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COLLAPSE OF A FLEXIBLE POLYMER CHAIN II

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Résumé. — On essaie de construire ici une description physique de la transition subie par une chaîne unique, longue (N monomères), et flexible, au point Θ de Flory, à partir des résultats de la littérature sur un point tricritique en dimension 3. On trouve que pour $T = \Theta + \Delta T$, la chaîne se comporte comme une séquence de *blobs*, chacun avec un certain nombre G_B de monomères

$$G_B \sim (\Theta/\Delta T)^2 \ln |\Theta/\Delta T|^{-3/11}.$$

A l'intérieur de chaque *blob* les conditions Θ sont remplies. Mais à plus grande échelle, le collier de *blobs* montre, soit un comportement de volume exclu ($T > \Theta$), soit un comportement effondré avec $R \sim N^{1/3}$ ($T < \Theta$). La partie singulière de l'énergie libre est $\sim kT$ par *blob*, d'où une anomalie de chaleur spécifique $C \sim (\ln \Theta/\Delta T)^{3/11}$. Plutôt que les mesures thermiques, une étude de l'hypochromisme en spectroscopie UV permettrait peut-être de tester ce point.

Abstract. — This note gives a physical description of the collapse transition for a long chain (N monomers) near the Θ point, based on existing renormalization group calculations.

1) at $T = \Theta$ exactly, the chain is ideal as regards the size ($R \sim N^{1/2}$) and the virial coefficient vanishes. However, some repulsive correlations remain due to 3 body interactions ;

2) for temperatures $T = \Theta + \Delta T$, a sufficiently long chain can be pictured as a sequence of blobs, each with G_B monomers $G_B = \left(\frac{\Theta}{\Delta T}\right)^2 \left(\ln \left|\frac{\Theta}{\Delta T}\right|\right)^{-3/11}$. Inside each blob, the Θ conditions still hold. But on a larger scale, the string of blobs shows excluded volume behaviour (if $T > \Theta$) or collapse, with $R \sim N^{1/3}$ (if $T < \Theta$). The singular part of the free energy is of order kT per blob : this gives a specific heat divergence of $\left(\ln \left|\frac{\Theta}{\Delta T}\right|\right)^{3/11}$. A better probe could be obtained with UV spectra, measuring the number of monomer-monomer contacts.

1. Introduction. — The conformations of a single chain near the Flory compensation point [1] are extremely delicate to handle. Numerical data on lattices suggest a specific heat anomaly [2]. The problem is related to a tricritical point [3] and is particularly difficult in 3 dimensions, where logarithmic singularities occur [4]. Tricritical behaviour is understood in the language of field theory [5] or parquet diagrams [6]. The translation of these results into polymer physics has been faced with difficulties [7]. Here we use a relatively simple approach based on a *decimation on the chemical sequence* [8].

In the Flory language [1], the free energy per site on the lattice, as a function of the density Φ , has the form :

$$\frac{F}{kT} \Big|_{\text{site}} = \frac{1}{2} u \Phi^2 + \frac{1}{6} t \Phi^3 + \dots \quad (1)$$

where

$$u = 1 - 2\chi \cong \frac{\Delta T}{\Theta}$$

is small, while t is positive and finite. The monomer size is a constant a . The three numbers a , u , t specify the problem entirely.

In the decimation method, we group the monomers into subunits of g monomers, and calculate the new parameters a_1 , u_1 , t_1 for the subunits. We then iterate the process m times. The resulting trajectories in the u , t plane are shown on figure 1. If we start from A, we go towards a fixed point $u = u^*$, $t = 0$. This means that large subunits repel each other like hard spheres [8] and give an excluded volume behaviour. If we start from B, we go towards large negative values of u = large subunits tend to collapse. If we start from a point C on the dividing line, we go towards the origin (ideal chain behaviour). The dividing line defines a certain u for each t , or a certain Θ point for each t . (In the original Flory picture, where all renormalizations of Θ are ignored, the dividing line is vertical : we shall also assume this, in what follows, since it simplifies the notation.)

FIG. 1.

2. **Chain behaviour at $T = \Theta$ exactly.** — Near the origin, the recurrence equations can be obtained by perturbation theory. On the dividing line, they reduce to ⁽¹⁾

$$a_{m+1} = a_m g^{1/2} (1 + Q_1 t_m^2) \quad (2a)$$

$$t_{m+1} = t_m (1 - Q_2 t_m) \quad (2b)$$

In equation (2a) the factor $g^{1/2}$ corresponds to ideal chain behaviour; the linear corrections (u_m and t_m) cancel out on the dividing line (by definition). In equation (2b) the coefficient of t_m is unity: ideal subunits of volume $a_1^3 = g^{3/2} a^3$ have a 3-body interaction $tg^3(a/a_1)^6 \equiv t$. From equation (2) we find a slow decrease:

$$t_m = \frac{Q_3}{m} \quad (m \gg 1). \quad (3)$$

However for sufficiently large subunits, t_m (and u_m) vanish: a dilute solution is ideal for $T = \Theta$. Inserting equation (3) into equation (2a) and integrating we get:

$$a_m = ag^{m/2} \left(1 + \frac{Q_4}{m} \right). \quad (4)$$

Choosing m such that one subunit of the final stage spans the whole chain ($g^{m/2} = N$), we see that the size R of the chain has the form first calculated by Stephen [9]

$$R = aN^{1/2} \left(1 + \frac{Q_5}{\ln N} \right). \quad (5)$$

In practice this correction is negligible and $R \sim N^{1/2}$. This result depends crucially on the fact that the corrections in equation (2a) are only of order t^2 . From it one can also show that the pair correlation function at the Θ point is ideal $\langle \rho(0) \rho(r) \rangle \sim 1/r$.

⁽¹⁾ $Q_1, Q_2, \dots$ are numerical constants; some of them depend on the choice of g , but the final results (as in eq. (5)) do not.

3. **Vicinity of the Θ point: the blob picture.** — The 3-body interaction t will turn out to be more important when we look at the approach of the Θ point: we now start at a point $A(u_0, t_0)$ just off the dividing line, and write the recurrence equation for u

$$u_{m+1} = u_m g^{1/2} (1 - Q_6 t_m) + O(u_m^2). \quad (6)$$

After renormalization of the Θ point, terms like t_m or t_m^2 cannot appear on the right hand side of (6). If $u_m = 0$, we must stay on the dividing line and $u_{m+1} \equiv 0$.

Let us assume first that t_m is still given by (3), and integrate, obtaining:

$$u_m = u_0 g^{m/2} m^{-p} \quad (7)$$

$$p = Q_3 Q_6 = 4/11 \quad (8)$$

where we have inserted the exact value of p taken from reference [5]. Physically u_m is the analog of the ζ parameter introduced in perturbation expansions [10]: if we use subunits of G monomers ($G = g^m$) we have

$$\zeta \cong G^{1/2} u_0 / (\ln G)^p. \quad (7')$$

The correlations at the Θ point have reduced ζ by a factor $(\ln G)^{-p}$.

Let us now return to the equation for t_m : off the dividing line it becomes instead of (2)

$$\begin{aligned} \frac{\partial t}{\partial m} = t_{m+1} - t_m = & -Q_2 t_m^2 + \\ & + Q_7 u_m^2 + Q_8 u_m t_m. \end{aligned} \quad (9)$$

(There are no linear terms in u : in first order a two point interaction cannot generate a three point interaction.) The dominant correction can be checked to be u_m^2 . Using (7), it gives a shift in t_m of value

$$\delta t_m \sim u_0^2 g^m m^{-2p}. \quad (10)$$

This will be negligible when compared to (3) provided that

$$u_0^2 \gtrsim g^{-m} m^{2p-1}. \quad (11)$$

This allows us to define a blob (G_B monomers): we impose that the inequality (10) be equivalent to $g^m < G_B$. Then we know that Θ point singularities are dominant inside a blob, but are negligible between blobs. (For $g^m > G_B$ we move off the dividing line.) From (10) we then have

$$G_B = u_0^{-2} |\ln u_0|^{-(1-2p)} \quad (12)$$

with $u_0 \sim \Theta / |\Delta T|$. Equation (12) is the key to the physics of the Θ region. From equation (5), each blob has a size $r_B = G_B^{1/2} a$.

4. **The many blob regime.** — For a fixed chain length N we have two regimes :

a) Inner Θ regime : $G_B > N$, very near $u_0 = 0$.

b) Outer Θ regime : $G_B < N$, for slightly larger $|u_0|$. We shall be concerned now with the second case, assuming $1 \ll G_B \ll N$. Consider first the size R of the chain for $u_0 > 0$. The blobs have a two body interaction

$$u_B = u_0 G_B^{1/2} |\ln u_0|^{-p} \cong |\ln u_0|^{-1/2} \quad (13)$$

and the three body interaction between blobs is irrelevant here. We can then apply the Flory formula to the string of blobs [1], and obtain :

$$R^5 = r_B^5 u_B \left(\frac{N}{G_B} \right)^3$$

$$R = N^{3/5} a \left[\frac{\Theta}{\Delta T} \left(\ln \frac{\Theta}{\Delta T} \right)^p \right]^{1/5} \quad (14)$$

Consider now the poor solvent side : here the analog of equation (1) is now written in terms of a number ρ of blobs per volume r_B^3

$$\frac{1}{kT} F_{\text{int}} = \frac{1}{2} |u_B| \rho^2 + \frac{1}{6} t_B \rho^3 \quad (1')$$

where $t_B \cong \left(\ln \frac{\Theta}{\Delta T} \right)^{-1}$ from equation (3). The opti-

mum ρ is $|u_B|/t_B$ and this defines the size R through $\rho(R/r_B)^3 = N/G_B$, [12]

$$R^3 \cong Na^3 \frac{\Theta}{\Delta T} \left[\ln \frac{\Theta}{\Delta T} \right]^{-7/11} \quad (15)$$

Note that equations (14, 15) do not crossover into $R = (N^{1/2} a)$ when $G_B = N$, but rather when $G_B \cong N/\ln N$. For instance, when $u_0 > 0$, the interval $N/\ln N < G_B < N$ corresponds to blobs between which excluded volume effects are weak.

Let us end up with the chain free energy F . From the diagram

we are led to a contribution of order

$$u_B^2 \int_a^{r_B} \frac{1}{r_{12}^3} dr_{12} \sim u_B^2 |\ln u_0| \sim 1 \quad (16)$$

for F/kT per blob. This then gives

$$\frac{F_{\text{tot}}}{kT} = \frac{N}{G_B} \sim N \left(\frac{\Delta T}{\Theta} \right)^2 \left(\ln \left| \frac{\Theta}{\Delta T} \right| \right)^{1-2p} \quad (17)$$

and a specific heat peak with a $\ln^{3/11}$ power. This differs slightly from the proposal of Moore [7]. Rather than thermal measurements, a study of hypochromism in UV spectroscopy would measure the number of binary contacts $N_c \sim \partial F / \partial u_0$ inside the chain. We then expect a singularity in $\partial N_c / \partial T \sim \ln^{3/11}$ which might be interesting to see.

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