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LETTER TO THE EDITOR

$O(n)$ field theory with n continuous as a model for equilibrium polymerisation

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Abstract. A grand canonical ensemble of continuous chains and rings is introduced for describing polymerisation equilibrium like that of sulphur. We show its equivalence to $O(n)$ field theory, with n continuous, $n \rightarrow 1$.

Equilibrium polymerisation of open polymer chains has been tentatively described by an n -vector lattice model, with $n \rightarrow 0$ (Wheeler *et al* 1980), with applications to liquid sulphur, and liquid sulphur solutions (Wheeler and Pfeuty 1981). However, for sulphur, the formation of large rings must be considered (Harris 1970). Lattice models of polymerisation including polymer loops have been very recently proposed (Pfeuty and Wheeler 1981, Rys and Helfrich 1982, Cordery 1981).

In the first two papers, an n -vector lattice model was proposed for *self-avoiding* chains and loops, with an anisotropy for l components among n . The rather odd limit $n \rightarrow 0$, l fixed, $0 < l \leq 1$, was taken. It was conjectured that (a) the critical behaviour should be that of an l -component model (Pfeuty and Wheeler 1981). In fact, for spin models on a lattice, like Sarma's (1978), the $n \rightarrow 0$ limit suppresses loops and crossings *at once*, which makes it unsuitable for self-avoiding loops on a lattice. The lattice model of Cordery (1981), on the other hand, involves chains and loops which can cross with a finite interaction energy E_{cell} . For a unique particular choice of E_{cell} the model happens to map onto the Ising model, and (b) corresponds therefore to the limit $n = l = 1$. This model presents two difficulties. For a different E_{cell} , it is no longer exactly an Ising model, and (c) the concentration of rings at equilibrium cannot be obtained from it.

In this Letter, we consider a continuous mathematical model of open chains and closed rings with any interaction between them. It represents infinitely thin polymers in solution. The polymerisation equilibrium is governed by three chemical potentials, associated with the number of polymerised links, the number of chains and the number of rings. Using functional integrals (Duplantier 1980), we show that this model is identical to an $O(n)$ field theory, where n is a continuous variable. This proves conjecture (a), where $l \equiv n$. A physical argument (for sulphur for instance) leads to the limit $n \rightarrow 1$ near the polymerisation point and this agrees with (b). Lastly, the concentration of rings is given by differentiating with respect to n , and this solves (c).

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The grand canonical partition function \mathcal{Q} of the system of continuous chains and rings at polymerisation equilibrium is defined by

$$\mathcal{Q}(n, a, h) = 1 + \sum_{\mathcal{M}=1}^{\infty} \frac{h^{2\mathcal{M}}}{\mathcal{M}!} \sum_{\mathcal{L}=1}^{\infty} \frac{n^{\mathcal{L}}}{\mathcal{L}!} \int_0^{\infty} \prod_{m=1}^{\mathcal{M}} dS_m \exp(-aS_m) \times \int_0^{\infty} \prod_{i=1}^{\mathcal{L}} dS'_i \exp(-aS'_i) + \mathcal{L}(S_1, \dots, S_{\mathcal{M}}; S'_1, \dots, S'_{\mathcal{L}}) \quad (1)$$

where ${}^+\mathcal{L}$ is the regularised partition function, with the proper symmetry factors, of an interacting system of \mathcal{M} continuous chains and \mathcal{L} continuous polymer rings, of Brownian areas S_m and S'_i (for chains made of N discrete links of length l , $S \equiv Nl^2$). \mathcal{Q} yields the average total Brownian area $\langle S \rangle$, the average number $\langle \mathcal{M} \rangle$ of polymer chains, and the average number $\langle \mathcal{L} \rangle$ of rings:

$$\langle S \rangle = \frac{\partial}{\partial a} \ln \mathcal{Q}, \quad \langle \mathcal{M} \rangle = \frac{h}{2} \frac{\partial}{\partial h} \ln \mathcal{Q}, \quad \langle \mathcal{L} \rangle = n \frac{\partial}{\partial n} \ln \mathcal{Q}. \quad (2)$$

Dimensionally (see below), $[n] = l^0$, $[a] = l^{-2}$, $[h] = l^{-1}$. The fugacities e^{-a} , n , h^2 correspond (up to dimensional factors due to the continuous limit) to *Gibbs factors* $\exp(-\Delta F/kT)$, where the ΔF measure the different polymerisation chemical steps (see for instance, Pfeuty and Wheeler (1981)). In the present model, we simply assume e^{-a} , n , h^2 to be functions of T such that

$$a(T) \rightarrow a_c^+ \quad \text{for } T \rightarrow T_c^-, \quad (3)$$

$$n(T) \rightarrow 1 \quad \text{for } T \rightarrow T_c^-, \quad (4)$$

where $a(T)$ is a decreasing function of T , T_c is the critical polymerisation temperature and a_c the critical value of 'a' such that $\langle S \rangle = \infty$. Equation (4) is a physical assumption: the probability of opening a ring to form a chain, h^2/n , equals that of cutting a chain into two chains, $(h^2)/h^2$. This holds for very long rings and chains and thus near T_c , where the polymerised objects are very long.

Considering (1) as a mathematical object by itself, we show now that it is exactly equal to the partition function of an $O(n)$ field theory.

Consider first for simplicity one continuous polymer chain and one continuous closed loop, of Brownian areas S and S' . Their configurations in d -dimensional space are given by vectors $\mathbf{r}(s)$, $0 \leq s \leq S$, and $\mathbf{r}'(s)$, $0 \leq s \leq S'$, with $\mathbf{r}'(0) \equiv \mathbf{r}'(S')$. The action (or energy) associated with the configuration $\{\mathbf{r}, \mathbf{r}'\}$ reads

$$A\{\mathbf{r}, \mathbf{r}'\} = A_0\{\mathbf{r}\} + A_0\{\mathbf{r}'\} + A_1\{\mathbf{r}, \mathbf{r}'\}, \quad (5)$$

$$A_0\{\mathbf{r}\} \equiv \int_0^S ds \left(\frac{d\mathbf{r}(s)}{ds} \right)^2, \quad (6)$$

$$A_1\{\mathbf{r}, \mathbf{r}'\} \equiv \frac{1}{2} \int_0^S ds \int_0^S ds' \mathcal{V}[\mathbf{r}(s) - \mathbf{r}(s')] + \frac{1}{2} \int_0^{S'} ds \int_0^{S'} ds' \mathcal{V}[\mathbf{r}'(s) - \mathbf{r}'(s')] + \int_0^S ds \int_0^{S'} ds' \mathcal{V}[\mathbf{r}(s) - \mathbf{r}'(s')]. \quad (7)$$

A_0 is the elastic energy of continuous chains or loops and A_1 represents the interactions. Potentials more general than the excluded volume interaction \mathcal{V} , like three-body potentials, etc, can be treated by the same method (Duplantier 1980). The regularised

partition function ${}^+\mathcal{Z}$ is defined by the functional integral

$${}^+\mathcal{Z}(S, S') = \frac{1}{2 \times 2S} \mathcal{Z}_0^{-1}(S) \mathcal{Z}_0^{-1}(S') \int d^d\{r\} d^d\{r'\} \delta[r'(0) - r'(S')] \exp(-A\{r, r'\}) \quad (8)$$

where the normalisation factor \mathcal{Z}_0 of a free chain or loop reads $\mathcal{Z}_0(S) \equiv V^{-1} \int d^d\{r\} \exp(-A_0\{r\})$, V being the total volume. A first factor $\frac{1}{2}$ corresponds to the exchange of the extremities of a chain, while the factor $1/2S'$ corresponds to the continuous cyclic invariance of a ring along itself and to the two possible orientations of the ring. The regularised partition function ${}^+\mathcal{Z}(S_1, \dots, S_M; S'_1, \dots, S'_L)$ of \mathcal{M} chains and \mathcal{L} rings is defined as in (8), with a symmetry factor $2^{-\mathcal{M}} 2^{-\mathcal{L}} \prod_{i=1}^{\mathcal{L}} (S'_i)^{-1}$. At the polymerisation equilibrium, there are no topological constraints for rings, which can be linked or not (at $d = 3$), and the whole phase space is accessible in (8).

For an arbitrary source field $J(x)$ (Duplantier 1980), define the Green function \mathcal{G}_J of a chain of Brownian area S , the extremities of which are fixed at x and y :

$$\mathcal{G}_J(x, y; S) \equiv \mathcal{Z}_0^{-1}(S) \int d^d\{r\} \delta[r(0) - x] \delta[r(S) - y] \exp\left(-A_0\{r\} + \int_0^S ds J[r(s)]\right). \quad (9)$$

Taking the trace of (9), $\text{Tr } \mathcal{G}_J \equiv \int d^d x \mathcal{G}_J(x, x; S')$, gives the partition function of a ring (without the symmetry factor). Following the method used in Duplantier (1980), one can show that (8) takes the very simple form

$${}^+\mathcal{Z}(S, S') = \left[\exp\left(-A_I \left\{ \frac{\partial}{\partial J} \right\} \right) \right]^{\frac{1}{2}} \int d^d x d^d y \mathcal{G}_J(x, y; S) (2S')^{-1} \text{Tr } \mathcal{G}_J(S') \Big|_{J=0} \quad (10)$$

where $A_I \{\partial/\partial J\}$ is the functional of the differentiation operator $\partial/\partial J$:

$$A_I \left\{ \frac{\partial}{\partial J} \right\} \equiv \frac{1}{2} \int d^d x d^d y \mathcal{V}(x - y) \frac{\partial}{\partial J(x)} \frac{\partial}{\partial J(y)}.$$

This operator reconstructs the interaction A_I by acting on the chains and loops coupled to exterior field J . The regularised partition function of \mathcal{M} chains and \mathcal{L} closed loops is given in the same way by

$$\begin{aligned} &{}^+\mathcal{Z}(S_1, \dots, S_M; S'_1, \dots, S'_L) \\ &= \left[\exp\left(-A_I \left\{ \frac{\partial}{\partial J} \right\} \right) \right]^{\frac{1}{2}} \frac{1}{2^{\mathcal{M}}} \prod_{m=1}^{\mathcal{M}} \int d^d x d^d y \mathcal{G}_J(x, y; S_m) \\ &\quad \times \frac{1}{2^{\mathcal{L}}} \prod_{i=1}^{\mathcal{L}} (S'_i)^{-1} \text{Tr } \mathcal{G}_J(S'_i) \Big|_{J=0}. \end{aligned} \quad (11)$$

One must notice that the functional of $\partial/\partial J$ acts on a term which is *completely factorised* in terms of the \mathcal{M} chains and the \mathcal{L} loops.

In order to calculate (1) we introduce the Laplace transform of (9)

$$G_J = \int_0^\infty dS e^{-aS} \mathcal{G}_J, \quad (12)$$

and for a ring, the Laplace transform of the partition function

$$z_J = \int_0^\infty dS' e^{-aS'} S'^{-1} \text{Tr } \mathcal{G}_J(S'). \quad (13)$$

This last integral is naturally logarithmically divergent for $S' \rightarrow 0$ and is regularised by some mean. In particular, a suitable regularisation is provided by introducing a minimal Brownian area s_0 for a loop and replacing $\int_0^\infty dS'$ by $\int_{s_0}^\infty dS'$.

Inserting (11), (12), (13) into (1) gives immediately

$$\mathcal{Q}(n, a, h) = \left[\exp\left(-A_1 \left\{ \frac{\partial}{\partial J} \right\}\right) \right] \exp\left(\frac{1}{2}h^2 \int d^d x d^d y G_J(x, y) + \frac{n}{2} z_J\right) \Big|_{J=0}. \quad (14)$$

G_J can be calculated directly with the help of definitions (12), (9). It is also well known from the correspondence between $n = 0$ field theory and polymer chain theory (de Gennes 1972, des Cloizeaux 1975, Emery 1975). We have, in the sense of integro-differential operators (Duplantier 1980),

$$G_J(x, y) = (-\Delta + a - J(x) \delta(x - y))^{-1} \quad (15)$$

where Δ is the Laplacian $\Delta = \partial/\partial x_1^2 + \dots + \partial/\partial x_d^2$. For $J = 0$, one recovers the propagator of a free field. The factor z_J , (13), satisfies $dz_J/da = -\text{Tr } G_J$, and integrating (15) formally with respect to 'a' gives

$$z_J = \text{Tr } \ln G_J \quad (16)$$

(a more refined calculation of z_J , (13), with the minimal area s_0 , gives for $s_0 \rightarrow 0$, $z_J = -CV + \text{Tr } \ln G_J/s_0$ (C : Euler's constant)).

We finally find for the grand partition function \mathcal{Q} (14), using $\exp(\text{Tr } \ln G) = \det G$,

$$\mathcal{Q} = \left[\exp\left(-A_1 \left\{ \frac{\partial}{\partial J} \right\}\right) \right] (\det G_J)^{n/2} \exp\left(\frac{1}{2}h^2 \int d^d x d^d y G_J(x, y)\right) \Big|_{J=0}. \quad (17)$$

Consider now an $O(n)$ field theory given by the action

$$A\{\varphi\} = \frac{1}{2} \sum_{j=1}^n \int d^d x \varphi_j(x) (-\Delta + a) \varphi_j(x) + \frac{1}{2} \int d^d x d^d y \varphi^2(x) \mathcal{V}(x - y) \varphi^2(y), \quad (18)$$

where $\varphi^2 \equiv \sum_{j=1}^n (\varphi_j)^2$. The partition function of this field theory, in an external field $h_j = \delta_{j1} h$, in the $j = 1$ direction, is defined by

$$Z_n(a, h) \equiv \int d^n \{\varphi\} \exp\left(-A\{\varphi\} + h \int d^d x \varphi^1(x)\right). \quad (19)$$

Introducing a source field $J(x)$ associated with the squared field $\varphi^2(x)$ (Fisher 1973), it has been shown (Duplantier 1980) that Z_n has exactly the form (17).

Thus we have

$$\mathcal{Q}(n, a, h) = Z_n(a, h) \quad (20)$$

where n can be a continuous variable.

Remarks

(1) Symmetry factors are essential. For a loop (factor $1/2S'$), factor $1/S'$ in (13) gives the logarithm in (16), and factor $\frac{1}{2}$ leads to the exponent $n/2$ in (17).

(2) The proof is quite general. In the physical case of polymerisation of sulphur, one takes at the end h small and $n \rightarrow 1$. One could generalise to $0 < n < 1$ by considering the formation of loops as less probable than that of chains.

A possible check is provided by the specific heat measurements for liquid sulphur (West 1959, Feher *et al* 1971). Near a critical point, the specific heat C is given by

$$C^{\pm} = A^{\pm}(|T - T_c|/T_c)^{-\alpha(n)} + B \quad (21)$$

where A^+ corresponds to T_c^- and A^- to T_c^+ . $A^+/A^-(n)$ and $\alpha(n)$ are universal and known (Bervillier 1976). The measurements cited above are not precise enough for distinguishing between $\alpha(0) = 0.236$ and $\alpha(1) = 0.166$. Cordery's fit for $n = 1$ is reasonably good, but too high a value for $n = 1$, $A^+/A^- \approx 0.6$, seems to have been taken. For $A^+/A^- \approx 0.5$ with $n = 1$, a value consistent with ε expansions (Bervillier 1976), and with a tentative inclusion of corrections to scaling (Chang and Houghton 1980), the fit is slightly less good, especially below T_c , where A^+ seems to be slightly higher than the theoretical prediction. Because $A^+/A^- \sim n$ one could even be tempted to take a value of n slightly higher than 1; however, more precise measures near the polymerisation temperature are certainly needed.

From a theoretical point of view, we have proved the isomorphism of a grand canonical set of *continuous chains* and *rings* to an $O(n)$ field theory, where n is continuous and can be differentiated. This relates mathematically a model of equilibrium polymerisation to standard field theory. Conversely, the latter can always be interpreted in terms of chains and rings. One could for instance derive exact results for chains and rings at $d = 1$ from the exact solution for the $O(n)$ model at $d = 1$ (Balian and Toulouse 1974). The model presented here can also be related to field theoretic models for branched polymers (Lubensky and Isaacson 1981).

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