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To cite this version:
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(Received 2 November 1994, revised in final form 21 December 1994, accepted 4 January 1995)

Abstract. — We study the effects of three- and fourfold crosslinks on wormlike micelles. This model is worked using a correspondence between magnetic models and equilibrium polymers. We obtain the phase diagrams and the critical behavior of the concentration of extremities and of crosslinks. These crosslinks generate a demixing for both three- and fourfold connections. We show that, due to the difference of parity between the three- and fourfold connections, the behavior is quite different for each case.

1. Introduction

Wormlike micelles in solution, liquid sulfur, etc. are known to be equilibrium polymers. They are also called living polymers. They are linear objects whose length is not fixed chemically but thermodynamically. They reach a dynamic equilibrium, where they do not cease to break and recombine or grow and retract. Hence these systems are different and apparently more complex than usual polymer solutions.

Some surfactant solutions were observed by S.A.N.S. to form worm like micelles [1]. Rheological measurements and their analysis gave an estimate of the micelle length [2, 3]. Recently these micelles showed some strange behavior: increasing salt concentration leads to an increase of the length as usual, but at high concentrations, an apparent decrease of the length [3] followed by a phase separation [4] was observed. This has been suspected to be the signature of the appearance of connections due to charge screening [3–5]. However, many doubts remain: are there really connections and is the demixing linked to the existence of these connections? It is clear that we now need a theoretical description of connected living polymers (Fig. 1).

The aim of this paper is to introduce a theoretical analysis of the role of crosslinks in equilibrium polymers more detailed than the previous one [6]. After recalling the magnetic model used to investigate such equilibrium polymers, we describe the phase diagram of the

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Fig. 1. — We are interested in a system of linear objects that have a chemical potential $\mu$ per unit of length. These chains can close in rings or have extremities of energy $E_1$. They can also form connections of energy $E_3$.

connected equilibrium polymers for both 3 functional and 4 functional connections. Finally, we discuss the consequences of these 3 and 4 connections on worm-like micellar systems.

2. Correspondence Between Ising Model and Equilibrium Polymers

A polymer theory taking excluded volume effects into account is difficult to work. An alternative way is to use the equivalence that exists between the polymers and the magnetic systems since they have been studied very deeply in the theory of critical phenomena.

Living polymers are different from classical polymers since they do not have a fixed length and also because they can sometimes polymerize into rings. It has been shown that such a fluctuating system corresponds to an Ising (one component) magnetic model [7].

Liquid sulfur is a representative example of a system that has been treated this way. Since the giant micelles are very similar to sulfur polymers, the former could also be described by an Ising model.

Our system will consist of a monomer ensemble (chemical potential $\mu$) that can assemble to form rings and chains. Their ends have a fugacity $K_1 = \exp(-E_1/kT)$, where $E_1$ is the end energy. These chains are placed in a good solvent so that there is an excluded volume interaction between them.

Let us establish the correspondence between the chains and rings of living polymers and the Ising model.

The ensemble of chains and rings has the following partition function [8]:

$$Z_p = \sum_{N_e, N_b} n(N_e, N_b) K_1^{N_e} K_p^{N_b}$$

(1)

$K_1$ and $K_p$ being the fugacity per end and per bond respectively.

$N_e, N_b$ are the number of chain ends and of bonds in chains and rings, respectively.

$n$ is the number of configurations for fixed $N_e$ and $N_b$. It must be noticed that it also takes into account the excluded volume effect by giving less weight to configurations where two polymers cross.
2.1. THREE-FOLD CROSSLINKS. — Following the same approach, we can write the partition function for a system with 3-fold crosslinks:

$$Z_p = \sum_{N_a, N_b, N_c} n(N_a, N_b, N_c) K_1^{N_a} K_2^{N_b} K_3^{N_c}$$  \hspace{1cm} (2)

where $K_c$ is the fugacity per crosslink and $N_c$ the number of these crosslinks.

This enables us to write the free energy per unit particle (we suppose $kT = 1$), $f_p = -1/N \ln Z_p$ and deduce the concentrations of ends, monomers and crosslinks that look like:

$$X_1 = \frac{\partial f_p}{\partial \ln K_1}, \quad \phi = \frac{\partial f_p}{\partial \ln K_2}, \quad X_3 = \frac{\partial f_p}{\partial \ln K_3}$$  \hspace{1cm} (3)

Let us now seek for the “magnetic” Hamiltonian that will correspond to this polymer system. The typical way to do it is to make a high temperature expansion and then identify both theories.

We rapidly review the main lines for the unlinked polymer theory. Let us start with the Hamiltonian:

$$H = - \sum_{<i,j>} J S_i S_j - \sum_i h S_i$$  \hspace{1cm} (4)

where $S_i$ is the spin variable; the second sum is over all sites of the lattice. The first is over the $i, j$ pairs of nearest neighbors.

The partition function $Z \equiv \sum e^{-\beta H}$ could then be expanded in $\beta$ (supposed to be small).

A schematic representation of the different terms of our expansion will surprisingly look like polymer and ring configurations [7]. The excluded volume is also taken into account in this one component model, even if it is not as strong as in the limit of zero spin components [9]. Considering universality, this repulsion is in fact sufficient.

In order to generate crosslinked polymers, it is easy to prove that the following Hamiltonian will do it nicely:

$$H = - \sum_{<i,j,k>} KS_i S_j S_k - \sum_{<i,j>} J S_i S_j - \sum_i h S_i$$  \hspace{1cm} (5)

The first sum is over the triplets of $i, j, k$ with $i, k$ two nearest neighbors of $j$.

The partition function can then be expanded in $\beta$ units and is in fact the partition function given in equation (2):

$$Z = \sum n(N_a, N_b, N_c) h^{N_a} J^{N_b} K^{N_c}$$  \hspace{1cm} (6)

Hence the polymer and the “magnetic” models belong to the same universality class. We deliberately write the two partition functions in the same form as in equations (2) and (6) and the two systems are equivalent in the sense that $K_1 \sim h, K_2 \sim J$ and $K_3 \sim K$.

As it is somewhat difficult to work on the discrete “magnetic” models, especially when including fluctuations, we will then work on the continuous formulation of the Ising model. Of course, it is also possible to do a direct diagrammatic correspondence between the continuous models, using the Feynman diagrams for the correlation functions of the “magnetic” model and identifying them to the continuous polymers [10].

$$H = \frac{1}{2}[(\nabla \varphi)^2 + u_2 \varphi^2] + u_0 \varphi^4 - h \varphi$$  \hspace{1cm} (7)
For the Ising model we will have in the continuous limit a Hamiltonian of the form: where $u_2$ is proportional to $(J - J_c)$, $h$ is the same as the one introduced before; $u_0$ is responsible for the excluded volume interaction and does not appear explicitly in the discrete Hamiltonian since it is intrinsically contained in the discreteness of the lattice.

Adding the 3-fold crosslink is equivalent to add a $-u_3\varphi^3$ term, with $u_3 \sim K$. The Hamiltonian will become:

$$H = \frac{1}{2}[(\nabla\varphi)^2 + u_2\varphi^2] - u_3\varphi^3 + u_0\varphi^4 - h\varphi$$  \hspace{1cm} (8)

We stress here that in the Hubbard transformation, $u_2$ is identified with $J - J_c$. Hence $u_2$ in the continuous model is the chemical potential per unit of length while $h$ and $u_3$ are fugacities. Calculating the density of the magnetic free energy $f = -1/N \ln Z$, we can deduce the end, the monomer and the crosslink concentration.

$$X_1 = \frac{\partial f}{\partial \ln K_1} = \frac{\partial f}{\partial \ln h}, \hspace{1cm} (9a)$$

$$\phi = \frac{\partial f}{\partial \ln K_2} = \frac{\partial f}{\partial \ln u_2}, \hspace{1cm} (9b)$$

$$X_3 = \frac{\partial f}{\partial \ln K_3} = \frac{\partial f}{\partial \ln u_3} \hspace{1cm} (9c)$$

For similar reasons, we could also calculate the monomer-monomer correlation function [11]:

$$I_0(x, x') \propto [\frac{1}{2}\varphi(x)^2\varphi(x')^2] - <\varphi(0)^2> \hspace{1cm} (10)$$

**Remark**: In order to describe networks, Lubensky et al. [12] used a Hamiltonian of a similar form but with a tensorial field. The upper critical dimension was then 6 and generated a rich topological variety. With our scalar field the critical dimension is 4 but the topology is fixed and does not allow us to distinguish between the different structures, i.e. for instance, we cannot separate the role of loops in the clusters. Hence, the information we get has nothing to do with cluster topology and percolation transition, which in fact has no thermodynamical role. The complete tensorial model is more complicated and uses a development in $\epsilon = 6 - d = 3$, which is a very crude approximation. Unfortunately, our scalar model does not allow us to get an insight into the topological structure of the clusters.

2.2. **Four-fold Crosslinks** [13]. — In the same way as previously, to include 4-fold connections with a fugacity $K_4$, we only have to add a $u_4\varphi^4$ term to our Hamiltonian, with $u_4 \sim K_4$.

$$H = \frac{1}{2}[(\nabla\varphi)^2 + u_2\varphi^2] + (u_0 - u_4)\varphi^4 + u_6\varphi^6 - h\varphi \hspace{1cm} (11)$$

$u_0$ engendering the excluded volume through the solvent quality, the addition of the $u_4$ term is in fact equivalent to a change of the solvent quality. We also added a $u_6\varphi^6$ term with $u_6 > 0$, since the $\varphi^2$ and $\varphi^4$ coefficients could vanish.

We can also deduce the 4-fold crosslink concentration:

$$X_4 = \frac{\partial f}{\partial \ln K_4} = \frac{\partial f}{\partial \ln u_4} \hspace{1cm} (12)$$
Then using the field theory and critical phenomenon techniques, we can calculate the previous quantities and principally find the phase diagram. For the sake of simplicity, let us first show the main mean-field results.

3. Mean Field

3.1. Three Fold Crosslink. — In the Landau mean-field approximation, the free energy can be written as

\[ F = \frac{1}{2} u_2 m^2 - u_3 m^3 + u_0 m^4 - hm \]  

At the transition point \( h = 0, u_2 = 0, u_3 = 0 \) and \( u_0 > 0 \), the concentrations of ends \( X_1 \), monomers \( \phi \) and crosslinks \( X_3 \) vary like (using Eq. (9)):

\[ X_1 \sim m, \quad \phi \sim m^2, \quad X_3 \sim m^3 \]

\( \phi \) being the polymer parameter that can be controlled (supposing that all the surfactant contribute to the polymerization), we get:

\[ X_1 \sim \phi^{1/2} \quad \text{and} \quad X_3 \sim \phi^{3/2} \]

These results were already derived by Cates and Drye [6] within the frame of the Gaussian approximation.

The phase diagram is shown in Figure 2. For \( h = 0 \) there is a critical point at \( u_2 = u_3 = 0 \) and three- first-order transition lines emerging from it.

![Phase Diagram](image)

Fig. 2. — The mean field phase diagram for threefold crosslinks. \( u_2 \) is the chemical potential and \( u_3 \) the crosslinks fugacity. The discontinuous lines are for \( h = 0 \) (no extremities). There are three first-order lines coming out of the critical point located at \( u_2 = u_3 = 0 \). The continuous lines are for \( h > 0 \) (with extremities). The critical point moves from the origin leaving a gap and creating a dissymmetry in the phase diagram.

If \( h \neq 0 \), then the phase diagram looks quite different with a region where no first-order transition can happen for weak \( u_3 \) (Fig. 2).
Fig. 3. — The mean-field phase diagram for fourfold crosslinks. $u_2$ is the chemical potential and $u_4$ the crosslink fugacity. $h = 0$ (no extremities) is represented by the discontinuous lines. A critical line appears for $u_2 = 0$ and $u_4 < u_0$. The point at $u_2 = 0$ and $u_4 = u_0$ is tricritical followed by a parabolic first-order line for $u_4 > u_0$.

3.2. FOUR-FOLD CROSSLINKS. — The Landau free energy is written

$$F = \frac{1}{2}u_2m^2 + (u_0 - u_4)m^4 + u_6m^6 - hm$$

(14)

The phase diagram is shown in Figure 3. If $h = 0$, the point where $u_4 = u_0$ and $u_2 = 0$ corresponds to a tricritical point, a critical line appears at $u_2 = 0$ and $u_4 < u_0$ and the parabolic line for $u_4 > u_0$ is of first order. When $h$ is non-zero, the tricritical point transforms into a critical one and the first-order line remains. If $h$ grows but remains close to zero, these critical effects will still be felt.

In the vicinity of the tricritical and critical parts of the phase diagram, the end and crosslink concentration will vary like: $X_1 \sim \phi^{1/2}$ and $X_4 \sim \phi^2$

4. Renormalization Group

While for the fourfold crosslink case the phase diagram will not show any qualitative difference when including fluctuations, in the case of threefold crosslink, the phase diagram will be affected by fluctuations and will be topologically different, as argued by Alexander and Amit [14].

For the threefold crosslink case, we can do the renormalization group calculation. In fact, as shown by Alexander and Amit, this problem can be transformed into an easier one. We are going to take up this demonstration again:

If we start with:

$$H = \frac{1}{2}(\nabla \phi)^2 + \frac{1}{2}u_2\phi^2 - u_3\phi^3 + u_0\phi^4 - h\phi$$

(15)

with the following change of variable $\phi = \psi + \frac{u_2}{4u_0}$ the Hamiltonian becomes:

$$H = \frac{1}{2}(\nabla \psi)^2 + \left(\frac{u_3}{4u_0}(u_2 - \frac{u_2^3}{2u_0}) - h\right)\psi + \left(\frac{u_2}{2} - \frac{3u_3^2}{8u_0}\right)\psi^2 + u_0\psi^4$$

(16)

We see that, since the order parameter is scalar, we can transform the original Hamiltonian with $\phi^3$ into a classical Hamiltonian $\psi^4$ with magnetic field.
Then the effective magnetic field and the effective $u_2$ parameter are given by

\[ h_{\text{eff}} = h - \frac{u_3}{4u_0}(u_2 - \frac{u_2^2}{2u_0}) \]

and

\[ u_{2\text{eff}} = u_2 - \frac{3u_3^2}{4u_0} \]

This kind of Hamiltonian is well-known and allows us to use the results already computed. For the following Hamiltonian:

\[ H = \frac{1}{2}(\nabla\psi)^2 + \frac{1}{2}a_2\psi^2 + a_4\psi^4 - h'\psi \]

there is a critical point at $a_2 = a_{2c}$ and $h' = 0$ and a first-order line for $a_2 < a_{2c}$ and $h' = 0$.

This enables us to find the phase diagram (Fig. 4) by mapping the following phase diagram on $u_2$, $u_3$ using $u_{2\text{eff}}$ and $h_{\text{eff}}$. There are three critical points and three first-order lines, one coming out of each critical point. The important difference with the mean field is the appearance of the gap for $u_2$ and $u_3$ weak. Thus this intermediate region between the two critical points is a crossover one.

The scaling part of the free energy is written

\[ F \sim (\Delta u_2)^{2-\alpha} f \left( \frac{h}{(\Delta u_2)\Delta} \right), \quad \Delta = \beta + \gamma \]

$f(x)$ being a regular function of $x$ and $\alpha$, $\beta$ and $\gamma$ the one component magnetic critical exponents, with the usual notation.
We can estimate the variation of ends and connections with the concentration in the vicinity of the critical points. Using equation (9), we get:

\[ X_1 \sim (\Delta u_2)^\beta \sim \phi^{\beta/(1-\alpha)} \]  

(20)

With the same scaling form of the free energy as in equation (19), we derive \( X_3 \). Including the \( u_3 \) term is just equivalent to replacing \( u_2 \) by \( u_{2\text{eff}} \) and \( h \) by \( h_{\text{eff}} \) (17a), (17b), in the previous equation.

Near the first critical point we have \( u_3 \to 0 \). Hence \( \Delta u_2 = u_2 - a_2 \) and \( h \sim u_3 \). Using equation (9c), we get easily:

\[ X_3 \sim (\Delta u_2)^{2-\alpha-\Delta} = (\Delta u_2)^\beta \sim \phi^{\beta/(1-\alpha)} \]  

(21)

which is the same variation in \( \phi \) as for \( X_1 \).

Near the second critical point, the situation is completely different and more complicated. \( X_3 \) and \( \phi \) varying with the same exponents, we have the very different result: \( X_3 \sim \phi \). Hence, the effect of fluctuations is to modify the topology of the phase diagram. Two critical points appear with a very different behavior of \( X_3 \).

**Remark:** We could also think of a mixture of three- and fourfold crosslinks. In this case, the critical effects will be dominated by the threefold connections in the critical region, \( u_3 \) like \( h \) removing the system from the tricritical point.

### 5. Consequences for Equilibrium Polymers

#### 5.1. Threefold Crosslink.

Let us just discuss the meaning of our parameters. Since \( u_3 \) and \( h \) are fugacities, the physical region corresponds to \( u_3 > 0 \) and \( h > 0 \); \( u_2 \) is the chemical potential per monomer and then, the conjugate of concentration. Then a decrease of \( u_2 \) is equivalent to an increase of concentration \( \phi \). On the other hand, \( h \) controls the concentration of extremity. Similarly a decrease of \( h \), i.e. an increase of the extremity energy, decreases the extremity concentration.

Varying \( \phi \), we are going to explore three regions in the phase diagram (Fig. 4). Increasing the chemical potential \( u_2 \) is equivalent to decrease the concentration.

Along line 1 (Fig. 4), we go near the critical point located at \( h = 0 \), \( u_3 = 0 \) and \( u_2 = u_{2c} \) (actually, we can reach this point only for a solution without any end nor crosslink). This critical transition corresponds to a merged polymerization and overlapping transition. Adding extremities will lower the critical effect and the signature of the overlapping transition will be a maximum for the correlation length and for the compressibility: adding extremities will increase the number of polymers, then shorten their length and soften the critical behavior. Putting connections between our chains will also move the system away from that criticality. The concentration near the critical point is the overlapping one.

Increasing \( h \) moves the critical point to the non-physical region of the phase diagram. The distance from this critical point is \( h_{\text{eff}} \sim h - u_3 u_{2c}/4u_0 \) (\( u_{2c} < 0 \)). We see that \( h \) and \( u_3 \) play a similar role.

This explains that \( X_1 \) (the extremity concentration) and \( X_3 \) (the crosslink concentration) have the same critical exponent \( (\phi^{\beta/(1-\alpha)}) \) (20), (21). Let us note that this exponent for \( X_1 \) has also been derived by Cates [15] using scaling arguments. It is suspected that the tadpole terms (Fig. 5a) are controlling the effect of \( u_3 \) near this first critical point because they engender effective ends.

Let us sweep line 2, decreasing the chemical potential \( u_2 \) hence increasing the concentration. Near the second critical point, the effects of \( u_2 \) and \( u_3 \) are mixed in the \( h_{\text{eff}} \) and \( u_{2\text{eff}} \). As
calculated before, \(X_3 \sim \phi\) while \(X_1\) remains in \(\phi^{\beta/(1-\alpha)}\) near the critical point. Since the ends vary slowly and the connections grow proportional to the monomer quantity, we suspect that we do not have a stretched network at all (in contrast with the arguments of Cates and Drye [6] of “saturated/unsaturated regime” in order to locate the phase separation). We guess that the system could be made of bubble structures (Fig. 5b). This would mean that, in this case, the connections are uniformly distributed on the polymers and not attracting two chains. Following fine 3, we cross a first-order line. Crossing this line, the concentration is discontinuous. This means that a phase separation occurs there between a dilute phase (up) and a dense phase (down).

5.2. FOURFOLD CROSSLINK. — We saw that the addition of the \(u_4\) term is equivalent to a change in the solvent quality. When the attraction due to \(u_4\) compensates the excluded volume effect \(u_0\), a phase separation will happen and that is what we can check by plotting the phase diagram (Fig. 3).

The concentration could be varied by changing the chemical potential as in the case of the threefold crosslink and we also see that we have three typical regions.

Since, in our physical system, ends are always present, we must have \(h > 0\). We saw that when \(h\) is small enough, we still feel the tricritical point if \(u_4 = u_0\) and \(u_2 = 0\) and the critical line for \(u_4 < u_0\).

The critical line will generate polymerization when \(u_4\) is weak. A first-order line starts from the tricritical point and represents the demixing. This demixing is in fact similar to that due to the change of solvent quality in classical polymers.

With a variation of the crosslink energy, we have a continuous passage from linear polymers to a compact reticulated system until the excluded volume effect is compensated by the attraction due to the crosslinks. Then we get a demixing between two phases, one compact and one dilute.

Around this tricritical point, \(X_4 \sim \phi^2\) which means that the density of entanglements is proportional to the density of the contact points and that the phase separation must be quite different from the threefold crosslink case.

We notice that apparently the three- and fourfold crosslinks have a similar phase diagram,
with a critical point followed by a first-order demixing line. However, the nature of the critical point and that of the transition are very different.

6. Conclusion

In this paper, we have studied the effects of crosslinks on equilibrium polymers. We have used field theory techniques, which are well adapted to treat fluctuations. We observed that fluctuations play a dominant role for this kind of system (mostly for threefold crosslinks).

The physical results are the following:

Both three- and fourfold crosslinks induce phase separations and these phase separations are of a different nature. The fourfold crosslink is equivalent to a solvent change and thus leads to a tricritical behavior, while the threefold crosslink leads to a critical behavior.

Surprisingly, for the threefold crosslink case, \( X_3 \sim \phi \) near the demixing critical point so that there is apparently no stretching of the polymer network close to the phase separation.

The drawback of our simple scalar model is that we are not able to characterize the topologies of our different phases.

It is certainly interesting to better understand the phase separation and the structure of such phases by performing more experiments and also numerical simulations.

Acknowledgments

We are grateful to L. Schäfer for extremely stimulating discussions and useful remarks.

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