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LETTER TO THE EDITOR

Polymer chains and vulcanisation†

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Abstract. We propose a discrete Hamiltonian to describe the vulcanisation which occurs when linear polymer chains are mixed with cross-linking units. Here the vulcanisation of the chains can occur via clusters of cross-linking units. The Hamiltonian is a simple combination of the n -vector model in the limit when n goes to zero, and the m -states Potts model when m goes to unity. We discuss the partition function. The Migdal renormalisation group shows that the chain behaviour is always controlled by the self-avoiding walk (SAW) fixed point. The vulcanisation is described by percolation exponents except in the vicinity of a higher-order critical point where it crosses over to the SAW exponents.

1. Introduction

Both linear polymer solutions and gels have received a renewed attention these last few years. Among other salient features, their relation to critical phenomena has been widely discussed both phenomenologically (Cotton *et al* 1976, Farnoux 1976, de Gennes 1975, Stauffer 1976) and microscopically (Domb *et al* 1965, de Gennes 1972, des Cloizeaux 1975, Lubensky and Isaacson 1978, Coniglio *et al* 1979). In the present Letter we wish to present a discrete Hamiltonian which allows us to study both polymer solutions and gelation of polyfunctional units (Flory 1953, Stockmayer 1943) as two limits. In between these two limits, it describes a situation where linear polymer chains can link together and eventually form an infinite molecule (vulcanisation). The limiting situations and the vulcanisation case are shown in figure 1. Let us remark here that by vulcanisation we mean not only the usual case where two neighbouring monomers of different chains can cross-link (Daoud 1979), but the more general case where two molecules which may be far apart from each other can be cross-linked by a cluster made of cross-linking units (wavy lines in figure 1). Hence, for instance, whereas the usual vulcanisation can occur in the semi-dilute regime only, we consider here the more general case where it can also take place in the dilute regime.

More specifically, we know that the linear polymer solutions may be described by an n -vector model in the limit when n goes to zero and in the presence of an applied external field (des Cloizeaux 1975):

$$\mathcal{H}_0 = \sum_{\alpha=1}^n JS_i^\alpha S_j^\alpha + H \sum_i S_i^1. \quad (1a)$$

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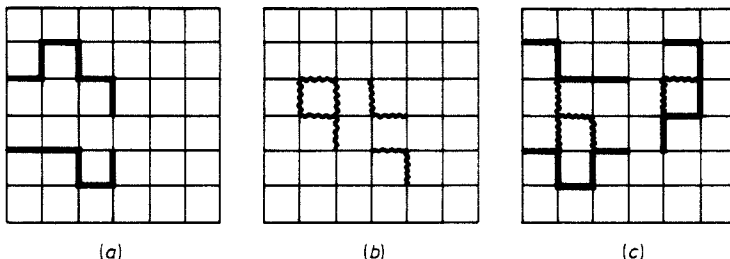


Figure 1. (a) Two polymer chains embedded on a square lattice. (b) Three clusters made of cross-links as in pure bond percolation. (c) Two clusters made of chains and cross-links. The cross-links (wavy lines) may connect two chains even if they do not have neighbouring monomers.

Alternatively, one can use the discrete version introduced by Hilhorst (1977a, b):

$$\bar{\mathcal{H}}_0 = nJ \sum_{\langle i,j \rangle} s_i s_j \delta_{\nu_i \nu_j} + \sqrt{n} H \sum_i s_i \delta_{\nu_i, 1}, \quad (1b)$$

where $s_i = \pm 1$ and $\nu_i = 1, 2, \dots, n$.

On the other hand, a useful model for gelation is bond percolation (Flory 1953, de Gennes 1975, Stauffer 1976), described by the m -states Potts model (Kasteleyn and Fortuin 1969, Wu 1978) in the limit when m goes to unity:

$$\mathcal{H}_P = \sum_{\langle i,j \rangle} \delta_{\sigma_i \sigma_j}. \quad (2)$$

We propose here a model Hamiltonian which is a simple combination of (1) and (2) which describes situations in between:

$$-\beta \mathcal{H} = \sum_{\langle i,j \rangle} (JS_i^\alpha S_j^\alpha + K) \delta_{\sigma_i \sigma_j} + H \sum_i S_i^1. \quad (3)$$

On each site, we have now two variables S and σ . The sum is restricted to nearest neighbours. Let us note:

(i) When $K = 0$, (3) describes the usual linear polymer solutions (figure 1(a)). This can be easily checked by using the discrete version 1(b) instead of 1(a) in (3).

(ii) When $J = 0$, it describes the gelation problem (figure 1(b)).

The purpose of this Letter is to investigate situations where both J and K are non-zero and to show that (3) is the most convenient form for the study of vulcanisation.

2. The partition function

The partition function for Hamiltonian (3) is

$$Z = \text{Tr}_{\{s\}} \text{Tr}_{\{\sigma\}} \prod_{\langle i,j \rangle} \exp(JS_i^\alpha S_j^\alpha + K) \delta_{\sigma_i \sigma_j}, \quad (4)$$

but we have

$$\prod_{\langle i,j \rangle} \exp(JS_i^\alpha S_j^\alpha + K) \delta_{\sigma_i \sigma_j} = \prod_{\langle i,j \rangle} \{1 + [(e^K - 1) + J e^K S_i^\alpha S_j^\alpha] \delta_{\sigma_i \sigma_j}\}, \quad (5)$$

where $e^{S_i^* S_j^*}$ has been developed. Only the terms linear in $S_i^\alpha S_j^\alpha$ have been kept, as they are the only ones which will survive in the limit $n = 0$ (Daoud *et al* 1975). The right-hand side of (5) can be written

$$\sum_{C \subseteq E} \prod_{\substack{\langle i,j \rangle \in C \\ \alpha}} (R + TS_i^\alpha S_j^\alpha) \delta(C), \tag{6}$$

where E is the set of all the bonds in the lattice, C is a subset of E , $\langle i, j \rangle$ denotes the bond connecting the two nearest-neighbour sites i and j , and

$$\delta(C) = \prod_{\langle i,j \rangle \in C} \delta_{\alpha_i \sigma_j}, \quad R = e^K - 1, \quad T = J e^K.$$

Clearly (6) is equal to

$$\sum_C \left(\sum_{C_1 \subseteq C} R^{|D_1|} T^{|C_1|} \prod_{\langle i,j \rangle \in C_1} S_i^\alpha S_j^\alpha \right) \delta(C), \tag{7}$$

where $C_1 + D_1 = C$, and by $|D_1|$ we mean the number of bonds in the subset D_1 . Now we can also develop the term $e^{HS_i^1}$ to second order,

$$e^{HS_i^1} = 1 + HS_i^1 + \frac{1}{2} H^2 (S_i^1)^2, \tag{8}$$

and from (8), (7) and (4) we obtain

$$Z = Z_0 \sum^* \lambda_e^D \lambda_K^{D_1} \lambda_J^{C_1} \lambda_H^{2N_P} m^{N_c(C)}, \tag{9}$$

where

$$Z_0 = \left(1 + \frac{H^2}{2} \right) \left(\frac{e^{-K}}{1+J} \right)^{|E|},$$

$$\lambda_e = e^{-K}/(1+J), \tag{10a}$$

$$\lambda_K = (1 - e^{-K})/(1+J), \tag{10b}$$

$$\lambda_J = J/(1+J), \tag{10c}$$

$$\lambda_H = H/(1 + H^2/2)^{1/2}, \tag{10d}$$

$$\tilde{J} = J(1 + H^2/2), \tag{10e}$$

with $N_c(C)$ the number of clusters in the 'configuration' C . Note that $C = C_1 + D_1$, where C_1 is a subset of bonds which can form linear chains only (these bonds will be called *links*), while the bonds in D_1 which have no restriction will be called *cross-linking units*.

A cluster in C is therefore a maximal set of sites connected by bonds of either C_1 or D_1 or both. One can see clearly from (9) that Z can be considered as the partition function of a grand ensemble with the following activities: λ_e = absence of bonds; λ_K = cross-linking units (wavy lines); λ_J = links (straight lines); λ_H = number of chains; m = number of clusters.

Note that these activities have been normalised:

$$\lambda_e + \lambda_J + \lambda_K = 1.$$

The mean number of clusters is

$$\langle N_c \rangle = \frac{1}{Z} \frac{\partial Z}{\partial m} \Big|_{m=1}$$

In principle, one might think of gelation processes in which $m \neq 1$ (Lubensky and Isaacson 1978). In this case, the critical exponents will not be the same as the percolation exponents.

3. Renormalisation group

Now we apply Migdal's renormalisation group (Migdal 1975, Kadanoff 1976) to the Hamiltonian (3) using the discrete version of the n -vector model. Let T be the transfer matrix and T_{ij} the elements of such a matrix; then the transformation that we use is (Nicoll 1979)

$$T'_{ij} = [T^b (T_{ij}^{b^{d-1}})]_{ij},$$

where b is the scaling factor and d is the dimensionality. For $b = 2$, $d = 2$ the recursion relations in the limit $n = 0$, $m = 1$ are

$$J' = 4J^2/(1 + H^2/2), \quad (11a)$$

$$H' = 2H + 8HJ/(1 + H^2/2), \quad (11b)$$

$$K' = \ln[e^{4K}/(2e^{2K} - 1)]. \quad (11c)$$

The first two equations are independent of K , and therefore coincide with the equations that one would have obtained from the pure n -vector model ($K = 0$). The eigenvalue exponents will be the same as for the SAW. From equations (1a, b) we find a non-trivial fixed point

$$H^* = 0, \quad J^* = \frac{1}{4},$$

with eigenvalue exponents $y_J = 1$ and $y_H = 2$. In this approximation the SAW exponent $\nu = y_J^{-1} = 1$. Other trivial fixed points are at: $H = 0, J = 0$; $H = 0, J = \infty$; $H = \infty, J = 0$. Equation (11c) is independent of J and H , and therefore is the same as for the pure Potts model. The eigenvalue exponent is the same as for the percolation problem. From equation (11c) we find the fixed point $K^* = 0.481$ and the eigenvalue exponent $Y_K = 0.612$. In this approximation the percolation exponent $\nu_p = Y_K^{-1} = 1.63$. This separation of the equations does not mean that the two problems are completely independent of each other. In fact, from equation (10b) we see that the activity for cross-links λ_K depends on K, J and H . Consequently, the presence of the chains affects the percolation problem. However, the activity of the links (of the chains) λ_J and the number of chains λ_H do not depend on K . Consequently the configuration of the chain is independent of whether or not there are cross-links, in particular whether or not the chain belongs to an infinite cluster, in agreement with experimental results (Duplessix 1976).

For $H = 0$ the interplay of the fixed points gives rise to the phase diagram and flow lines given in figure 2. The line $\lambda_J = \lambda_J^* = J^*/(1 + J^*)$ corresponds to the divergence of the radius of gyration of the single chain. The critical exponents along the whole line are given by the usual SAW exponents. The left of point 0^* in the diagram corresponds to the absence of an infinite cluster, while the right corresponds to the presence of an infinite cluster. The line $\lambda_K = (1 - e^{-K^*})/(1 + J)$ ($0 < J < J^*$) corresponds to the divergence of a single cluster, part of which is made of a chain. It starts at $\lambda_K^* = 1 - e^{-K^*}$, and ends at a critical point 0^* whose coordinates are λ_J^* and $\Lambda_K^* = (1 - e^{-K^*})/(1 + J^*)$. Such a point 0^* is characterised by the divergence of both the cluster and the chain.

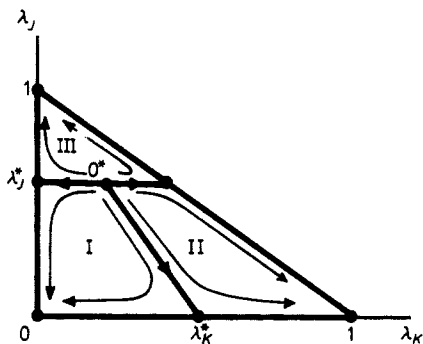


Figure 2. Fixed points and flow lines, for $H = 0$, dividing the λ_K, λ_J plane into three regions: I: finite clusters and finite chain; II: infinite cluster and finite chain; III: macroscopic chain whose density (number of links)/(number of sites) $\neq 0$.

The linear dimension of the cluster ξ_P near the point O^* behaves as

$$\xi_P \sim (K - K^*)^{-\nu_P} f\left(\frac{|J - J^*|}{|K - K^*|^\Delta}\right), \tag{12}$$

where $\Delta = \nu_P/\nu$ is the cross-over exponent, and

$$f(x) \sim \begin{cases} \text{const} & \text{if } x \ll 1 \\ x^{-\nu} & \text{if } x \gg 1. \end{cases} \tag{13}$$

The two critical lines divide the phase diagram into three regions: region I corresponds to finite clusters and a finite chain; region II corresponds to an infinite cluster and a finite chain; and region III corresponds to a macroscopic chain whose density (number of links)/(number of sites) $\neq 0$.

So far we have considered the critical behaviour of a single chain in a cluster or the critical behaviour of a single cluster, part of which is made of a chain.

Now we consider the case $H \neq 0$ which corresponds to a finite density of chains. The critical threshold for percolation λ_{K_c} is given from (10b), putting the scaling field $B - B^* = 0$, by

$$\lambda_{K_c} = (1 - e^{-K^*}) / (1 + \tilde{J}), \tag{14}$$

where $\tilde{J} = J / (1 + H^2/2)$.

Note that the critical surface given by (14) is controlled by the fixed point ($K = K^*$, $H = \infty$, $J = 0$) with percolation exponents.

In particular, if H is small and J large enough (long chains) equation (14) describes vulcanisation of chains. We note that in the usual way of treating vulcanisation (Daoud 1979), cross-linking occurs only between neighbouring monomers of different chains. Here, the chains can also be linked via large clusters of cross-linking units. Of course, the two situations coincide in the limit of small λ_{K_c} .

A similar behaviour occurs in the site-bond correlated percolation problem (Coniglio and Klein 1979). If the value of $\lambda_K \neq \Lambda_K^*$, the critical line ends at a critical end-point.

In figure (3) we have plotted the critical curve obtained from (15) for fixed value of λ_{K_c} . An interesting situation occurs if we choose $\lambda_{K_c} = \Lambda_K^* = (1 - e^{-K^*}) / (1 + J^*)$. In this case the line ends at a critical point where the length of the chain diverges. This point

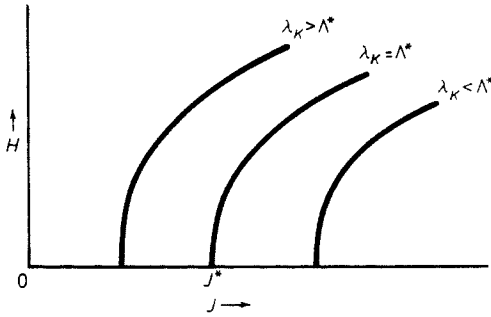


Figure 3. Critical curves of vulcanisation for fixed value of cross-link activity λ_K in the plane H, J . There is a particular value $\lambda_K = \Lambda^* = (1 - e^{-K^*})/(1 + J^*)$ such that the critical line of vulcanisation ends at a higher-order critical point $H = 0, J = J^*$. This is the critical point for the SAW problem, where the exponents cross over from percolation to SAW.

can be considered as a higher-order critical point for vulcanisation, and critical exponents will cross over from percolation exponents to SAW exponents. Although we have restricted our discussion to dimensionality $d = 2$, the previous results are valid also for $d = 3$ since the structure of the RG equations does not change.

4. Conclusions

In conclusion, we have exhibited a model Hamiltonian which incorporates the features of the m -states Potts model and the n -vector model. In the two limiting cases it describes gelation (pure m -states Potts model) and linear polymer solution (pure n -vector model), while in the intermediate case it describes vulcanisation of polymer chains. The Migdal RG has been used to study the model.

All the vulcanisation processes are controlled by the percolation exponents. However, for a particular choice of the cross-linking activity, there is a critical line of vulcanisation which ends at a higher-order critical point. This is the critical point for the SAW problem, where the exponents cross over from percolation to SAW.

The chain problem is always controlled by the SAW fixed point. More explicitly, the radius of gyration of a chain which is part of the infinite network has the SAW exponent (Duplessix 1976).

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