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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  $\Theta$  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  $\Theta$  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  $\Theta$  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  $\rho$ , 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

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

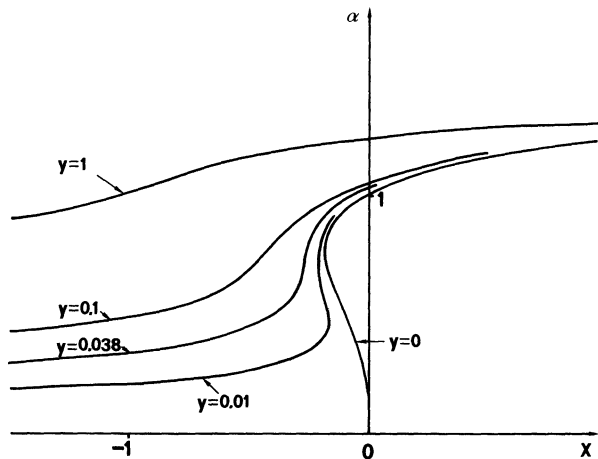


FIG. 1. — Size of a polymer chain as a function of reduced temperature in an extended Flory approximation (eq. (4)). The curves are shown for various values of a parameter  $y$ , which is large if the chain has some side groups, and small if the chain is slightly stiff.

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  $\tau$  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  $r_0 \sim (\tau - \tau_0)$ ,  $\tau_0$  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  $\tau$  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  $\Theta$  point:  $\tilde{\Theta} = \Theta[1 - g(y) N^{-\Phi_t}]$ .

$\nu_t$  is a tricritical exponent defined as in reference [8]. The constant  $\Phi_t$  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  $\nu$  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  $\nu_c$  in the collapsed state is equal to  $1/d$ : for fixed (negative)  $W_1$  the density  $\rho$  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  $\nu_c$  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  $\nu_t$  may be extracted from the results of an

expansion in powers of  $\varepsilon = 3 - d$ , carried to order  $\varepsilon^2$  [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  $\Phi_t$  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.

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