème magnétique.

Abstract. — The behavior of a single, flexible polymer chain near the Flory temperature Θ is analysed in analogy with a magnetic phase transition. The transition to a collapsed state is related to a *tricritical point* for the magnetic problem.

A solute polymer chain expands in a good solvent, and collapses in a poor solvent [1]. By suitable changes in temperature, or in solvent composition, it is possible to cross over from one behavior to the other. In experiments on solutions, a demixing process replaces the collapse [1]. However, the transition from an extended shape to a globular form, for a single coil, may be of some interest for studies on protein folding [2]; it is also of theoretical interest as a first step towards the understanding of micellar structures.

The collapse has been studied by numerical methods on lattice models, where the polymer chain is described as a self avoiding walk, and attractive interactions between neighboring monomers are added: the results have been reinterpreted recently by Domb [3]. In the present note, we present a slightly different approach, based on an analogy with the phase transitions of a magnetic system, which is already known to be useful for the simple excluded volume problem [4].

1. Self consistent field approximation. — As usual, it is helpful to start by a simple calculation of the Flory type [1] suitably extended to cover collapsed situations. This is based on the following free energy

$$\frac{F}{k_B T} = 3[\alpha^2/2 - \ln \alpha] + \frac{N}{2} [\rho W_1(T) + \rho^2 W_2(T) + \dots] \quad (1)$$

Here $\alpha = R/R_0$ is the expansion factor, and

$$R_0 = N^{1/2} a$$

is the r.m.s. radius of an ideal coil. N is the number

of monomers along the chain. The average monomer concentration in the coil is

$$\rho = kN/R^d = ka^{-d} N^{1-d/2} \quad (2)$$

where d is the dimensionality and k a numerical constant. The parameters W_1, W_2, \dots are essentially the successive virial coefficients of the monomer interaction. $W_1(T)$ is the excluded volume coefficient and has the form

$$W_1(T) = v \frac{T - \Theta}{\Theta} \left(\left| \frac{T - \Theta}{\Theta} \right| \ll 1 \right) \quad (3)$$

Here Θ is the Flory compensation temperature. (To be specific we assume $v > 0$.) The second coefficient W_2 may be taken as positive and temperature independent in the range of interest. It is important to realise that *both* W_1 and W_2 are relevant for a discussion of the region $T = \Theta$ in three space dimensions. For $T \sim \Theta$, $\alpha \sim 1$ and the W_2 term is of order N^{3-d} : this is to be compared with the extensional term $\frac{1}{2}\alpha^2 - \ln \alpha$ which is of order unity. Thus W_2 is relevant for $d \leq 3$. The higher terms (W_3, W_4, \dots) are irrelevant for $d = 3$.

Specializing now to $d = 3$, retaining only W_1 and W_2 in eq. (1) inserting the form (2) for ρ , and minimizing the free energy, one arrives at the following amended form of the Flory equation [1]:

$$\alpha^5 - \alpha^3 - \frac{y}{\alpha^3} = kN^{1/2} \frac{W_1}{a^3} = x \quad (4)$$

where $y = k^2 W_2 a^{-6}$ is a dimensionless parameter. [Physically, y can be increased by adding side groups to the chain; it can be decreased by choosing chains which are somewhat rigid.] A plot of $\alpha(x)$ for various

values of y is shown on figure 1. For good solvents ($x \gg 1$) the Flory curve is maintained and $R \sim N^{3/5}$. For poor solvents ($x \ll 0$) we have a strong collapse and

$$R \sim \left[N \frac{\Theta}{-T + \Theta} \right]^{1/3}. \quad (5)$$

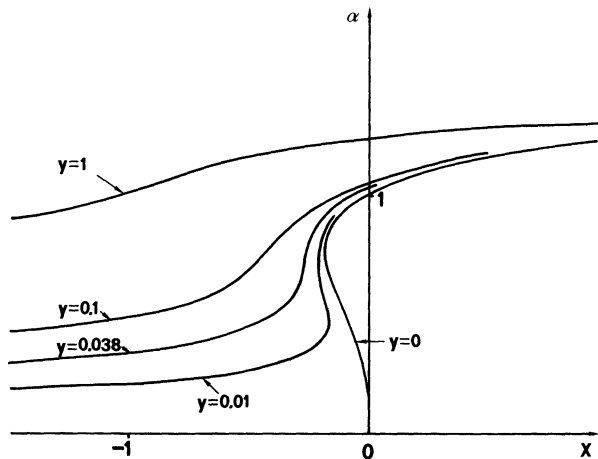


FIG. 1. — Size of a polymer chain as a function of reduced temperature in an extended Flory approximation (eq. (4)). The curves are shown for various values of a parameter y , which is large if the chain has some side groups, and small if the chain is slightly stiff.

For $|x| \sim 1$ (crossover region) we find two regimes depending on the value of the constant y . If $y > 0.038$ the coil contracts smoothly upon cooling. But if $y < 0.038$ eq. (4) predicts an unstable branch; if this were taken literally, it would imply an abrupt transition to the collapsed state, at a certain critical value of x for which the free energies on the two (locally) stable branches become equal. In fact, since we are dealing with a finite system, the sharp transition may be an artefact of the self consistent field method: but it is probably indicative of a very steep slope, as is indeed confirmed by numerical experiments [3]. The main weakness of the latter is that they are usually performed at one single value of y , depending on the particular model chosen.

A more elaborate (local) version of this self consistent field method has been considered by Edwards [5] (without the W_2 term) and by Lifschitz [6] (with a saturation term); the Lifschitz results are very similar to those deduced from eq. (4).

2. Relation between collapse and a tricritical point. —

The interaction terms in eq. (1) can be used as a starting point for a rigorous theory of chain conformations, just as the Landau free energy F_L [7] can be used as a weight function for calculations on critical points [8]. Let us consider in fact a magnetic system with magnetisation M , temperature τ and Landau

free energy :

$$F_L = \frac{1}{2} r_0 M^2 + U_1 M^4 + U_2 M^6 + \dots + \frac{1}{2} (\nabla M)^2. \quad (6)$$

[Where $r_0 \sim (\tau - \tau_0)$, τ_0 being the mean field transition point.]

There is a correspondence between the diagrams for the correlation function $\langle M(0) M(r) \rangle$ of the magnetic problem (in zero field, and above the transition point, $\tau > \tau_c$) and the statistical weight for a chain extending from 0 to r [4]. The bare vertex coefficients U_1, U_2, \dots are essentially identical (apart from normalization coefficients) to the virial coefficients W_1, W_2, \dots . The polymer length N is related to τ by a Laplace transform, but from dimensional considerations on a single chain it suffices to say that $N \sim (\tau - \tau_c)^{-1}$. We are interested here in the limit $N \rightarrow \infty$ ($\tau \rightarrow \tau_c$).

The diagrams for the two problems coincide provided that certain closed loops, present in the magnetic case but absent for the single chain, are eliminated: this is achieved formally by setting the number n of components of the vector M equal to zero [4].

The standard excluded volume problem corresponds to a strongly positive W_1 (or U_1): in this regime U_2, U_3, \dots are irrelevant. The problem discussed here corresponds to W_1 small: i.e. to a tricritical point [8]. An assumption of generalised scaling then leads to a coil radius (or correlation length) of the form

$$R = a N^{\nu_t} f(\tilde{x}, y) \quad (7)$$

$$\tilde{x} = \frac{\tilde{W}_1}{a^3} N^{\Phi_t}. \quad (8)$$

Here \tilde{W}_1 is defined as in eq. (3), but with a shifted Θ point: $\tilde{\Theta} = \Theta[1 - g(y) N^{-\Phi_t}]$.

ν_t is a tricritical exponent defined as in reference [8]. The constant Φ_t is a cross-over exponent. For

$$|\tilde{x}| \ll 1$$

the function f remains finite and $R \sim N^{\nu_t}$. For $\tilde{x} > 1$, f becomes independent of y and proportional to a power of x ; then $R \sim N^{\nu}$ where ν is the excluded volume exponent. For $\tilde{x} < -1$, f is strongly dependent on y and again behaves like a power of $|\tilde{x}|$:

$$\left. \begin{aligned} f(\tilde{x}, y) &= |\tilde{x}|^{-\mu} b(y) \\ R &\cong N^{\nu_t - \Phi_t \mu} |W_1|^{-\mu} \cong N^{\nu_c} |W_1|^{-\mu} \\ \mu &= (\nu_t - \nu_c) / \Phi_t \end{aligned} \right\}. \quad (9)$$

Eq. (1) suggests that the exponent ν_c in the collapsed state is equal to $1/d$: for fixed (negative) W_1 the density ρ is finite and the interaction terms (of order N)

dominate the free energy : the extensional term (of order 1) can be omitted. This conclusion for ν_c is probably valid even beyond the self consistent field approximation.

For $d = 3$ the tricritical exponents have the mean field values $\nu_t = \Phi_t = \frac{1}{2}$. However, this is a marginal case (confluence of two fixed points in the renormalisation group approach) and corrections involving $(\ln N)$ are expected [9]. For $d = 2$ an approximate value of ν_t may be extracted from the results of an

expansion in powers of $\varepsilon = 3 - d$, carried to order ε^2 [10] :

$$\nu_t = \frac{1}{2} + \frac{1}{3} \frac{(n+2)(n+4)}{(3n+22)^2} \varepsilon^2 \left. \vphantom{\nu_t} \right|_{n=0, \varepsilon=1} \cdot \quad (10)$$

$$\cong 0.5055$$

The exponent Φ_t has not been calculated for $n = 0$. But the trend is clear : even for two dimensions, the tricritical exponents are very close to the mean field values.

References

- [1] See for instance FLORY, P. J., *Principles of polymer chemistry*, (Cornell University Press, NY), 5th ed. 1966.
STOCKMAYER, W. A., *Makromol. Chemie* **35** (1960) 54.
- [2] See for instance LIQUORI, A. M., *Quartely Reviews of Biophys.* **2** (1969) 1.
- [3] DOMB, C., *Polymer* **15** (1974) 259.
See also RAPAPORT, D. C., *Phys. Lett.* **48A** (1974) 339.
- [4] DE GENNES, P. G., *Phys. Lett.* **38A** (1972) 339.
See also DES CLOIZEAUX, J., *J. Physique* **36** (1975) n° 4 (to be published).
- [5] EDWARDS, S. F., in *Critical phenomena* eds. M. S. Green and J. V. Sengers (Nat. Bur. Stand. Miscell. Pub.) 273 (1966) p. 225.
- [6] LIFSHITZ, I. M., *Sov. Phys. JETP* **28** (1969) 1280.
See also EIZNER, *Polymer Science USSR* **11** (1969) 409; **14** (1972) 1965.
- [7] LANDAU, L., LIFSHITZ, I. M., *Statistical Physics*, Chap. 14 (Pergamon Press London) 1958.
- [8] GRIFFITHS, R. B., *Phys. Rev.* **B 7** (1973) 545.
- [9] RIEDEL, E., WEGNER, F., *Phys. Rev. Lett.* **29** (1972) 349.
- [10] STEPHEN, M., MCCAULEY, J., *Phys. Lett.* **44A** (1973) 89.