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## Equilibrium polymerization with a free surface

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Received 23 May 1991, in final form 7 October 1991

**Abstract.** Equilibrium polymerization of a monomer to long chain polymers has been shown to be described by the formal  $n \rightarrow 0$  limit of the  $n$ -vector model of magnetism. We address the problem of equilibrium polymerization with a substrate represented by a free surface. Thus we obtain the mean-field solution of the cubic symmetric  $n$ -vector model on a semi-infinite lattice and study its thermodynamic properties. We consider the situation in which the surface attracts polymer ends. We also examine the possibility of an attractive interaction between the surface and polymer bonds. We obtain the profiles for the densities of polymers and of monomers incorporated into polymers. The behaviour of the mean molecular weight is also studied.

### 1. Introduction

The problem of thermodynamic properties of flexible polymer chains has been the subject of a considerable amount of work [1], both experimental and theoretical. In particular, it was shown by de Gennes [2] that there exists an analogy between the statistics of a self-avoiding walk on a lattice and the magnetic problem of the  $n$ -vector model, in the formal limit  $n \rightarrow 0$ . This allowed the renormalization group methods, well suited to magnetic systems, to be applied to the polymer problem. The correspondence was later extended to the multiple chain problem by des Cloiseaux [3].

On a lattice, the analogy between the equilibrium polymerization and the magnetic problems was explicitly stated independently by Wheeler and Pfeuty [4] and by Gujrati [5], in slightly different but equivalent ways. The equilibrium polymerization transition of elemental sulphur [6] was recognized to be an experimental realization of the problem, although it is still an open question whether polymeric rings do play a relevant part in this transition. If this is the case, the appropriate model for equilibrium polymerization of sulphur would be an  $n = 1$  vector model [7–9].

A natural question to consider is how the equilibrium polymerization model would be affected by the presence of a free surface. For magnetic models, we refer to the review article by Binder [10] and Diehl [11]. For the polymer problem, the effect of a free surface, particularly the problem of adsorption of polymer chains by an attractive surface, was also considered, both theoretically and experimentally. De Gennes [12] proposed a scaling theory for the problem, and early work may be found in the

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references of his paper. This scaling theory was further developed by des Cloiseaux [13]. The scaling predictions were tested through series expansions [14], and the exact scaling form in four dimensions was found [15]. The scaling description was further extended by Eisenriegler *et al* [16], who performed thorough Monte Carlo simulations on the problem.

In this paper, we obtain the mean-field solution for the  $n$ -vector model with cubic symmetric spins [17] in the presence of a free surface. Although it is usual to consider the continuous  $n$ -vector model, we choose the cubic symmetric one for its simplicity. In the particular limit  $n \rightarrow 0$ , where we will focus our attention, both models are equivalent. It should be remarked, however, that it is possible to find reasonable polymeric problems which are equivalent to the  $n$ -vector model with continuous symmetry for general  $n$ ; this no longer the case for the model with discrete cubic spins [18]. We then proceed to investigate the properties of the solution of the mean-field solution in the  $n \rightarrow 0$  limit. Although we obtained the mean-field solution of the model in the magnetic representation, the discussion of the physical properties was done in polymer variables, since it is as a polymeric system that the model has physical meaning. Also, in this paper we focus our attention on the profiles of polymeric densities close to the surface.

It should be stressed that the correspondence between the polymer model and the  $n \rightarrow 0$  vector model was originally developed to calculate the limit where scaling laws apply [2]. However, it was verified explicitly that mean-field approximations to the  $n \rightarrow 0$  vector model lead to precisely the same results as direct Flory-like approximations on the polymer model, both in the problems of equilibrium polymerization [4] and equilibrium polymerization in a solvent [19]. Therefore, we are confident that our calculations lead to the same results, in the  $n \rightarrow 0$  limit, as direct calculations for the polymer model in Flory-like approximations.

In section 2, we define the model we are considering and present the mean-field solution in the presence of a free surface. Some limiting analytic properties of this solution are developed. In section 3 we review the correspondence between the model considered and the equilibrium polymerization problem in the presence of a surface. In particular, we consider two distinct possibilities. In the first case, we investigate the effect of an attractive interaction between the substrate and polymer endpoints. This situation is related to the problem of grafted polymers [20], which has attracted much attention recently, particularly related to the study of polymer brushes [21]. The case we are studying is the one of 'soft' grafting, such as that encountered when the chain is terminated by a special chemical group that adsorbs on to the surface. However, both ends of the chain are equally adsorbed in our model. The second investigation concerns the problem of the adsorption of polymer bonds on to the surface. We proceed in this section by presenting and discussing our results. Finally, we present conclusions in section 4.

## 2. Definition of the model and mean-field solution

We consider the  $n$ -vector model with cubic symmetric spins [17] defined on a semi-infinite  $d$ -dimensional lattice bounded by a  $(d-1)$ -dimensional hyperplane, which represents the substrate. The model is described by the Hamiltonian

$$H = -J \sum_{(jk, j'k')} S_{jk} \cdot S_{j'k'} - \sum_j (h + h_j) \sum_k S_{jk}^{(1)} \quad (2.1)$$

where the subscripts  $j$  and  $k$  describe the localization of a site on the lattice. A layer parallel to the wall is indexed by  $j$ . The substrate occupies the layer  $j = 0$ , while the free surface hyperplane corresponds to  $j = 1$ . The index  $k$  defines a site inside a layer. Each classical spin  $S_{jk}$ , which has  $n$  components, may assume  $2n$  configurations, each with only one non-zero component. We choose the norm of the vector to be  $\sqrt{n}$ . So, for example, we may have

$$S_{jk} = (0, \dots, 0, \pm n^{1/2}, 0, \dots, 0). \tag{2.2}$$

When  $n = 1$ , the Ising model is recovered. The interaction is only between spins on first-neighbour sites. We choose the magnetic field to point in the 1 direction, and in each layer the field corresponds to the sum of a bulk value  $h$  with a layer-dependent field  $h_j$ .

The partition function is given by

$$Z = \text{Tr}[e^{-\beta H}] \tag{2.3}$$

where  $\beta \equiv (k_B T)^{-1}$  and the trace operation over the configurations of the spins is defined as

$$\text{Tr}[\psi] \equiv \frac{\sum_{\{S_{jk}\}} \psi}{\sum_{\{S_{jk}\}} 1} = \frac{1}{(2n)^N} \sum_{\{S_{jk}\}} \psi \tag{2.4}$$

$\psi$  is an arbitrary function of the spins and  $N$  is the total number of spins. The normalization factor in the denominator, although not having any effect on the thermodynamic properties of the free energy per  $kT$

$$F = -\ln Z \tag{2.5}$$

assures that

$$\lim_{T \rightarrow \infty} F = 0 \tag{2.6}$$

even in the formal limit  $n \rightarrow 0$ .

To obtain the mean-field approximation of the model, we follow a standard procedure [22]. Starting with the Gibbs-Bogoliubov inequality for the free energy

$$-k_B T F \leq \Phi = \text{Tr}(\rho H) + k_B T \text{Tr}(\rho \ln \rho) \tag{2.7}$$

we consider a mean-field ansatz for the density matrix  $\rho$

$$\rho_0 = \prod_{jk} \rho_j(S_{jk}) \tag{2.8}$$

the product is over all sites in the lattice and we suppose that, given the symmetry of the problem, a different function  $\rho_j$  is defined on each layer  $j$ . We proceed to calculate the right-hand side of inequality (2.7) for the Hamiltonian (2.1) and the choice (2.8) for  $\rho$ . We obtain

$$\begin{aligned} \frac{\Phi}{A} = & -J \sum_j \left\{ \frac{1}{2} a [\text{Tr}(\rho_j S_{jk}^{(1)})]^2 + b [\text{Tr}(\rho_j S_{jk}^{(1)})][\text{Tr}(\rho_{j+1} S_{(j+1)k}^{(1)})] \right\} \\ & - \sum_j (h + h_j) [\text{Tr}(\rho_j S_{jk}^{(1)})] + k_B T \sum_j \text{Tr}(\rho_j \ln \rho_j) \end{aligned} \tag{2.9}$$

where  $A = L^2$  is the number of sites in each layer so that  $N = AL$ . Each site has first neighbours in the same layer and  $b$  first neighbours in the layer just above it. Also, it is reasonable to consider only the 1 component of the spin, since the interaction in (2.1) is isotropic and the symmetry-breaking field is in this direction.

Now we find the best choice for the  $\rho_j$  by minimizing  $\Phi/A$  with respect to  $\rho_j$  under the constraints  $\text{Tr } \rho_j = 1, \forall_j$ . This leads to

$$\rho_j = \frac{\exp(-\beta H_j S_{jk}^{(1)})}{\text{Tr}[\exp(-\beta H_j S_{jk}^{(1)})]} \quad (2.10)$$

where

$$H_j \equiv +J[am_j + b(m_{j+1} + m_{j-1})] + (h + h_j) \quad (2.11)$$

and the layer magnetization  $m_j$  is given by

$$m_j = \text{Tr}(\rho_j S_{jk}^{(1)}). \quad (2.12)$$

We may now perform the trace operation in (2.12), with the choice (2.10) for  $\rho_j$ , obtaining

$$m_j = t_n(\beta H_j) \quad (2.13)$$

where  $H_j$  is given by equation (2.11) and  $t_n(x)$  is the function defined by

$$t_n(x) = \frac{\sqrt{n} \sinh(\sqrt{n} x)}{n - 1 + \cosh(\sqrt{n} x)}.$$

Notice that

$$t_1(x) = \tanh(x)$$

and that

$$t_0(x) = \frac{x}{1 + x^2/2}.$$

To obtain the surface properties, we first find the bulk properties. As we let  $m_i = m$  and  $h_j = 0$ , and recalling that the coordination of the lattice is  $q = a + 2b$ , we obtain

$$m = t_n(\beta(qJm + h)) \quad (2.14)$$

and the bulk free energy  $f$  per  $kT$  per site

$$f = -\frac{1}{2}q\beta Jm^2 + r_n(\beta(qJm + h)) \quad (2.15)$$

where  $r_n(x)$  is the function defined by

$$r_n(x) = \ln \frac{n - 1 + \cosh(\sqrt{n} x)}{n}.$$

Notice that  $t_n(x) = (d/dx)r_n(x)$ . Particular cases are

$$r_1(x) = \ln(\cosh x)$$

and

$$r_0(x) = 1 + \frac{x^2}{2}.$$

It is easy to compare these equations with earlier results. In the limit  $n \rightarrow 0$ , the mean-field results for the continuous  $n \rightarrow 0$  vector model are recovered [4], and when  $n = 1$  we reobtain the mean-field results for the Ising ferromagnet.

The surface free energy  $f_s$  per  $kT$  and per unit area is defined by

$$f_s = \lim_{L \rightarrow \infty} \frac{(\Phi - Nf)}{A} \tag{2.16}$$

From equations (2.9) and (2.16) we obtain

$$f_s = \sum_j \left\{ -\beta J \left( a \frac{m_j^2}{2} + b m_j m_{j+1} \right) + r_n(\beta H_j) - f \right\} \tag{2.17}$$

where  $H_j$  is given by equation (2.11).

It is not difficult to obtain the phase diagram of the model for general  $n$  in the mean-field approximation, for the case of zero magnetic field ( $h = h_j = 0$ ) and an interaction  $J_s$  between pairs of first-neighbour spins in the surface layer and  $J_b$  between other pairs of first-neighbour spins. In the case  $n \rightarrow 0$ , this situation corresponds to an interaction between the substrate and the polymer bonds.

The quantities  $H_j$  will then be given by

$$\begin{aligned} H_1 &= J_s a m_1 + J_b b m_2 \\ H_i &= J_b [a m_i + b(m_{i+1} + m_{i-1})] \quad i > 1. \end{aligned} \tag{2.18}$$

Equations (2.13), in this case, allows three types of solution: a *paramagnetic* solution ( $m_i = 0$ , for all  $i$ ), a *bulk ferromagnetic* solution ( $m_b \neq 0$ , where  $m_b = \lim_{i \rightarrow \infty} m_i$  is the bulk magnetization), and a *surface ferromagnetic* solution ( $m_1 \neq 0, m_b = 0$ ). It is possible to study the stability of these solutions analytically, and the resulting phase diagram (for  $a = 4, b = 1$ ; corresponding to a simple cubic lattice) is shown in figure 1, where we introduced the variables

$$T = \frac{1}{\beta J_b} \quad \Delta \equiv \frac{J_s}{J_b} - 1. \tag{2.19}$$

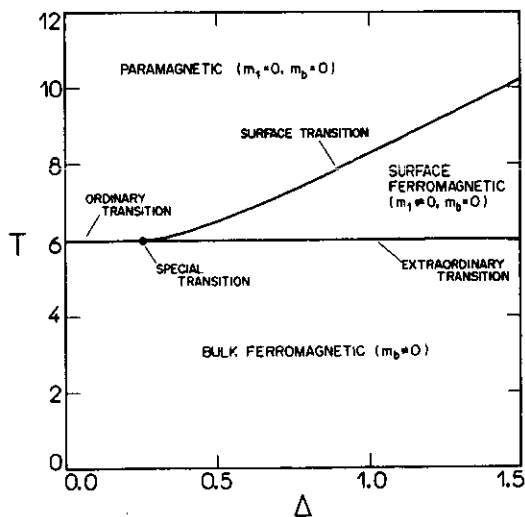


Figure 1. Phase diagram for the semi-infinite  $n$ -vector model on a cubic lattice ( $a = 4, b = 1$ ) with  $h = h_j = 0$ , in the mean-field approximation. Surface first-neighbour spins interact with an exchange constant  $J_s$  and other pairs interact with  $J_b$ .  $T$  is defined as  $J_b/\beta$  and  $\Delta$  stands for  $J_s/J_b - 1$ . Three phases are observed: a paramagnetic, a bulk ferromagnetic and a surface ferromagnetic phase. In the  $n \rightarrow 0$  limit, they correspond to a non-polymerized, a bulk polymerized and a surface polymerized phase, respectively.

This phase diagram has the usual features for this kind of model [10]. The special transition point is located at  $T_c = 6$ ,  $\Delta_c = 0.25$ . In the vicinity of the special transition point, the surface transition line is described approximately by

$$T - 6 \approx (4\Delta - 1)^2. \quad (2.20)$$

This quadratic behaviour is identical to that obtained via a Landau mean-field calculation for the Ising model ( $n = 1$ ) [10]. It is interesting to observe that all phase boundaries are independent of  $n$ . This, however, is not true for other results, such as the magnetization profiles.

We will now concentrate our attention on the  $n \rightarrow 0$  vector model. In this limit, equations (2.13) and (2.17) become

$$m_j = t_0(\beta H_j) \quad (2.21)$$

$$f_s = \sum_j \left\{ -\beta J \left( a \frac{m_j^2}{2} + b m_j m_{j+1} - q \frac{m_j^2}{2} \right) + r_0(\beta H_j) - r_0(\beta(Jqm + h)) \right\}. \quad (2.22)$$

The thermodynamic properties of the cubic  $n \rightarrow 0$  vector model in the mean-field approximation are obtained by solving the coupled equations (2.21) for the layer magnetizations, under proper boundary conditions; the free energy of the system may then be found through equation (2.22).

In general, it was necessary to use numerical methods to find the solutions for equations (2.21). Moreover, we usually considered only 40 layers, forcing the magnetization to vanish in the zeroth layer (the substrate), and to be equal to the bulk magnetization on the 41st layer. In our numerical calculations we found that this truncation does not introduce significant errors in the results. For simplicity, we particularized our discussion for a cubic lattice limited by a 2D surface, so that  $a = 4$  and  $b = 1$ . In this case equations (2.21) become

$$\begin{aligned} m_1 &= t_0(\beta(J(4m_1 + m_2) + h + h_1)) \\ m_j &= t_0(\beta(J(4m_j + m_{j+1} + m_{j-1}) + h + h_j)) \quad j > 1. \end{aligned} \quad (2.23)$$

In the particular case  $h = 0$  and  $h_j = 0$ ,  $j > 1$ , it is easy to find a solution for equations (2.23), valid in the limit of vanishing layer magnetizations and  $h_1 \approx 0$ . In this case the equations will be asymptotically linear and we find the solution

$$m_1 = \frac{\beta h_1}{1 - \beta J(4 + \alpha)} \quad m_j = \alpha m_{j-1} \quad j > 1$$

where

$$\alpha = \frac{1}{2} \left\{ \left( \frac{1}{\beta J} - 4 \right) \times \left( 1 - \left[ 1 - \left( \frac{2}{1/\beta J - 4} \right)^2 \right]^{1/2} \right) \right\}. \quad (2.24)$$

This solution is valid for  $\beta J \leq (\beta J)_c = \frac{1}{6}$  (the bulk critical value). For  $\beta J \rightarrow (\beta J)_c$ , we see that  $\alpha \rightarrow 1$  (no decay in the layer magnetizations) and for  $\beta J \rightarrow 0$ ,  $\alpha \rightarrow 0$ .

### 3. Correspondence with an equilibrium polymerization model and numerical results

In section 2 we obtained the mean-field solution of the  $n$ -vector model with cubic symmetric spins. In the formal limit  $n \rightarrow 0$ , this model is not expected to display reasonable thermodynamic properties viewed as a magnetic model. For example,

negative susceptibilities occur in some regions of its phase diagram [4]. Thus we choose to present some thermodynamic properties of the mean-field solution in polymer variables, and we start this section by reviewing the connection between the magnetic and polymeric models, referring to the paper by Wheeler and Pfeuty [4] for more details.

We consider a lattice model suitable for describing equilibrium polymerization of elemental sulphur, as proposed by Wheeler and Pfeuty [4]. Each site of the lattice (monomer) may or may not be incorporated into polymeric chains, which are self- and mutually avoiding. The statistical weight of a chain with  $m$  monomers will be

$$\begin{aligned} K_1 & \quad \text{if } m = 1 \\ 2K_1(K_p)^{m-1} & \quad \text{if } m > 1. \end{aligned} \tag{3.1}$$

The thermodynamic properties of this model may be obtained from the partition function

$$Y = \sum_{N_p} \sum_{N_b} \sum_{N_1} (2K_1)^{N_p} (K_p)^{N_b} \left(\frac{1}{2}\right)^{N_1} \Gamma(N_p, N_b, N_1; N) \tag{3.2}$$

where  $N_p$  is the number of chains in the configuration,  $N_b$  is the total number of bonds and  $N_1$  is the number of chains which comprise one site only.  $\Gamma(N_p, N_b, N_1; N)$  is the number of configurations on the  $N$ -site lattice described by  $N_p, N_b$  and  $N_1$ . This partition function may be shown to be identical with the magnetic partition function (2.3), in the limit  $n \rightarrow 0$ . In the bulk problem ( $h_j = 0$ ), we identify

$$K_p = \beta J \quad K_1 = \frac{1}{2}(\beta h)^2. \tag{3.3}$$

The average number of bonds and polymers are therefore given by

$$\begin{aligned} \langle N_b \rangle &= K_p \left( \frac{\partial \ln Y}{\partial K_p} \right)_{K_1} = (\beta J) \left( \frac{\partial \ln Z}{\partial (\beta J)} \right)_{(\beta h)} \\ \langle N_p \rangle &= K_1 \left( \frac{\partial \ln Y}{\partial K_1} \right)_{K_p} = \frac{1}{2} (\beta h) \left( \frac{\partial \ln Z}{\partial (\beta h)} \right)_{(\beta J)}. \end{aligned} \tag{3.4}$$

Thus the density of monomers incorporated into polymers and the density of polymers will be

$$\varphi_u = \frac{\langle N_p + N_b \rangle}{N} = \frac{1}{2} \beta h m + \beta J e \quad \varphi_p = \frac{\langle N_p \rangle}{N} = \frac{1}{2} \beta h m \tag{3.5}$$

where  $e$  is the dimensionless energy per spin

$$e = \left( \frac{\partial \ln Z}{\partial (\beta J)} \right)_{(\beta h)}. \tag{3.6}$$

Another quantity of interest is the mean molecular weight of the polymers

$$M = \frac{2\varphi_\mu}{\varphi_p}. \tag{3.7}$$

It is straightforward to generalize the correspondences above (equations 3.4–3.7) to the situation where the model is defined on a semi-infinite lattice with layer-dependent statistical weights.  $\varphi_\mu$  and  $\varphi_p$  should be layer-dependent in this case. We remark that there is no simple way to calculate a layer-dependent mean molecular weight in this case; the global value is given by

$$M = \frac{2 \sum_j \varphi_\mu(j)}{\sum_j \varphi_p(j)}. \tag{3.8}$$



In the mean-field solution of the bulk problem [4] the energy per spin  $e$  will be given by

$$e = \frac{1}{2}qm^2. \quad (3.9)$$

This expression, in the layer-dependent case, will be replaced by

$$e(j) = \frac{1}{2}am_j^2 + bm_jm_{j-1}. \quad (3.10)$$

We considered a simple cubic lattice (so that  $a = 4$  and  $b = 1$ ) and investigated two distinct situations. In the first one we imagine that the substrate provides an extra attractive interaction to the endpoints of polymer chains, so we consider a larger value of  $K_1$  in the vicinity of the substrate. Thus, in this case, polymer chains are grafted onto the substrate. The second calculation corresponds to the situation where the substrate attracts polymer bonds, thus represented by a larger value of  $K_p$  close to the wall. This second situation might be verified experimentally, by measuring the density profiles of elemental sulphur close to the wall of a vessel made of an appropriate material, at temperatures around the bulk polymerization transition.

### 3.1. Endpoints are attracted

To model this situation we simulated a system in which the statistical weight  $K_1$  in the bulk was made very small, while the one associated with the substrate, acting on the free surface (first layer), was much larger. The value of  $K_p$  was chosen slightly above the bulk critical value. In figure 2(a) we show the profile obtained for the density

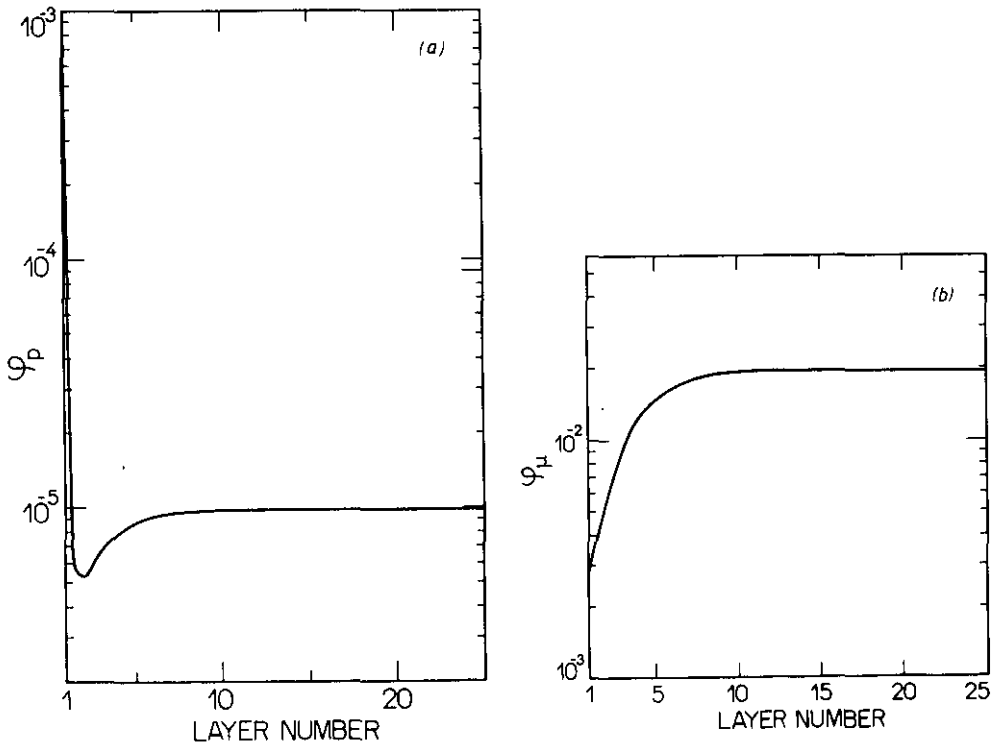


Figure 2. (a) Profile of the density of polymers.  $K_p = 0.17$ ;  $K_1^{\text{bulk}} = 5.00 \times 10^{-9}$ ;  $K_1^{\text{surf}} = 2.00 \times 10^{-4}$ . (b) Profile of the density of monomers incorporated in to polymers.  $K_p = 0.17$ ;  $K_1^{\text{bulk}} = 5.00 \times 10^{-9}$ ;  $K_1^{\text{surf}} = 2.00 \times 10^{-4}$ .

of polymers and in 2(b), for the density of monomers incorporated into polymers. The non-monotonic behaviour of the  $\varphi_p$ -profile may be understood by the fact that, since the density of endpoints at the surface is much higher than in the bulk, we observe a correlation hole effect [1] close to the surface (it is less likely to find a polymer end in the close neighbourhood of another one). The  $\varphi_\mu$ -profile shows that, for that given set of parameters, the density of monomers incorporated into polymers increases to its value in the bulk. In figure 3 we observe that the latter feature does not always hold; in fact, as we increased the ratio  $K_1^{\text{surf}}/K_1^{\text{bulk}}$  we obtain a non-monotonic profile and even an inversion of the behaviour observed in figure 2(b). This feature is due to the competition between geometric and energetic factors. The presence of the wall restricts the number of ways of attaching a monomer to a given chain (the connectivity of the lattice is smaller); on the other hand, the substrate offers an extra attractive interaction to polymer endpoints which ultimately induces a larger concentration of bonds in its vicinity. If the  $K_1^{\text{surf}}/k_1^{\text{bulk}}$  ratio is small, the geometric factor dominates and the density of monomers incorporated into polymers is smaller than its bulk value; in the opposite situation, this behaviour is inverted.

We extended the idea of having the substrate as an attractor of endpoints. For this purpose we considered a model where the first  $q$  layers are sensitive to the presence of the wall and attract endpoints according to

$$K_1(j) = \begin{cases} K_1^{\text{surf}}/j^{2\delta} & \text{for } j \leq q \\ K_1^{\text{bulk}} & \text{for } j > q. \end{cases} \quad (3.11)$$

We chose arbitrarily  $\delta = 3$ . Figure 4 shows the profile of the density of polymers. We see that the dip observed for  $q = 1$  (also shown in figure 2(a)) disappears as  $q$  increases.

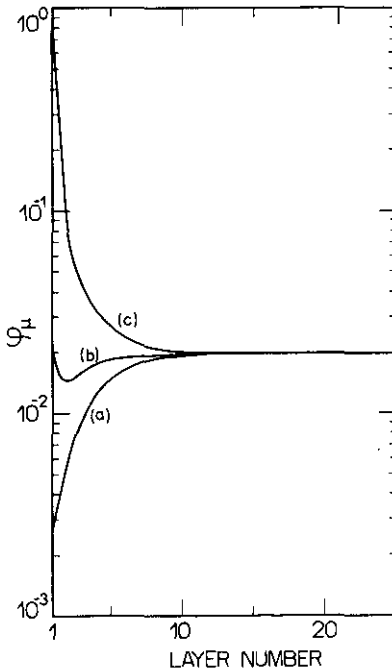


Figure 3. Profile of the density of monomers incorporated into polymers.  $K_p = 0.17$ ;  $K_1^{\text{bulk}} = 5.00 \times 10^{-9}$ ; (a)  $K_1^{\text{surf}} = 2.00 \times 10^{-4}$ ; (b)  $K_1^{\text{surf}} = 8.45 \times 10^{-3}$ ; (c)  $K_1^{\text{surf}} = 2.00$ .

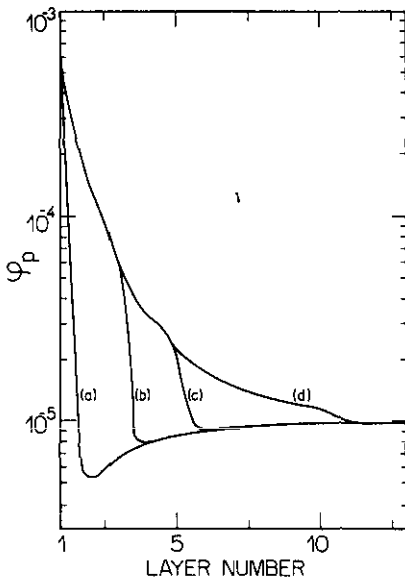


Figure 4. Profile of the density of polymers.  $K_p = 0.17$ ;  $K_1^{bulk} = 5.00 \times 10^{-9}$ ; (a)  $q = 1$ ; (b)  $q = 3$ ; (c)  $q = 5$ ; (d)  $q = 10$ .

A possible explanation of this fact is that in the case  $q = 1$ , we are imposing an extremely large potential gradient; the dip arises as the system is bound to satisfy markedly different boundary conditions within a very small region. The profile of the density of monomers incorporated into polymers for  $q > 1$  (not shown here), does not show any unexpected behaviour. We just mention that in the vicinity of the wall, this density increases with increasing  $q$ .

In figure 5 we show a plot of the mean molecular weight  $M$ , as a function of  $K_p^{bulk}$ , calculated according to (3.8). Notice that, below the critical bulk value  $(K_p^{bulk})_c = \frac{1}{6}$ ,

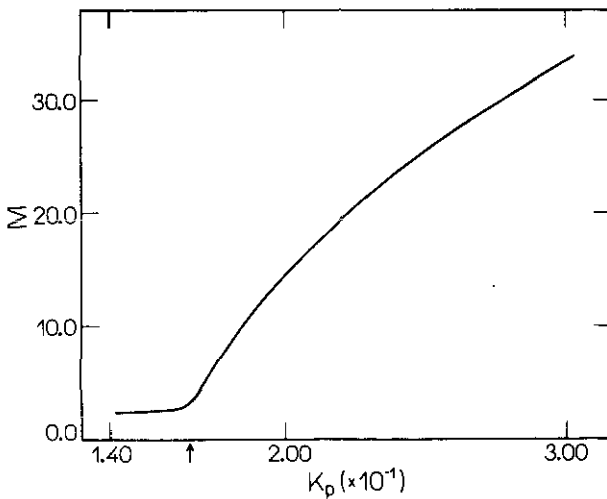


Figure 5. Dimensionless mean molecular weight versus  $K_p$ ,  $K_1^{bulk} = 5.00 \times 10^{-9}$ ;  $K_1^{surf} = 2.00$  ( $q = 1$ ). The arrow shows the location of  $(K_p^{bulk})_c$ .

$M$  decreases not to zero, but to a value slightly over unity. This means that for small values of  $K_p^{\text{bulk}}$ , we find, far from the wall, one-monomer chains while, close to the wall, the chains are somewhat longer.

In the next subsection we discuss the results obtained for the case where the substrate attracts polymer bonds.

### 3.2. Bonds are attracted

This condition is obtained as we let the statistical weight  $K_p^{\text{surf}}$  on the free surface (first layer) be larger than the value  $K_p^{\text{bulk}}$  assigned to the remaining layers,

$$K_p^{\text{surf}} = K_p^{\text{bulk}}(1 + \Delta). \quad (3.12)$$

In this case, we again chose  $K_p^{\text{bulk}}$  slightly larger than  $(K_p^{\text{bulk}})_c$ .

Here we followed a route similar to that of the last subsection. We started calculating the profiles of the density of polymers and of the density of monomers incorporated into polymers for various values of  $\Delta$  (figures 6 and 7). Figures 6(a) and 6(b) display the density profiles for  $\Delta = 0$  and  $\Delta = 0.1$ .  $\Delta = 0$  corresponds to the situation where the wall just plays the role of a geometric constraint; the  $\Delta = 0.1$  case represents a small attractive potential: an effect added to the geometric factor. Both figures show that the extra potential produces an increase of  $\varphi_p(j)$  and  $\varphi_\mu(j)$  near the wall. This was of course expected. Figures 7(a) and 7(b) show the behaviour of the profiles as one increases the potential  $\Delta$ . For small values of  $\Delta$ ,  $\varphi$  increases to the bulk value, whereas

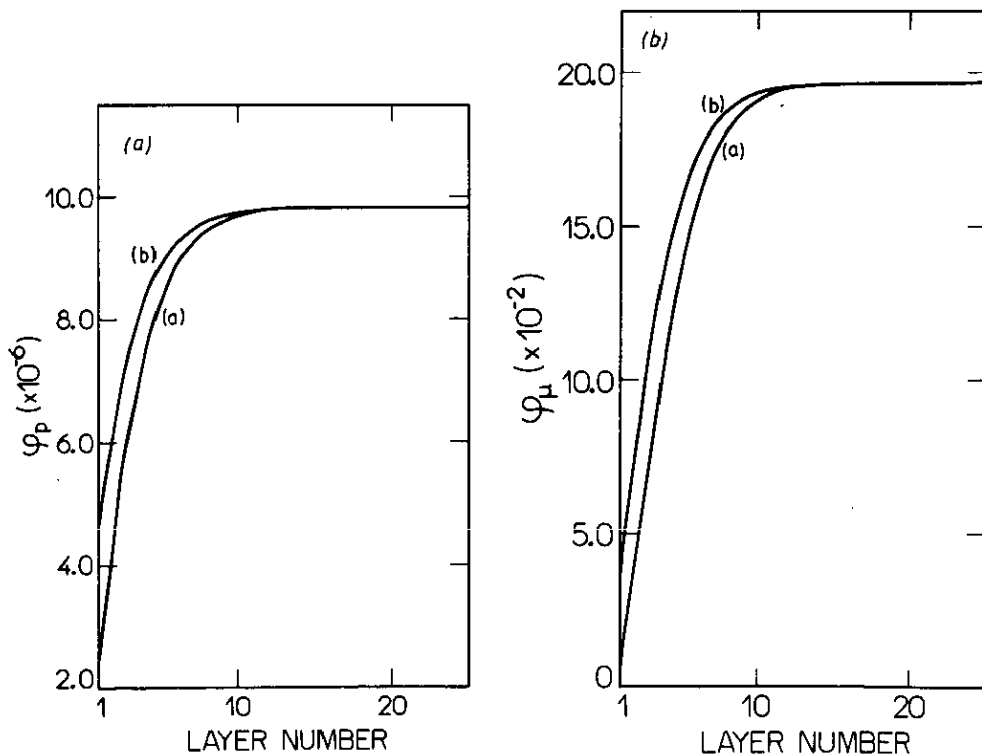


Figure 6. (a) Profile of the density of polymers.  $K_1 = 5.00 \times 10^{-9}$ ;  $K_p^{\text{bulk}} = 0.17$ ; (a)  $\Delta = 0$ ; (b)  $\Delta = 0.1$ . (b) Profile of the density of monomers incorporated into polymers.  $K_1 = 5.00 \times 10^{-9}$ ;  $K_p^{\text{bulk}} = 0.17$ ; (a)  $\Delta = 0$ , (b)  $\Delta = 0.1$ .

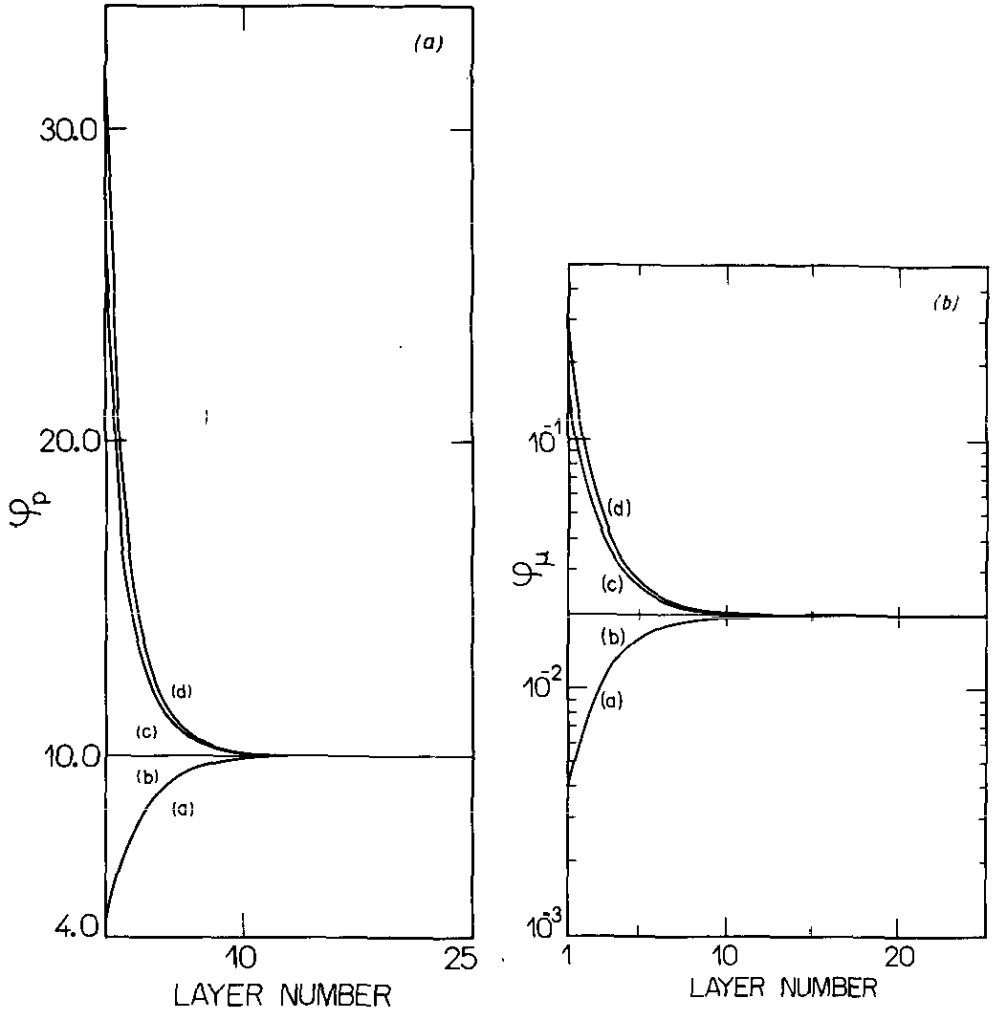


Figure 7. (a) Profile of the density of polymers.  $K_1 = 5.00 \times 10^{-9}$ ;  $K_p^{bulk} = 0.17$ ; (a)  $\Delta = 0.1$ ; (b)  $\Delta = 0.2$ ; (c)  $\Delta = 0.5$ ; (d)  $\Delta = 0.8$ . (b) Profile of the density of monomers incorporated into polymers.  $K_1 = 5.00 \times 10^{-9}$ ;  $K_p^{bulk} = 0.17$ ; (a)  $\Delta = 0.1$ ; (b)  $\Delta = 0.2$ ; (c)  $\Delta = 0.5$ ; (d)  $\Delta = 0.8$ .

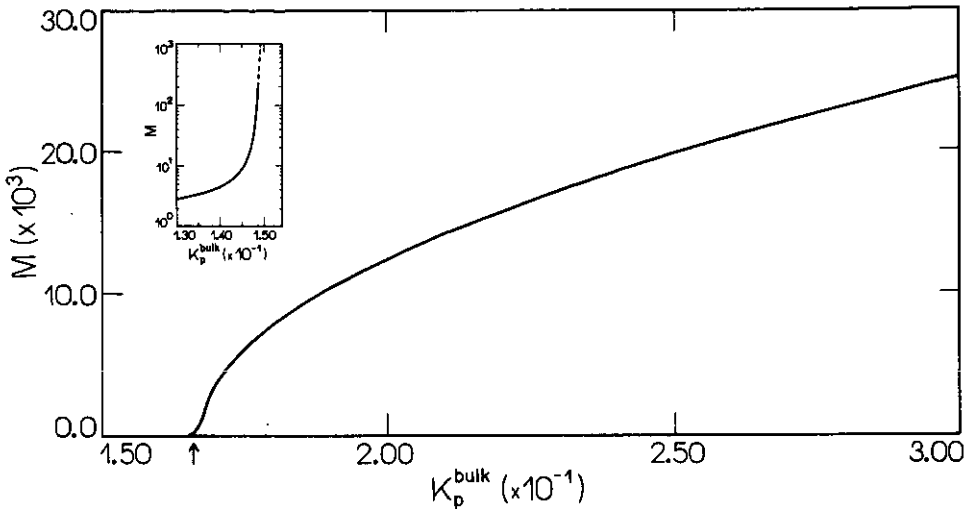
for larger  $\Delta$  (actually  $\Delta = 0.2$  seems to be the cross-over value),  $\varphi$  decreases to the bulk value. The discussion that led to the understanding of figure 3 (section 3.1), in terms of the competition between geometric and energetic effects, also applies here to explain the change of behaviour with varying  $\Delta$ .

Here again we tried to extend the idea of the substrate attracting bonds. So we assumed that the first  $q$  layers imposed an additional attraction

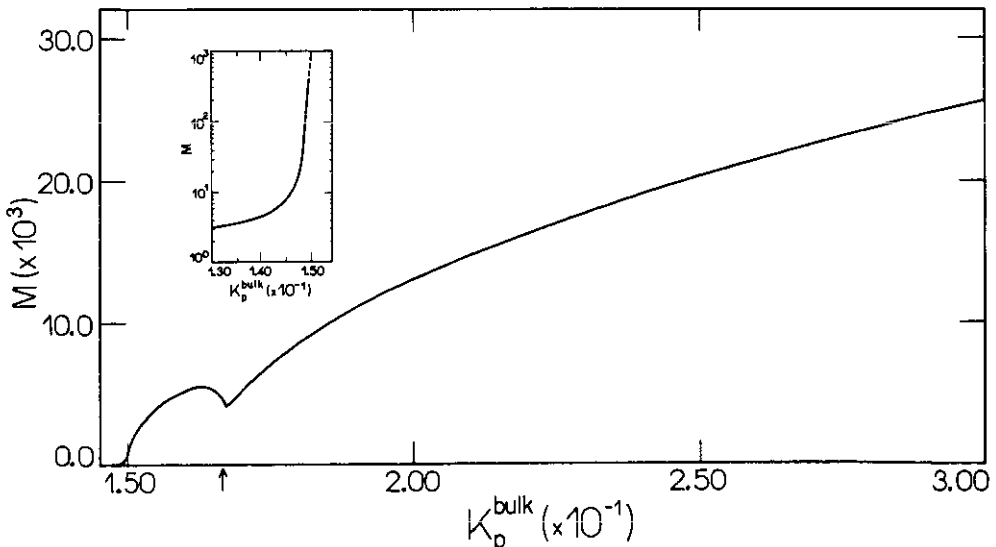
$$K_p(j) = \begin{cases} K_p^{bulk}(1 + \Delta/j^\delta) & \text{for } j \leq q \\ K_p^{bulk} & \text{for } j > q. \end{cases} \quad (3.13)$$

Again we made  $\delta = 3$ . The profiles for  $\varphi_p$  and  $\varphi_\mu$  (not presented here) do not show any relevant feature. As expected, near the wall the magnitudes of  $\varphi_p(j)$  and  $\varphi_\mu(j)$  increase with increasing  $q$ .

Finally we calculated the mean molecular weight  $M$  as a function of  $K_p^{\text{bulk}}$ , using the ratio (3.8). In the case  $\Delta = 0$ , where just the geometric effect is considered, we obtain a smooth behaviour (figure 8): for  $K_p^{\text{bulk}} < (K_p^{\text{bulk}})_c$ ,  $M$  decreases to a value a little larger than unity. Nevertheless, for sufficiently large  $\Delta$  (figure 9), we find a cusp at  $K_p^{\text{bulk}} = (K_p^{\text{bulk}})_c$ ; at lower values of  $K_p^{\text{bulk}}$ ,  $M$  decreases to about unity. We are now investigating the reason for this surprising behaviour. At present we understand it as follows. Although we plot  $M$  against  $K_p^{\text{bulk}}$ , our physical system consists of two



**Figure 8.** Dimensionless mean molecular weight versus  $K_p^{\text{bulk}}$ .  $K_1 = 5.00 \times 10^{-9}$ ;  $\Delta = 0$ . The arrow shows the location of  $(K_p^{\text{bulk}})_c$ . The inset shows that for low values of  $K_p^{\text{bulk}}$ ,  $M$  converges to a finite value.



**Figure 9.** Dimensionless mean molecular weight versus  $K_p^{\text{bulk}}$ .  $K_1 = 5.00 \times 10^{-9}$ ;  $\Delta = 0.5$ . The arrow shows the location of  $(K_p^{\text{bulk}})_c$ . The inset shows that for low values of  $K_p^{\text{bulk}}$ ,  $M$  converges to a finite value.

subsystems: one represented by the bulk, where the properties are determined by  $K_p^{\text{bulk}}$  (and  $K_1$ ), and another one, the neighbourhood of the wall, where the properties are determined by  $K_p^{\text{surf}}$  (and  $K_1$ ). As  $K_p^{\text{rbulk}}$  decreases beyond  $(K_p^{\text{bulk}})_c$ , we start to sample a different subsystem, detached from the whole: the vicinity of the wall, which has its  $M$  versus  $K_p^{\text{surf}}$  curve. The cusp is then a consequence of the cross-over between the bulk-dominated and the surface-dominated regimes.

#### 4. Conclusion

A mean-field solution for the problem of equilibrium polymerization with a wall has been presented. By extending the equivalence between the magnetic  $n$ -vector model in the  $n \rightarrow 0$  limit, we have been able to obtain density profiles and the mean molecular weight of a system constituted of one type of polymer. Two particular cases were studied: the case in which *polymer ends* are adsorbed on to the surface (grafted polymers) and the case where *polymer bonds* are adsorbed (polymer adsorption), and we considered in some detail density profiles close to the surface. In these systems, the investigation of adsorption isotherms and scaling properties is an important subject and will be the object of later work.

#### Acknowledgments

We wish to acknowledge helpful initial conversations with Dr J Noolandi. This work was partially supported by CNPq, FAPESP and FINEP (Brazilian agencies).

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