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CRITICAL BEHAVIOUR FOR VULCANIZATION PROCESSES

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Résumé. — Nous considérons un système de chaînes fondues, avec N monomères/chaîne et une fraction ρ des monomères pontés par un agent de vulcanisation. Au voisinage de la transition sol-gel ($\rho = \rho_c/\Delta\rho$) nous trouvons que la théorie de Flory est acceptable à $N > (\rho_c/\Delta\rho)^3$. Pour des chaînes plus courtes on doit retrouver les exposants critiques de la percolation.

Abstract. — We consider a polymer melt, with polymerization index N and a fraction ρ of cross linked monomers, for values of ρ close to the gelation threshold ($\rho = \rho_c + \Delta\rho$). Using a Ginsburg argument, we find that (in three dimensions) the Flory theory is qualitatively correct whenever $N > (\rho_c/\Delta\rho)^3$. For shorter chains the critical exponents are expected to be of the percolation type.

1. Introduction. — The classical theory of gelation for branched polycondensates [1, 2] is based on a *tree approximation* : the trees are generated by a random branching process. Cyclizations are either neglected, or included only at the level of short cycles. This approach gives rather good numerical values for the gelation threshold ρ_c . But it is qualitatively incorrect for all critical exponents describing the behaviour near threshold [5, 6]. The critical exponents are in fact known from numerical studies on the related percolation problem [7] :

a) the gel fraction θ , as a function of the fraction ρ of reacted bonds is expected to behave (near threshold) like :

$$\theta \cong \left(\frac{\rho - \rho_c}{\rho_c} \right)^\beta = \left(\frac{\Delta\rho}{\rho_c} \right)^\beta \quad \beta = 0.39 \quad (1.1)$$

b) the correlation length $\xi(\rho)$ behaves like

$$\xi = \xi_0 \left(\frac{\Delta\rho}{\rho_c} \right)^{-\nu} \quad \nu \simeq 0.9 \quad (1.2)$$

c) the average polymerization index Z of the finite clusters diverges like

$$Z = \left(\frac{\Delta\rho}{\rho_c} \right)^{-\gamma} \quad \gamma = 1.8. \quad (1.3)$$

These exponents differ strongly from the predictions of the tree approximation

$$\beta_t = 1 \quad \gamma_t = 1 \quad \nu_t = 1/2. \quad (1.4)$$

In the present note, we discuss another sol-gel transition : the *vulcanization* process, where a system of flexible chains, of large polymerization index N , becomes cross linked through the action of small agents such as a sulphur atom [3, 4]. We have discussed in the past some features of vulcanization between dilute, ideal chains in solution [8]. In the present note, we come to a much more practical problem, where the chains form a *concentrated* solution and have realistic interactions. We shall show that, for large N , and for three dimensional systems, the critical exponents of the vulcanization transition have their classical values (eq. (1.4)) : the tree approximation is in better shape for long chains than for the branching of small units.

We have reached this result by two methods :

a) direct discussion of fluctuations inside one correlation volume (section 2),

b) introduction of a *generalized Potts model* which defines a correspondence between vulcanization and a certain type of magnetic phase transitions (section 3).

Method (a) is more accessible to physical chemists, while method (b) is rather directed towards solid state physicists.

2. Direct Ginsburg argument. — The deviations from mean field exponents are due to fluctuations in the number of connected monomers inside one correlation volume. We shall now estimate three fluctuations following the spirit of an early argument by Ginsburg for phase transitions [9] :

a) we compute the fluctuations assuming that the classical exponents are valid,

b) we compare them to the average gel fraction θ : whenever the fluctuations are small with respect to θ ,

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we conclude that the tree approximation is qualitatively correct. All our arguments will be written for an arbitrary space dimensionality d .

We consider a volume $\Omega = \xi^d$ containing an average number of monomers

$$v_{\text{tot}} = c_0 \Omega. \quad (2.1)$$

(where $c_0 \sim a^{-d}$ is the monomer concentration). We choose a reaction level ρ slightly larger than the threshold ρ_c : then we have an average number v_{gel} of monomers inside Ω , belonging to the gel fraction

$$v_{\text{gel}} = c_0 \theta \Omega. \quad (2.2)$$

The fluctuations of v_{tot} are negligible. Thus the fluctuations of v_{gel} and those of v_{fc} (number of monomers belonging to finite clusters) are related by

$$\Delta v_{\text{gel}} + \Delta v_{\text{fc}} = 0. \quad (2.3)$$

In a volume Ω we have v_{fc} monomers grouped into $g = v_{\text{fc}}/Z$ clusters, where Z is the average number of monomers/clusters. In the free approximation

$$Z \cong N \rho_c / \Delta \rho \quad (2.4)$$

Thus we expect relative fluctuations

$$\left(\frac{\Delta v_{\text{fc}}}{v_{\text{fc}}} \right)^2 \sim \frac{1}{g} = \frac{Z}{v_{\text{fc}}}$$

or since v_{fc} is nearly equal to $v_{\text{tot}}(\theta \rightarrow 0)$

$$\langle \Delta v_{\text{gel}}^2 \rangle = \langle \Delta v_{\text{fc}}^2 \rangle \cong v_{\text{tot}} Z. \quad (2.5)$$

The relative importance of the fluctuations is measured by the quantity

$$X = (\Delta v_{\text{gel}}/v_{\text{gel}})^2 \cong Z/(\theta^2 c_0 \xi^d) \quad (2.6)$$

We now insert for Z , θ , and ξ the classical exponents of eq. (1.4). One coefficient is important: the prefactor ξ_0 in eq. (1.2) is of the order of the size on one chain. For a dense system we know both from theory [1] and from neutron experiments [10] that the chains are ideal: thus

$$\xi_0 \cong N^{1/2} a \quad (2.7)$$

We also note that $\rho_c \sim 1/N$ as explained in reference [4]. Then

$$X \cong N^{1-d/2} (\rho_c / \Delta \rho)^{3-d/2}. \quad (2.8)$$

a) Consider first the usual case ($d = 3$). Then eq. (2.8) shows that X is small except in a very narrow range $|\Delta v| \lesssim \Delta \rho^*$

$$\frac{\Delta \rho^*}{\rho_c} \sim N^{-1/3} \quad (d = 3). \quad (2.9)$$

Thus for $N = 10^3$ the classical exponents should hold except for a small interval of order $1/10 \rho_c$ (where the system crosses over towards the percolation indices).

b) Eq. (2.8) shows that for $d \geq 6$ the fluctuations are always weak as is known for percolation [11].

c) For $d = 2$, $X = [\rho_c / \Delta \rho]^2$ is large in all the critical region and the percolation indices must be observed. This could possibly be studied on monomolecular films.

3. A Potts model for vulcanization. — The s -state Potts model is a generalization of the Ising model of magnetism where each magnetic moment can be in s different states [12]. Kastelejn and Fortuin have shown that taking the formal limit $s \rightarrow 1$ in the Potts model, one generates a percolation transition [13]. In the present section, we construct a slight generalization of the Potts model which, in the same limit $s \rightarrow 1$, generates a vulcanization problem. We then show how the Ginsburg criterion can be discussed in this representation.

Let us start with a random set of chains, represented by a set of non-intersecting random walks on a periodic lattice. We consider only concentrated systems; each lattice site carries one and only one monomer.

To each lattice site (i) we associate a spin S_i : this is a classical vector in an $s - 1$ dimensional space; it can take s different positions at the corners of a regular polyhedron [14].

For a given arrangement of the chains, we introduce a hamiltonian $\mathcal{H}$ describing certain couplings J_{ij} between *nearest neighbour* spins

$$\mathcal{H} = - \sum_{i < j} J_{ij} S_i \cdot S_j \quad (3.1)$$

$$J_{ij} = \begin{cases} J_0 & \text{if } (i, j) \text{ belong to the same chain} \\ J & \text{if } (i, j) \text{ belong to different chains} \end{cases} \quad (3.2)$$

$$J_0 \gg NJ > 0.$$

To the system described by (3.1) we associate a fictitious temperature τ (which has nothing to do with the physical temperature of the chains) and we restrict our attention to the temperature region

$$\tau \sim NJ \ll J_0. \quad (3.3)$$

Then all spins along one chain are locked and parallel to each other.

From reference [13] we know that if we take the formal limit $s \rightarrow 1$ in the system described by (3.1), we generate a percolation problem, where two nearest neighbour sites i and j have a probability p_{ij} of being connected

$$p_{ij} = 1 - \exp(-2 J_{ij}/\tau). \quad (3.4)$$

With our choice of J_{ij} , and the inequality (3.2), we see that

$$p_{ij} = \begin{cases} 1 & \text{if } (i) \text{ and } (j) \text{ belong to the same chain} \\ p = 1 - \exp - \frac{2J}{\tau} \cong \frac{2J}{\tau} & \text{if not.} \end{cases} \quad (3.5)$$

This corresponds exactly to a vulcanization problem, where the cross-linking species is spread over all bonds between different chains with a (small) probability p of building up a cross link : the fraction of cross linked monomers ρ and the probability p are proportional [$\rho \cong p(Z_1 - 2)$, where Z_1 is the coordination number of the lattice].

For the temperature interval of interest, the Landau Ginsburg free energy [14] corresponding to eq. (3.1) has the form

$$F/\tau = A \left[\frac{\tau - \tau_c}{N\tau} \right] \theta^2 + \frac{B}{N} \theta^3 + \frac{C\tau_c}{N\tau} \xi_0^2 (\nabla\theta)^2 + \dots \quad (3.6)$$

where F is an energy per unit cell, A, B, C are numerical constants and θ is the average of S_i .

Eq. (3.6) is justified as follows :

a) the terms

$$\frac{A}{N} \theta^2 + \frac{B}{N} \theta^3 + \dots$$

come from the entropy of partially aligned spins. The $1/N$ factor expresses the fact that all spins in one chain are in unison. The existence of an θ^3 term is related to the lack of centrosymmetry of the basic polyhedron (for $s \neq 2$);

b) the term $-\frac{A\tau_c}{N} \theta^2$ describes the J interaction between neighbour chains (τ_c/N is proportional to J);

c) the coefficient of the gradient term $(\nabla\theta)^2$ can be understood as follows : two neighbouring sites (i) and (j) belonging to different chains have a difference of magnetization

$$\theta_i - \theta_j \sim \nabla\theta \cdot (\bar{\mathbf{R}}_{(i)} - \bar{\mathbf{R}}_{(j)}) \quad (3.7)$$

where $\bar{\mathbf{R}}_i$ is the center of gravity of the chain to which (i) belongs, and :

$$\langle (\bar{\mathbf{R}}_{(i)} - \bar{\mathbf{R}}_{(j)})^2 \rangle \sim \xi_0^2.$$

We may eliminate τ and write the free energy in terms of θ and of the percolation probability p (eq. (3.5)) :

$$\frac{F}{\tau p_c} = A\theta^2 \frac{p_c - p}{p_c} + B\theta^3 + C\xi_0^2 (\nabla\theta)^2 \dots \quad (3.8)$$

Eq. (3.8) leads to a critical behaviour in agreement with the tree approximations : for instance when $p > p_c$ the optimum of F corresponds to

$$\theta = \frac{2A}{3B} \frac{p - p_c}{p_c} \cong (\rho - \rho_c)/\rho_c. \quad (3.9)$$

Starting from eq. (3.8) it is easy to calculate the fluctuations of θ in the mean field approximation, and to apply the Ginsburg approach [5] : the results coincide with eq. (2.6-8).

Remark. — In the transition from the hamiltonian $\mathcal{H}$ to the mean field free energy F , we ignored any complication related to the disorder of the chains, or the resulting disorder of the coupling constants J_{ij} . In certain systems, a weak randomness in the coupling constants is enough to alter the critical exponents [15]. This complication is not expected to occur here, since the specific heat is not singular for the $s = 0$ Potts model.

4. Conclusions. — For very long chains, we expect that the sol-gel transition induced by a weak cross-linking, to follow the classical picture, with the critical exponents (1.4). For shorter chains, we predict a cross over between classical behaviour, not too close from threshold and percolation behaviour (eq. 1.1-3), very close to threshold.

The fact that cyclisations become less important for long chains is intuitively obvious. But the merit of the Ginsburg approach is to tell us exactly *how long* the chains must be if we want the classical theory to apply at a given (small) distance from threshold : this is given by eq. (2.9).

Precise measurements of the weight average molecular mass (Z) below threshold and of the gel fraction (θ) above threshold, for *various chain lengths* (N) are not currently available, but would be of great interest.

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