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# A new approach to polymer solution theory

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**Abstract.** We show that in the usual treatment of the  $O(n)$  symmetric Ginzburg–Landau–Wilson field theory Goldstone modes induce a negative susceptibility for  $n < 1$  as the co-existence curve is approached. By using the des Cloizeaux formalism, in which in the limit  $n \rightarrow 0$  one maps the field-theoretic problem into a polymer solution problem, we find that this ridiculous situation affects the whole of the semi-dilute regime of polymer solutions. To examine the role of Goldstone modes within this formalism, we consider the generalised Heisenberg model of Stanley with self-avoiding constraint on a  $d = 2$  square lattice in the limit  $n \rightarrow 0$ . By taking highly anisotropic couplings, we take the continuum limit in one direction for the transfer matrix and obtain a quantum mechanical Hamiltonian on a  $d = 1$  lattice. This is used to obtain perturbation series in the coupling between lattice sites for the inverse correlation length and susceptibility and estimates of the exponents  $\nu$  and  $\gamma$  are obtained. We obtain the equation of state to second order, and show the existence of spontaneous magnetisation even though it is absent in  $d = 1$ . The susceptibility is well behaved and positive. Finally, we obtain a van der Waals type expression for the osmotic pressure of a semi-dilute polymer solution to lowest order in the perturbation expansion. The calculations can be readily extended to systems of higher dimensionality.

## 1. Introduction

In an isotropic ferromagnet at temperatures below the Curie temperature,  $T_c$ , the transverse susceptibility behaves as

$$\chi_T = M/h, \quad (1)$$

where  $M$  is the magnetisation and  $h$  the absolute value of the applied magnetic field. This expression is easily derived if a relation of the form

$$h = Mf(M^2, t) \quad (2)$$

is assumed, where  $t = (T - T_c)/T_c$  is the reduced temperature. In the model that is usually used to study phase transitions, the  $n$ -dimensional spin field-theoretic model with Ginzburg–Landau–Wilson Hamiltonian

$$H = \int d^d \mathbf{x} \left[ \frac{1}{2} \sum_{i=1}^n (\nabla \phi_i)^2 + \frac{t}{2} \sum_{i=1}^n \phi_i^2 + \frac{\nu}{8} \left( \sum_{i=1}^n \phi_i^2 \right)^2 - h \phi_1 \right], \quad (3)$$

equation (1) may be derived as a Ward identity (Brezin *et al* 1973). The fact that  $\chi_T$  diverges as  $h \rightarrow 0$  is an example of Goldstone's theorem (Goldstone *et al* 1962). The occurrence of spontaneous magnetisation breaks the isotropy of  $n$ -dimensional spin space (see equation (3) with  $h = 0$ ); the direction of the magnetisation is not fixed *a priori*, however, and so there exist long-wavelength Goldstone modes or spin-wave

excitations which rotate the local magnetisation for an arbitrary small cost in energy. It has long been recognised that the singular behaviour of  $\chi_T$  as  $h \rightarrow 0$  induces further singularities in other thermodynamic quantities; in particular, the longitudinal susceptibility

$$\chi_L = (\partial M / \partial h), \quad (4)$$

is predicted to diverge on the co-existence curve ( $t < 0, h \rightarrow 0, M \neq 0$ ). Spin-wave calculations (Vaks *et al* 1968) predict

$$\chi_L \sim h^{-1/2}, \quad h \rightarrow 0, t < 0, \quad (5)$$

in three dimensions. Patashinskii and Pokrovskii (1973), using a Ginzburg–Landau form of potential, showed this to be a general result within mean-field theory. A general argument, similar in spirit to the spin-wave approach, can be formulated (Brezin and Wallace 1973, Wallace and Zia 1975) in which it is demonstrated that

$$\chi_L \sim c_1 + c_2 h^{-\epsilon/2}, \quad (6)$$

where  $\epsilon = 4 - d$  and  $c_1$  and  $c_2$  are critical amplitudes depending only on  $n$  and  $\epsilon$ , with  $c_2$  vanishing for the Ising case  $n = 1$ . These amplitudes have been calculated within the framework of the  $\epsilon$ -expansion to  $O(\epsilon)$  by Wallace and Zia (1975) to be

$$c_1 = \frac{1}{n+8} \left[ 9 - \frac{\epsilon}{2(n+8)} \left( 9(n+8) \ln 2 - 81 \ln 3 + \frac{25n^2 + 142n + 76}{n+8} \right) \right],$$

$$c_2 = \frac{n-1}{n+8} \left[ 1 + \frac{\epsilon}{2(n+8)} (9(n+8) \ln 3 - n^2 + 6n + 52) \right]. \quad (7)$$

Suppose the theory is now analytically continued to non-integral values of  $n$ , in particular to  $n < 1$ ; then, since  $c_2$  is proportional to the  $n - 1$  transverse Goldstone modes, from (6) we see that  $\chi_L$  becomes negative as  $h \rightarrow 0$ , i.e. when the co-existence curve is approached. A negative longitudinal susceptibility is impossible, since by linear response theory

$$\chi_L = \beta \langle (\phi_1(k=0) - M)^2 \rangle \geq 0,$$

where  $\beta = 1/k_B T$ . At first sight, this might not be thought to be a serious problem but just another example of the curious results which can sometimes be obtained by analytic continuations in  $n$  (see Balian and Toulouse (1974), who showed that in certain circumstances even negative specific heats could be obtained on analytic continuation to negative values of  $n$ ). However, in this instance the problem is very serious, since there is at least one physical system lying in the domain of  $n < 1$ . Des Cloizeaux (1975) showed that there was an analogy between the  $n = 0$  limit of a Lagrangian field theory with external field  $h$  and the properties of polymer solutions in the so-called semi-dilute regime where the polymer concentration is such that they overlap significantly. In this theory, the longitudinal correlation function, to which  $\chi_L$  is the long-wavelength limit, is related to the correlations between the ends of one polymer and the ends of *all* the other polymers in solution. These correlations can be measured by neutron scattering experiments in which the end groups of the polymer chains are deuterated. The explicit relations between field-theoretic correlation functions and polymer correlation functions are given by Schäfer and Witten (1977). In particular,

$$\int d^d \mathbf{x} [\langle \sigma(\mathbf{x}) \sigma(0) \rangle - \langle \sigma(0) \rangle^2] \equiv \langle (\hat{\sigma}(\mathbf{k}=0) - \langle \sigma(0) \rangle)^2 \rangle = \hbar^2 \chi_L$$

where  $\sigma(\mathbf{x})$  is the density of chain end-points and  $\hat{\sigma}(\mathbf{k})$  is the Fourier transform of this quantity. A negative  $\chi_L$  implies that a physically measurable entity (namely, the structure function  $S(\mathbf{k})$  for the deuterated end groups), positive definite at  $\mathbf{k} = 0$ , has apparently become negative!

This difficulty in analytic continuation of a field-theoretic expression for a measurable quantity of polymer solutions prompts several questions. To see if this is a real problem for polymer solutions, we show in § 2 that a large region of the Daoud–Jannink (1976) plot of temperature versus concentration is affected, including the whole of the semi-dilute region. How far is the des Cloizeaux analogy valid? Predictions based on this theory and associated scaling ideas are in good agreement with experiments (Daoud *et al* 1975). It is well known that the field-theoretic formalism suffers from uncontrollable polydispersivity (des Cloizeaux 1975, Daoud *et al* 1975, Schäfer and Witten 1977, Moore 1977) due to the grand canonical ensemble of polymer chain lengths considered. However, one of us (Moore 1977) has shown that, by using this formalism, no errors are produced if the quantity under investigation is molecular weight independent. Indeed, in the semi-dilute poor solvent region where the excluded volume effect is 'weak' and it is possible to calculate quantities such as the screening length  $\xi$  and osmotic pressure  $\pi$  directly using straightforward perturbation theory (Edwards 1966), the agreement with the field-theoretic formalism is good (Moore 1977). However, the fact that the usual perturbation expansion, when analytically continued to  $n = 0$ , gives a negative  $\chi_L$  suggests that there must be something fundamentally wrong, even though everything apparently works well in low-order perturbation theory. In this paper we present a formalism which does not involve the conventional perturbation expansion and does not suffer from a negative  $\chi_L$ . We start by considering the  $O(n)$  symmetric generalised Heisenberg model of Stanley (Stanley 1969, Stanley *et al* 1970), with the constraint that the square of the modulus of the spins is equal to  $n$ . In the limit  $n \rightarrow 0$  such a model reduces to the self-avoiding walk. By considering the transfer matrix of the model in two dimensions in which the coupling strengths are highly anisotropic, we are led to consider a quantum mechanical formulation in which the 'time' axis is continuous and a spatial axis discrete. This is the  $n = 0$  version of the models considered by Fradkin and Susskind (1978), Hamer *et al* (1979) and Kogut (1979) to develop systematic strong-coupling expansions of the Ising,  $XY$  and Heisenberg ( $n = 3$ ) models. While throughout this paper the calculations are presented only for  $d = 2$ , there is no reason either in practice or principle why they cannot be extended to  $d = 3$ . Also, there is no reason in principle why the procedure need be applied only to the generalised Heisenberg model. It also works for the model of equation (3), but the complexity of the calculation is considerably increased.

The use of such a model is essentially an expansion about one dimension where there exists an exact solution (Stanley *et al* 1970), analytically continued for  $n < 1$  by Balian and Toulouse (1974). Considerable simplification occurs in the limit  $n \rightarrow 0$ , in that only the two lowest energy levels of the one-dimensional quantum mechanical problem need be considered. Perturbation expansions in the weak coupling between the one-dimensional chains are then possible. A particularly simple graphical expansion for the mass gap or inverse correlation length of the two-dimensional self-avoiding walk is obtained which allows an estimate of the critical exponent  $\nu$  to be determined in § 4.

By considering the effect of an external field, we are also able to find a perturbation series for the susceptibility and an estimate of  $\gamma$ . From the equation of state we are able to show that spontaneous magnetisation is possible, despite there being none in one

dimension (Balian and Toulouse 1974). The susceptibility is found to be well behaved and non-negative with no evidence of Goldstone mode problems. By Legendre transformation we construct the effective potential of the model which, by use of the des Cloizeaux (1975) 'dictionary', allows us to relate this to polymer variables and give an expression for the osmotic pressure.

The layout of this paper is as follows. In § 2 we review the spin-wave type of argument that leads to equation (6) and the mechanism by which the transverse susceptibility induces singular behaviour in the longitudinal susceptibility. By relating the susceptibilities to polymer variables we determine the affected regions of the Daoud–Jannink plot. Section 3 introduces the model and its quantum mechanical formulation. Section 4 is devoted to the perturbation expansion for the mass gap and estimation of  $\nu$  for  $d=2$ . Section 5 concerns the susceptibility series and § 6 the equation of state and spontaneous magnetisation. Section 7 relates the effective potential to polymer variables. Section 8 is a discussion of the results and conclusions.

## 2. The negative susceptibility and the affected region of the Daoud–Jannink plot

In this section we review the cause of the induced singularity in  $\chi_L$  by means of diagrammatic perturbation theory. We also recall the general argument leading to equation (6), and finally determine the region of the Daoud–Jannink plot that is affected by the difficulty in analytic continuation for  $n=0$ .

For the Hamiltonian (3) with  $t < 0$  and  $M \neq 0$  we 'shift' the field  $\phi_1$  by the transformation

$$L = \phi_1 - M, \quad (8)$$

with

$$M = \langle \phi_1 \rangle \quad \text{so that} \quad \langle L \rangle = 0, \quad (9)$$

and where the thermal average is defined by the functional integral

$$\langle A \rangle = \int D\phi A\{\phi\} e^{-H(\phi)} / \int D\phi e^{-H(\phi)}, \quad (10)$$

which leads to  $H = H_0 + H_1$  where

$$H_0 = \frac{1}{2} \int d^d \mathbf{x} [(\nabla \phi_T)^2 + (\nabla L)^2 + r_T \phi_T^2 + r_L L^2], \quad (11)$$

$$\phi_T^2 = \sum_{i=2}^n \phi_i^2, \quad (12)$$

and the perturbation is

$$H_1 = \int d^d \mathbf{x} \left\{ \frac{1}{8} v (L^2 + \phi_T^2)^2 + \frac{1}{2} v M L (L^2 + \phi_T^2) + [(r_0 + \frac{1}{2} v M^2) M - H] L \right\} + \text{counter terms}. \quad (13)$$

$r_L$  and  $r_T$  are respectively the inverse longitudinal and transverse susceptibilities defined by

$$r_L^{-1} = \int d^d \mathbf{x} [\langle \phi_1(\mathbf{x}) \phi_1(\mathbf{0}) \rangle - M^2], \quad (14)$$

$$r_T^{-1} = \int d^d x \langle \phi_i(x) \phi_i(\mathbf{0}) \rangle, \quad 2 \leq i \leq n. \tag{15}$$

For the unperturbed longitudinal and transverse correlation functions in momentum space, we have

$$\begin{aligned} g_L(k) &= \int d^d x e^{ik \cdot x} [\langle \phi_1(x) \phi_1(\mathbf{0}) \rangle_{H_0} - M^2] \\ &= \langle L(k) L(-k) \rangle_{H_0} \\ &= (r_L + k^2)^{-1}, \end{aligned} \tag{16}$$

$$\begin{aligned} g_T(k) &= \int d^d x e^{ik \cdot x} \langle \phi_i(x) \phi_i(\mathbf{0}) \rangle_{H_0}, \quad 2 \leq i \leq n, \\ &= (r_T + k^2)^{-1}. \end{aligned} \tag{17}$$

Using these as ‘propagators’, a graphical perturbation expansion can be developed for the full longitudinal susceptibility. In treating the terms of equation (13) as perturbations, it should be noticed that the new vertex  $vM$  is  $O(v^{1/2})$ , since  $M^2 = O(t/v)$  as may be shown in mean-field theory by minimising equation (3). The expansion to  $O(v)$  of the longitudinal susceptibility is given by the diagrams of figure 1. The source of the induced singularity is the closed loop of transverse modes shown in figure 2, with a contribution proportional to

$$(n-1)v^2 M^2 \int \frac{d^d q}{(q^2 + r_T)^2} \propto (n-1)v^2 M^2 r_T^{-\epsilon/2}, \tag{18}$$

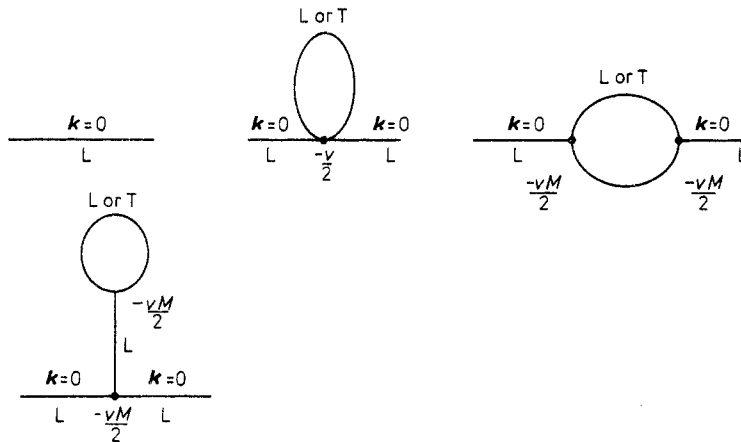


Figure 1. Diagrammatic expansion of the longitudinal susceptibility to  $O(v)$ . Labels L and T refer to unperturbed longitudinal and transverse correlation functions respectively.

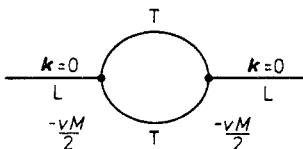


Figure 2. Source of induced singularity in longitudinal susceptibility due to closed loop of transverse modes. The weighting of this graph is  $(n-1)$ .

with  $r_T$  given by (1) as  $r_T = h/M$ . The graph has an  $(n-1)$  weighting due to  $(n-1)$  transverse modes. Evaluating the diagrams of figure 1 gives

$$\begin{aligned} \chi_L = & \frac{1}{r_L} - \frac{v}{2r_L^2} [3F(r_L) + (n-1)F(r_T)] + 2\left(\frac{vM}{2}\right)^2 \frac{1}{r_L^2} [9\pi(r_L) + (n-1)\pi(r_T)] \\ & + 3\left(\frac{vM}{2}\right)^2 \frac{1}{r_L^3} [3F(r_L) + (n-1)F(r_T)], \end{aligned} \quad (19)$$

where

$$r_L = t + 3vM^2/2, \quad r_T = t + \frac{1}{2}vM^2, \quad (20)$$

$$F(r) = \frac{1}{(2\pi)^d} \int d^d q \left( \frac{1}{q^2+r} - \frac{1}{q^2} \right) = -R_d r^{2-\epsilon/2}, \quad (21)$$

$$\pi(r) = \frac{1}{(2\pi)^d} \int d^d q \frac{1}{(q^2+r)^2} = \frac{2-\epsilon}{2} R_d r^{-\epsilon/2}, \quad (22)$$

with

$$R_d = \frac{\pi K_d}{2 \sin \frac{1}{2}\pi\epsilon} \quad \text{and} \quad K_d = \frac{2}{(4\pi)^{d/2} \Gamma(d/2)}. \quad (23)$$

Putting  $n < 1$  (in particular  $n = 0$ ) and  $r_T = h/M$ , it is evident that as  $h \rightarrow 0$  the term given by equation (18) dominates and drives  $\chi_L$  negative. The perturbation expression is consistent with the general form of equation (6). Further support is given by what is essentially a spin-wave type approach (Brezin and Wallace 1973, Wallace and Zia 1975).

For  $T < T_c$ , i.e.  $t < 0$ , and for  $h$  small the dominant fluctuations are expected to be those transverse to the magnetisation. Therefore consider the effective Hamiltonian obtained from equation (3) by elimination of the longitudinal mode  $\phi_1$  in favour of the  $(n-1)$  transverse modes by the constraint  $\sum_{i=1}^n \phi_i^2 = M^2$ , a constant, i.e.

$$\phi_1 = (M^2 - \phi_T^2)^{1/2} \quad (24)$$

which is understood as a power series in  $1/M$ . The effective Hamiltonian is

$$H = \int d^d x \left\{ \frac{1}{2} (\nabla \phi_T)^2 + \frac{1}{2} [\nabla (M^2 - \phi_T^2)^{1/2}]^2 - h (M^2 - \phi_T^2)^{1/2} \right\}. \quad (25)$$

If we expand the last term, it is easily seen that  $r_T = h/M$ , and so as  $h \rightarrow 0$  we are examining the critical behaviour of this Hamiltonian. Under a renormalisation group transformation, the only interactions relevant for inducing anomalous dimensions or non-classical exponents are terms of the form  $(\sum_{i=2}^n \phi_i^2)^2$  (Wilson and Kogut 1974). Since such a term occurs in the Hamiltonian (25) with a factor of  $h$ , which tends to zero, the dimensions of the fields are expected to be classical. Denoting the transverse correlation length by  $\xi$ , we have from equation (15)

$$r_T \sim \xi^{d-2d_\phi} \sim \xi^2, \quad (26)$$

since  $2d_\phi = d - 2$  ( $\eta = 0$ ). For the longitudinal susceptibility, we have from equation

(15), substituting from equation (24) for  $\phi_1$ ,

$$\begin{aligned} r_L^{-1} &\sim c_1 + c_2' \int d^d \mathbf{x} \langle \phi_T^2(\mathbf{x}) \phi_T^2(\mathbf{0}) \rangle \\ &\sim c_1 + c_2 \xi^{d-2d_\phi^2} \sim c_1 + c_2 \xi^{d-4d_\phi}, \\ r_L^{-1} &\sim c_1 + c_2 \xi^\epsilon, \end{aligned} \tag{27}$$

with  $c_2 = c_2'(n-1)$ .

Elimination of  $\xi$  between (26) and (27) gives

$$r_L^{-1} \sim c_1 + c_2 r_T^{-\epsilon/2}, \tag{28}$$

which is basically equation (6).

Turning now to the application of field theory to polymer solutions, we follow the treatment of Moore (1977) and quote the results of the des Cloizeaux (1975) formalism required to relate magnetic variables to polymer quantities. Given the effective potential  $\Gamma(M, t)$  of the field theory with Hamiltonian (3), in the limit  $n \rightarrow 0$  polymer quantities are given by the relations

$$c = \partial\Gamma/\partial t, \tag{29}$$

$$c/N = \frac{1}{2}M(\partial\Gamma/\partial M), \tag{30}$$

$$\pi/k_B T = M(\partial\Gamma/\partial M) - \Gamma, \tag{31}$$

where  $c$  is the concentration of monomers,  $N$  is the average chain length and  $\pi$  the osmotic pressure. We determine the region of the Daoud-Jannink plot (figure 3) relating to  $\chi_L$  becoming negative when analytically continued.

In the poor solvent regime (region III of figure 3) the perturbation expressions (19)–(23) are valid (Moore 1977). Converting to polymer variables using (29) and (30), we have

$$r_L = 1/N + 2vc \approx 2vc, \quad \text{for } N \gg (2vc)^{-1}, \tag{32}$$

$$r_T = 1/N, \tag{33}$$

with

$$\chi_L = \frac{1}{2vc} \left( 1 + \frac{3}{4}(5-3\epsilon)R_d v (2vc)^{-\epsilon/2} - \frac{2-\epsilon}{4} R_d v N^{\epsilon/2} \right). \tag{34}$$

Hence the criterion for  $\chi_L < 0$  is

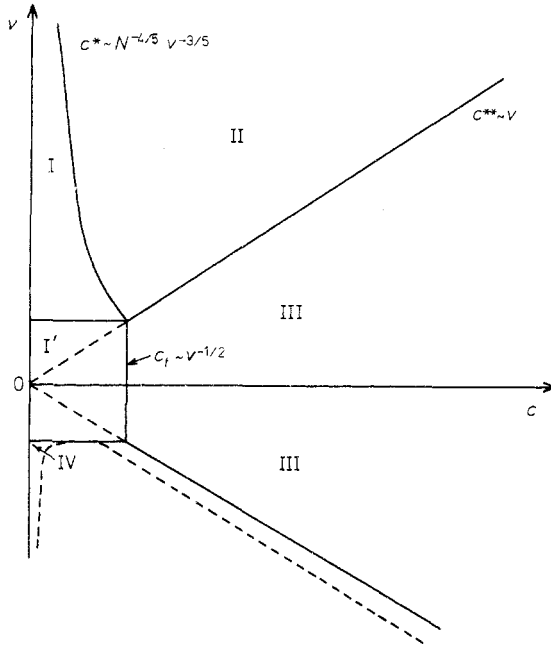
$$N^{\epsilon/2} > \text{constant } (2vc)^{-\epsilon/2} \quad \text{or} \quad N > \text{constant } (2vc)^{-1}, \text{ in } d = 3. \tag{35}$$

This is just the criterion for the semi-dilute poor solvent regime (Moore 1977). Since the cross-over line between semi-dilute poor and good solvent regimes (regions III and II) is given by  $c^{**} \sim v$ , and so  $v < c$  in III, an alternative way of expressing (35) is

$$c > N^{-1/2}. \tag{36}$$

In the good solvent regime (region II) we use the renormalisation group method of Rudnick and Nelson (1976) in which the recursion relations for  $t(\tau)$  and  $v(\tau)$  are integrated out of the critical region to give a non-critical Hamiltonian  $H[\tau^*]$ . The perturbation approach of the beginning of this section can then be used with  $t(\tau^*)$ ,  $v(\tau^*)$





**Figure 3.** The Daoud-Jannink plot of polymer solutions. The cross-over values are for  $d = 3$ . Regions II and III are the semi-dilute good and poor solvent regimes respectively. In both  $\chi_L$  is negative. NB Strictly speaking, the plot is meaningless for  $v < 0$ , as to ensure stability three-body or non-local two-body interactions have to be introduced.

and  $M(\tau^*)$ , and then relating back to the initial values  $t$  and  $v$  through

$$t(\tau^*) = t e^{2\tau^*} / Q^\Delta(\tau^*), \tag{37}$$

$$v(\tau^*) = v e^{\epsilon\tau^*} / Q(\tau^*), \tag{38}$$

where

$$Q(\tau^*) = 1 + [8K_d v(\tau^*) / \epsilon] (e^{\epsilon\tau^*} - 1) \quad \text{and} \quad \Delta = \frac{1}{4} \text{ for } n = 0. \tag{39}$$

From equation (B20) of Rudnick and Nelson (1976) (with our different normalisation of the  $v$  term in (3)), we have

$$\begin{aligned} \chi_L(t, v, h) = \frac{e^{2\tau^*}}{T_L(\tau^*)} & \left[ 1 - \left( \frac{3K_d v(\tau^*) [t(\tau^*) + \frac{9}{2}v(\tau^*)M^2(\tau^*)]}{2T_L(\tau^*)} \right) \ln T_L(\tau^*) \right. \\ & \left. - \frac{1}{4}(n-1)K_d v(\tau^*) \ln T_T(\tau^*) - \frac{(n+8)K_d v^2(\tau^*)M^2(\tau^*)}{4T_L(\tau^*)} \right], \end{aligned} \tag{40}$$

where

$$T_L(\tau^*) = t(\tau^*) + \frac{3}{2}v(\tau^*)M^2(\tau^*), \tag{41}$$

$$T_T(\tau^*) = t(\tau^*) + \frac{1}{2}v(\tau^*)M^2(\tau^*). \tag{42}$$

Using the same matching condition  $T_L(\tau^*) = 1$  as Moore (1977), we find

$$\chi_L(t, v, h) = e^{2\tau^*} [1 + (K_d/4)v(\tau^*) \ln T_T(\tau^*) - 2K_d v^2(\tau^*)M^2(\tau^*)], \tag{43}$$

and the criterion for  $\chi_L < 0$  is

$$T_T(\tau^*) < 1. \tag{44}$$

Converting to polymer variables, we note

$$\begin{aligned} T_T(\tau^*) &= e^{2\tau^*} (t/Q^\Delta(\tau^*) + vM^2/Q(\tau^*)) \\ &= (e^{2\tau^*}/Q^\Delta(\tau^*)) [t + vM^2Q^{\Delta-1}(\tau^*)], \end{aligned} \tag{45}$$

but  $1/N = t + vcQ(\tau^*)^{2\Delta-1}$  and  $c = \frac{1}{2}M^2Q^{-\Delta}(\tau^*)$  (cf Moore 1977) so

$$T_T(\tau^*) = e^{2\tau^*}/Q^\Delta(\tau^*)N. \tag{46}$$

In the good solvent region where  $Q$  is large, we have  $2vcQ^{\Delta-1}(\tau^*) = e^{-2\tau^*}$ , so that the condition (44) becomes

$$1/2vcQ^{2\Delta-1}(\tau^*)N < 1$$

or, substituting for  $Q^{2\Delta-1}(\tau^*)$  (Moore 1977),

$$\frac{1}{2Nvc} \left( \frac{8K_d v}{\epsilon} (2vc)^{-\epsilon/2} \right)^{-2(d\nu-2)/\epsilon(d\nu-1)} < 1. \tag{47}$$

For  $d = 3$  ( $\epsilon = 1$ ), and using the Flory value  $\nu = \frac{3}{5}$ , this is equivalent to

$$c > \text{constant } N^{-4/5} v^{-3/5} \tag{48}$$

which is the criterion for being in the semi-dilute regime (Daoud and Jannink 1976). Hence the problem of negative  $\chi_L$  exists throughout the entire semi-dilute regime.

### 3. The model: a quantum mechanical lattice Hamiltonian

The  $O(n)$  symmetric  $\phi^4$  Hamiltonian of equation (3) generates in the limit  $n \rightarrow 0$  the conventional model for interacting polymers with excluded volume  $v$  (although the polydispersivity is somewhat unusual). To avoid the problems associated with a negative  $\chi_L$ , we wish to present in this section an alternative perturbation expansion which is based essentially on an expansion about a one-dimensional limit. While in principle it is possible to carry out this expansion for the  $\phi^4$  Hamiltonian, the calculational complexities it would entail make it desirable to introduce a simplified model Hamiltonian. We believe that it is in the same universality class as that of the  $\phi^4$  model, and the numerical values of its exponents are consistent with this belief. The starting point for the derivation of the new model Hamiltonian is a generalisation of the  $n$ -vector Heisenberg Hamiltonian (Stanley 1969, Stanley *et al* 1970), which in the limit  $n \rightarrow 0$  models self-avoiding walks. The version we consider is the anisotropic case

$$H = - \sum_{\mathbf{R}} [K_x \mathbf{n}(\mathbf{R}) \cdot \mathbf{n}(\mathbf{R} + \delta_x) + K_y \mathbf{n}(\mathbf{R}) \cdot \mathbf{n}(\mathbf{R} + \delta_y)], \tag{49}$$

where  $\mathbf{n}(\mathbf{R})$  is an  $n$ -dimensional spin vector at a site  $\mathbf{R}$  of a two-dimensional lattice with  $\delta_x$  and  $\delta_y$  nearest-neighbour vectors. (We shall discuss explicitly the case  $d = 2$ ; the extension to higher dimensions is straightforward.) In the limit of large anisotropy  $K_x \gg K_y$ , it is possible by standard methods to reduce the two-dimensional Hamiltonian of equation (49) to a one-dimensional quantum mechanical Hamiltonian, which then forms the basis for the subsequent calculations.

A factor of  $(k_B T)^{-1}$  has been included in the exchange constants  $K_x$  and  $K_y$  for convenience. We choose the spins to be of length  $n^{1/2}$ , i.e.

$$\sum_{\alpha=1}^n n^\alpha(\mathbf{R}) n^\alpha(\mathbf{R}) = n. \quad (50)$$

In  $d = 1$ , in which  $K_y = 0$  and  $\mathbf{R}$  is a scalar, the model may be solved by using the transfer matrix

$$T = \exp[K_x \mathbf{n}(\mathbf{R}) \cdot \mathbf{n}(\mathbf{R} + 1)], \quad (51)$$

which acts on the  $n$ -dimensional sphere of radius  $n$ . Rescaling the spins  $\mathbf{n} = n^{1/2} \mathbf{S}$  allows the Funk–Hecke theorem to be used to determine the eigenvalues of  $T$  (Stanley *et al* 1970), which are

$$\lambda_l = \Gamma(n/2) (nK_x/2)^{1-n/2} I_{l+n/2-1}(nK_x), \quad (52)$$

where  $I_\nu$  is the modified Bessel function of the first kind of order  $\nu$  and  $l = 0, 1, 2, \dots$ . The eigenfunctions are the generalised spherical harmonics in  $n$  dimensions. The degeneracies of the above  $\lambda_l$  are given by

$$D_l^n = \frac{(l+n-3)!(2l+n-2)}{l!(n-2)!}. \quad (53)$$

For the  $s(l=0)$  and  $p(l=1)$  states we recover the familiar results  $D_0^n = 1$ ,  $D_1^n = n$ . Since the partition function is given by

$$Z = \text{Tr } T^N = \sum_l \lambda_l^N, \quad (54)$$

where  $N$  is the number of sites in the linear chain, the free energy per site, in the thermodynamic limit, is

$$F = -k_B T \ln \lambda_m, \quad (55)$$

where  $\lambda_m$  is the maximum eigenvalue of  $T$ . The correlation function between two spins a distance  $z$  apart is

$$\begin{aligned} \langle n^\alpha(z) n^\alpha(0) \rangle &= \sum_l |\langle m | n^\alpha | l \rangle|^2 \left( \frac{\lambda_l}{\lambda_m} \right)^z \\ &= \sum_l |\langle m | n^\alpha | l \rangle|^2 \exp[-z(\ln \lambda_m - \ln \lambda_l)]. \end{aligned} \quad (56)$$

Balian and Toulouse (1974) have investigated this model with the spins normalised to one. For  $n > 1$  the  $s$  state has the largest eigenvalue, but for  $0 < n < 1$  it is possible for a  $p$  state to cross this state for sufficiently low temperature. However, in both the high-temperature and low-temperature phases there is no spontaneous magnetisation.

Returning to the model here, we note from equation (52)

$$\begin{aligned} \lambda_l &= \Gamma\left(\frac{n}{2}\right) \left(\frac{nK_x}{2}\right)^{1-n/2} \sum_{p=0}^{\infty} \frac{(nK_x/2)^{n/2-1+l+2p}}{p! \Gamma(n/2+l+p)} \\ &= \frac{\Gamma(n/2)}{\Gamma(n/2+l)} \left(\frac{nK_x}{2}\right)^l \left[ 1 + O\left(\frac{(nK_x)^2}{n/2+l}\right) \right], \end{aligned} \quad (57)$$

where the series expansion for  $I_\nu$  has been used. As  $n \rightarrow 0$  with  $K_x$  fixed we note

$$\begin{aligned} \lambda_0 &= 1 + O(n), & \lambda_1 &= K_x [1 + O(n^2)], \\ \lambda_l &= O(n^{l-1}), & l &\geq 2, \end{aligned} \tag{58}$$

so that only the  $s$  and  $p$  levels survive in the self-avoiding walk ( $n \rightarrow 0$ ) limit, with a critical point defined by  $K_x = 1$ .

We now return to  $d = 2$  and write the transfer matrix between two rows or chains of spins (figure 4) as

$$T(\tau) = \exp\left(K_x \sum_m \mathbf{n}(m) \cdot \mathbf{n}'(m) + \frac{1}{2} K_y \sum_m (\mathbf{n}(m) \cdot \mathbf{n}(m+1) + \mathbf{n}'(m) \cdot \mathbf{n}'(m+1))\right), \tag{59}$$

where  $\tau$  is the lattice spacing in the  $x$  direction and primes denote nearest-neighbour chains. To develop a quantum mechanical formulation, we take the continuum limit in the  $x$  (or  $\tau$ ) direction so that

$$T(\tau) = \exp(-\tau H),$$

or

$$H = \lim_{\tau \rightarrow 0} -\frac{1}{\tau} \ln T. \tag{60}$$

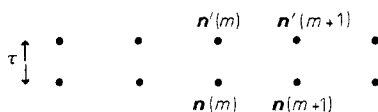


Figure 4. Two neighbouring chains of spins.

In order to find a simple form for  $H$ , it is necessary for  $K_x$  to be large and  $K_y/K_x \equiv x \ll 1$ . Such an approach has been used by Wilson and Kogut (1974) and Stoeckly and Scalapino (1975) for  $\phi^4$  models. It has also been used by Fradkin and Susskind (1978) and Hamer *et al* (1979) to develop strong coupling expansions for the Ising, O(2), O(3) and O(4) models. It is found that  $H$  takes the form

$$H = \sum_m [H_0(m) - x \mathbf{n}(m) \cdot \mathbf{n}(m+1)], \tag{61}$$

where  $H_0$  is a single-site operator whose eigenvalues are given by

$$\Gamma_l = -\ln \lambda_l, \tag{62}$$

where  $\lambda_l$  are the eigenvalues of the  $d = 1$  transfer matrix (51). For example, for the model with spins normalised to 1, Balian and Toulouse give

$$-\ln \lambda_l = -K_x + \frac{1}{2}(n-1) \ln(K_x/2\pi) + (1/8K_x)(2l+n-3)(2l+n-1), \tag{63}$$

which up to (arbitrary) constants is

$$-\ln \lambda_l \sim (1/2K_x)l(l+n-2). \tag{64}$$

$l(l+n-2)$  is the spectrum of the squared angular momentum operator  $J^2(m)$  in  $n$  dimensions, and so is consistent with the Hamiltonian derived in a different way by

Hamer *et al* (1979) for  $n = 2, 3, 4$ . From (64) we see that the  $p$  level is always below the  $s$  level for  $n < 1$ .

Applying (62) to the eigenvalues (58) of our model, we see that, in the limit  $n \rightarrow 0$ ,

$$\Gamma_0 = 0, \quad \Gamma_1 = -\ln K_x \equiv \Delta, \quad \Gamma_l \rightarrow \infty \quad l \geq 2. \quad (65)$$

So for  $H_0(m)$  we may consider a two-level system of an  $s$  state and  $n$   $p$ -states. We consider  $\Delta$  to take both positive and negative values, and perform perturbation expansions in the 'hopping' term

$$H_1 = -x \sum_m \mathbf{n}(m) \cdot \mathbf{n}(m+1). \quad (66)$$

We can also consider the effect of an external magnetic field by adding a term

$$-h \sum_m n^1(m) \quad (67)$$

to (61) where we have chosen  $h$  to be in the 1-direction. The rest of this paper is concerned with the quantum mechanical Hamiltonian

$$H = \sum_m [H_0(m) - xn(m) \cdot \mathbf{n}(m+1) - hn^1(m)] \quad (68)$$

on a one-dimensional lattice. This is a model for polymers in two dimensions. The generalisation of equation (68) to spins in a plane would be the appropriate model for polymers in three dimensions.

#### 4. Perturbation expansion for the mass gap

In this section we take  $h = 0$  and  $\Delta > 0$ . Let  $H_0 = \sum_m H_0(m)$  and denote the eigenvalues of  $H$  and  $H_0$  by  $\epsilon_j$  and  $\epsilon_j^{(0)}$ . The two-point correlation function is

$$G(z) = \sum_j |\langle \Psi_0 | n^\alpha(m) | \Psi_j \rangle|^2 \exp[-z(\epsilon_j - \epsilon_0)], \quad (69)$$

where  $\{|\psi_j\rangle\}$  are the eigenfunctions of  $H$ .

The quantity of most interest is the inverse correlation function or mass gap,  $\xi^{-1}$ , which is the difference between the lowest energy level and the first excited state:

$$\xi^{-1} = \epsilon_1 - \epsilon_0. \quad (70)$$

(A knowledge of  $\xi$  enables one to determine the polymer size exponent  $\nu$ .) We investigate this by a perturbation expansion in the 'hopping' term (66) about  $H_0$ . Denote the ground state  $|0\rangle$  of  $H_0$  by

$$H_0|0\rangle = 0, \quad (71)$$

i.e. all sites are in an  $s$  state and  $\epsilon_0^{(0)} = 0$ . The first excited state  $|1\rangle$  of  $H_0$  that is translationally invariant is the zero-momentum state of a spin wave,

$$|1\rangle = L^{-1/2} \sum_{m=1}^L n^1(m)|0\rangle, \quad \epsilon_1^{(0)} = \Delta, \quad (72)$$

where  $L$  is the number of sites of the lattice. By virtue of (50) we have

$$\langle 0 | n^\alpha(m) n^\beta(m') | 0 \rangle = \langle n^\alpha(m) n^\beta(m') \rangle_A = \delta_{\alpha\beta} \delta_{mm'}, \quad (73)$$

$$\langle 0 | \sum_{\alpha=1}^n [n^\alpha(m)]^2 | 0 \rangle = n, \tag{74}$$

where  $\langle \dots \rangle_A$  denotes the angular average over the sphere in  $n$  dimensions. Using these and the simplicity of a two-level system, we find that the effect of  $H_1$  is to (1) raise a spin from the  $s$  state to a  $p$  state at a site and at a neighbouring site or (2) lower from  $p$  to  $s$  at two neighbouring sites or (3) lower a  $p$  to  $s$  at a site and raise from  $s$  to  $p$  at a neighbouring site. Following Hamer *et al* (1979) and Kogut (1979), we use graphs to represent terms of the Rayleigh–Schrödinger perturbation series for  $\epsilon_1$  and  $\epsilon_0$  which may be obtained to high order from the formal expression

$$\epsilon_j - \epsilon_j^{(0)} = \sum_{k=0}^{\infty} \langle j | xV [g(\epsilon_j^{(0)} - \epsilon_j + xV)]^k | j \rangle, \tag{75}$$

where  $g$  is the resolvent

$$g = \frac{1 - |j\rangle\langle j|}{\epsilon_j^{(0)} - H_0}, \tag{76}$$

and

$$H_1 = xV, \quad V = -\sum_m \mathbf{n}(m) \cdot \mathbf{n}(m+1),$$

i.e.

$$\epsilon_j = \epsilon_j^{(0)} + \epsilon_j^{(1)}x + \epsilon_j^{(2)}x^2 + \epsilon_j^{(3)}x^3 + \dots$$

with

$$\begin{aligned} \epsilon_j^{(1)} &= \langle j | V | j \rangle, & \epsilon_j^{(2)} &= \langle j | VgV | j \rangle, \\ \epsilon_j^{(3)} &= \langle j | VgVgV | j \rangle - \langle j | V | j \rangle \langle j | Vg^2 | j \rangle. \end{aligned} \tag{77}$$

We use a single vertical line to denote a  $p$  state at a site  $m$  and a cross for the single-site operator

$$X = \sum_m n^1(m). \tag{78}$$

Thus the state  $|1\rangle$  is shown in figure 5. Interaction terms  $xV$  are shown by horizontal lines joining neighbouring sites. The first- and second-order graphs for  $\epsilon_1$  are shown in figure 6 and contribute

$$\epsilon_1^{(1)} = -2x, \quad \epsilon_1^{(2)} = 2x^2(-1/2\Delta). \tag{79}$$

Intermediate state denominators are determined by drawing dotted lines through a diagram: if such a line cuts only one vertical line, that graph is disallowed since the resolvent excludes such intermediate states.

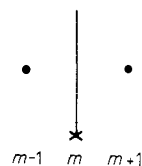


Figure 5. The state  $|1\rangle$  of equation (72).

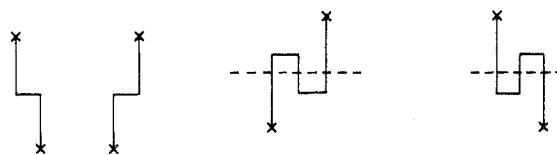


Figure 6. First- and second-order graphs for  $\epsilon_1$ .

Since  $V$  can ‘flip’ to left or right in the lattice, the graphs have a mirror reflective symmetry. A possible diagram for  $\epsilon_1$  at  $O(x^2)$  is shown in figure 7. However, this graph does not contribute in the limit  $n \rightarrow 0$ , since the closed loop has an unrestricted sum over spin components which gives a factor of  $n$ . Two or more vertical lines cannot be drawn at a site, since this corresponds to values of  $l \geq 2$  for states of the single-site Hamiltonian  $H_0(m)$ . In consequence, our graphical series are considerably simpler than those of Hamer *et al* (1979); in particular, we do not have the complication of non-Abelian graphs.

The graphs for  $\epsilon_1$  have been calculated to  $O(x^5)$ . It should be noted that, beyond second order, disconnected products have to be included; these are shown in brackets in the third-order graphs of figure 8. At fourth order, the new type of graph of figure 9 appears†. The graphs for  $\epsilon_0$  always have an even number of interactions  $V$ . The second-order graph is shown in figure 10. However, since this graph always consists of closed loops, there is no contribution in the limit  $n \rightarrow 0$ , and  $\epsilon_0 = 0$ , to all orders in perturbation theory.

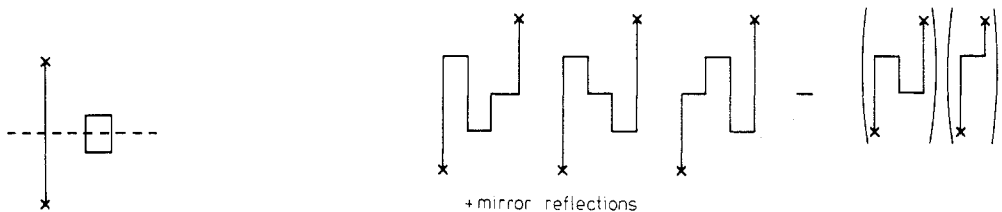


Figure 7. Graph with zero contribution to  $\epsilon_1$ . Figure 8. Third-order graphs for  $\epsilon_1$ .



Figure 9. A graph with two ‘horses’ in the same lane. Figure 10. Second-order graph for  $\epsilon_0$ .

To order  $x^5$  we find

$$\epsilon_1 - \epsilon_0 = \Delta(1 - 2y - y^2 - \frac{1}{2}y^3 - \frac{5}{4}y^4 - \frac{5}{4}y^5) = \Delta F(y), \tag{80}$$

where  $y = x/\Delta$ . Referring to (65) for  $\Delta$ , we see that the expansion (80) is effectively a high-temperature series expansion. Since we expect

$$\xi^{-1} \sim (y_c - y)^\nu, \quad y \rightarrow y_c, \tag{81}$$

at some critical value  $y_c$ , we form the logarithmic derivative of  $F$

$$\frac{d}{dy} \ln F(y) = \frac{F'(y)}{F(y)} \underset{y \rightarrow y_c}{\sim} \frac{\nu}{y - y_c}. \tag{82}$$

By forming Padé approximants of the logarithmic derivative, we may estimate the

† We found it useful to consider interactions as horses in a race in which the Jockey Club ruled that no two horses could have the same place. Stewards’ inquiries were quite common.

position and residue of the pole and hence estimate  $y_c$  and  $\nu$ . The results are shown in table 1. We see there is consistent evidence for a pole at

$$y_c = 0.37 \pm 0.02. \tag{83}$$

The estimates of  $\nu$  from the residues may be compared to the Flory value of  $\frac{3}{4}$ , exact enumeration techniques (McKenzie 1976) which give  $\nu = 0.74$  to  $\nu = 0.75$ , and the renormalisation group calculation of Hilhorst (1977) on a triangular lattice which gave  $\nu = 0.74$ .

**Table 1.** The positions and residues (in brackets) of poles on the positive, real  $y$  axis in Padé approximants to the mass gap.

$N$	$[N/N-1]$	$[N/N]$	$[N/N+1]$
0			0.33 (0.67)
1		0.39 (0.90)	0.37 (0.79)
2	0.36 (0.73)	0.37 (0.81)	

### 5. The susceptibility

We now find a perturbation expansion for the susceptibility. Let

$$\tilde{H} = \sum_m [H_0(m) - xn(m) \cdot n(m+1)] = H_0 + xV,$$

and

$$\tilde{H}|\Psi_0\rangle = \epsilon_0|\Psi_0\rangle, \tag{84}$$

so that  $|\Psi_0\rangle$  is the exact ground state. Consider the term (67) as a perturbation

$$-h \sum_m n^1(m) = -hX$$

to calculate the ground-state eigenvalue

$$\epsilon = \epsilon_0 - h\langle\Psi_0|X|\Psi_0\rangle + h^2 \sum_{m,m'} \langle\Psi_0|n^1(m) \frac{Q}{\epsilon_0 - \tilde{H}} n^1(m')|\Psi_0\rangle,$$

where

$$Q = 1 - |\Psi_0\rangle\langle\Psi_0|. \tag{85}$$

The susceptibility  $\chi$  is then given by

$$\chi = -\left. \frac{\partial^2 F}{\partial h^2} \right|_{h \rightarrow 0} = -L^{-1} \left. \frac{\partial^2 \epsilon}{\partial h^2} \right|_{h \rightarrow 0} = -2L^{-1} \sum_{m,m'} \langle\Psi_0|n^1(m) \frac{Q}{\epsilon_0 - \tilde{H}} n^1(m')|\Psi_0\rangle, \tag{86}$$

with  $\epsilon_0 = 0$ . However, we note from the previous section that  $\epsilon_0 = 0$  to all orders in  $x$ . The state  $|\Psi_0\rangle$  is given in perturbation theory in  $V$  by

$$|\Psi_0\rangle = \sum_{k=0}^{\infty} [g(\epsilon_0^{(0)} - \epsilon_0 + xV)]^k |0\rangle = \sum_{k=0}^{\infty} (gxV)^k |0\rangle, \tag{87}$$

where

$$g = (1 - 0)\langle 0| / (\epsilon_0^{(0)} - H_0).$$



The state  $\Psi_0\rangle$  is properly normalised to 1, since  $\langle\Psi_0\Psi_0\rangle$  will only contain graphs of closed loops beyond zeroth order. Noting that  $V$  is an even operator, so that  $\Psi_0\rangle$  only contains an even number of excited states, we see that

$$\sum_m \langle\Psi_0 n^1(m) \Psi_0\rangle = \langle\Psi_0 X \Psi_0\rangle = 0, \tag{88}$$

so that  $Q$  may be replaced by 1 in equation (86). Thus we obtain a perturbation expression for  $\chi$ ,

$$\chi = 2L^{-1} \sum_{m,m'} \sum_{k,k'} \langle 0 (xVg)^k n^1(m) \frac{1}{H} n^1(m') (gxV)^{k'} 0\rangle,$$

with

$$\frac{1}{H} = \frac{1}{H_0} \left( 1 - xV\frac{1}{H_0} + xV\frac{1}{H_0}xV\frac{1}{H_0} - \dots \right). \tag{89}$$

Since  $V$  is defined by (76) with a minus sign, we see that all terms of (89) are positive. A diagrammatic expansion can also be developed for the terms of (89) with the same rules as before, except that single vertical lines are allowed since the resolvent  $g$  now projects out the ground state  $0\rangle$ , not the state  $1\rangle$ . The diagrams up to second order are shown in figure 11, and give

$$\chi = (2/\Delta)(1 + 4y + 12\frac{1}{2}y^2). \tag{90}$$

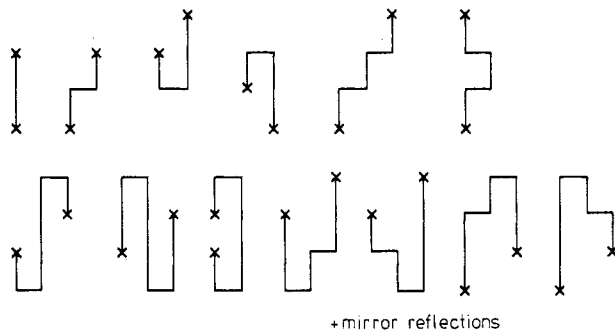


Figure 11. Graphs to  $O(x^2)$  for the susceptibility.

Since all the terms in (89) are positive, we can use it to find a lower bound to  $\chi$  and an estimate of  $y_c$ . The dominant diagrams are the 'shortest path' type, e.g. figure 12 shows those of this type at  $O(x^3)$ . These diagrams have all intermediate states equal to 1, and so have the smallest energy denominators.

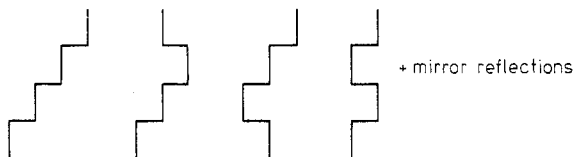


Figure 12. Dominant graphs at  $O(x^3)$  for the susceptibility.

At  $N$ th order the number of such diagrams is

$$\sum_{r=0}^N \binom{N}{r} = 2^N$$

and so

$$\chi > \frac{2}{\Delta} \sum_{N=0}^{\infty} 2^N y^N,$$

i.e.

$$\chi > \frac{2}{\Delta} \left[ \frac{1}{1-2y} \right]. \tag{91}$$

Therefore  $\chi$  diverges before  $y = 0.5$ . The estimates of  $y_c$  from table 1 are consistent with this.

We have developed the expansion (89) to  $O(x^4)$ , and find

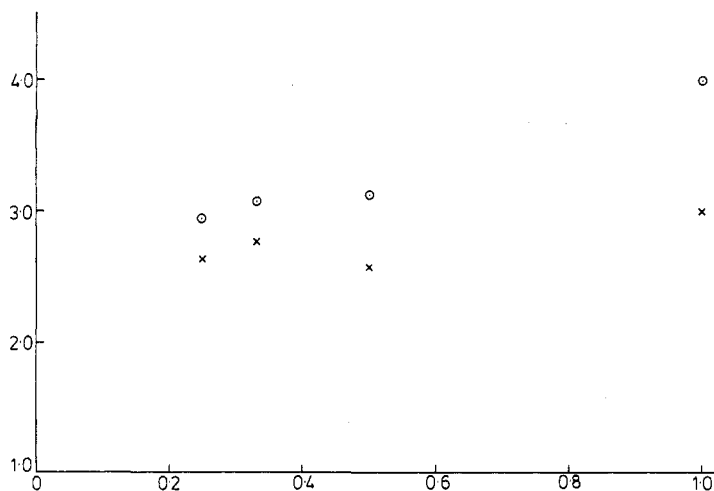
$$\chi = (2/\Delta)(1 + 4y + 12\frac{1}{2}y^2 + 38\frac{1}{2}y^3 + 113y^4). \tag{92}$$

Whilst the ratios of successive terms  $R_l$  versus  $1/l$  (figure 13) indicate that asymptotic behaviour has not been reached, we find for the  $[1, 2]$  Padé approximant to the logarithmic derivative,

$$\frac{4 + 8.5135y}{1 - 0.1216y - 7.1014y^2} = \frac{d}{dy} \ln \chi(y), \tag{93}$$

a pole at 0.37 with residue  $-1.34$ . The pole is consistent with the estimates for the mass gap of table 1, and the residue estimate for  $\gamma$  can be compared to  $\gamma = \frac{4}{3}$  from enumeration techniques (Watts 1975).

The estimates for  $\nu$  and  $\gamma$  from such short series encourage us to believe the model merits further investigation.



**Figure 13.** Graph of ratios  $R_l$  versus  $1/l$  for the  $l$ th term of the series for  $\chi$  (O) and  $\log$  (mass gap), (x).

## 6. The equation of state

In this section we consider the model in the presence of an external field  $h$ , and take  $\Delta$  both positive and negative. For  $h \rightarrow 0$ , spontaneous magnetisation is shown to be possible without a negative susceptibility.

First we diagonalise the single-site Hamiltonian  $H_0(h; m) = H_0(m) - hn^1(m)$ . Since we have

$$\langle s|n^1|s\rangle = \langle p^\alpha|n^1|p^\beta\rangle = 0, \quad \text{for all } \alpha, \beta = 1, \dots, n, \quad (94)$$

and

$$\langle s|n^1|p^\alpha\rangle = \delta_{\alpha 1},$$

we only have to consider the reduced Hamiltonian

$$H_0(h; m) = \begin{pmatrix} 0 & -h \\ -h & \Delta \end{pmatrix}. \quad (95)$$

This has eigenvalues

$$\lambda_1 = \frac{1}{2}\Delta\{1 - [1 + (2h/\Delta)^2]^{1/2}\}, \quad \lambda_2 = \frac{1}{2}\Delta\{1 + [1 + (2h/\Delta)^2]^{1/2}\}, \quad (96)$$

and eigenvectors

$$|\psi_1(m)\rangle = \cos \frac{1}{2}\theta|s\rangle + \sin \frac{1}{2}\theta|p^1\rangle, \quad |\psi_2(m)\rangle = -\sin \frac{1}{2}\theta|s\rangle + \cos \frac{1}{2}\theta|p^1\rangle, \quad (97)$$

where the mixing angle  $\theta/2$  is given by

$$\tan \frac{1}{2}\theta = -\lambda_1/h \quad \text{or} \quad \tan \theta = 2h/\Delta; \quad (98)$$

hence

$$\lambda_i = \frac{1}{2}\Delta(1 \mp \sec \theta), \quad i = 1, 2. \quad (99)$$

The eigenvalues of the other  $n - 1$   $p$ -states are unaffected and remain at  $\Delta$ . For the lattice, to zeroth order in  $x$ , we have  $H = H_0(h) = \sum_m H_0(h; m)$  and

$$|\Psi_0\rangle = \prod_m |\psi_i(m)\rangle \quad \text{where} \quad \begin{array}{l} i = 1 \quad \text{for } \Delta > 0, \\ i = 2 \quad \text{for } \Delta < 0, \end{array} \quad (100)$$

and the free energy  $F$  is

$$\begin{aligned} F &= \frac{\epsilon_0}{L} = \lambda_i, & i = 1, \Delta > 0, \\ & & i = 2, \Delta < 0, \\ &= \frac{1}{2}\Delta(1 \mp \sec \theta). \end{aligned} \quad (101)$$

(We shall use the convention of top sign for  $\Delta > 0$ .)

The magnetisation  $M$  is obtained by differentiation:

$$\begin{aligned} M &= -\frac{\partial F}{\partial h} = -\frac{\partial \lambda_i}{\partial \theta} \frac{\partial \theta}{\partial h}, \\ M &= \pm \sin \theta. \end{aligned} \quad (102)$$

Legendre transformation gives the effective potential

$$\begin{aligned} \Gamma &= F + Mh \\ &= \frac{1}{2}\Delta(1 \mp \cos \theta) \\ &= \frac{1}{2}\Delta[1 \mp (1 - M^2)^{1/2}], \end{aligned} \quad (103)$$

and the equation of state follows from

$$h = \partial\Gamma/\partial M = \pm \frac{1}{2}\Delta M(1 - M^2)^{-1/2}, \quad (104)$$

and the susceptibility

$$\partial M/\partial h = \pm(2/\Delta)(1 - M^2)^{3/2}. \quad (105)$$

For  $h \rightarrow 0$  we have  $M \rightarrow 0$  and no spontaneous magnetisation, as expected from the  $d = 1$  solution of Balian and Toulouse (1974). If we consider the effect of the perturbation  $H_1 = xV$ , however, spontaneous magnetisation is possible. To first order in  $x$ , the ground-state energy is

$$\begin{aligned} E &= \epsilon_0 + x\langle\Psi_0|V|\Psi_0\rangle = \epsilon_0 - x\langle\Psi_0|\sum_m \mathbf{n}(m) \cdot \mathbf{n}(m+1)|\Psi_0\rangle \\ &= L(\lambda_t - x \sin^2 \theta) \end{aligned} \quad (106)$$

since

$$\begin{aligned} \langle\psi_1(m)|n^\alpha(m)|\psi_1(m)\rangle &= (\langle s|\cos \frac{1}{2}\theta + \langle p|\sin \frac{1}{2}\theta)n^\alpha(\cos \frac{1}{2}\theta|s) + \sin \frac{1}{2}\theta|p\rangle) \\ &= 2 \sin \frac{1}{2}\theta \cos \frac{1}{2}\theta \delta_{\alpha 1}, \end{aligned} \quad (107)$$

and similarly

$$\langle\psi_2(m)|n^\alpha(m)|\psi_2(m)\rangle = -2 \sin \frac{1}{2}\theta \cos \frac{1}{2}\theta \delta_{\alpha 1},$$

so that we obtain

$$\begin{aligned} F &= \frac{1}{2}\Delta(1 \mp \sec \theta - 2y \sin^2 \theta), \\ M &= \pm \sin \theta(1 \pm 4y \cos^3 \theta), \\ \Gamma &= \frac{1}{2}\Delta[1 \mp \cos \theta - 2y \sin^2 \theta(1 - 2 \cos^2 \theta)]. \end{aligned} \quad (108)$$

Solving for  $\theta$  in terms of  $M$ , we have

$$\cos \theta = (1 - M^2)^{1/2}[1 \pm 4y(1 - M^2)^{1/2} \mp 4y(1 - M^2)^{3/2}] + O(y^2), \quad (109)$$

which leads to

$$\Gamma = \frac{1}{2}\Delta[1 \mp (1 - M^2)^{1/2} - 2yM^2], \quad (110)$$

and the equation of state to first order

$$h = \pm \frac{1}{2}\Delta M[(1 - M^2)^{-1/2} \mp 4y]. \quad (111)$$

For  $h \rightarrow 0$  we obtain either  $M = 0$  or

$$M = [1 - (1/4y)^2]^{1/2}, \quad (112)$$

i.e. for  $\frac{1}{4} < |y| < \infty$  spontaneous magnetisation is possible. The susceptibility is again well behaved:

$$\partial M/\partial h = \pm(2/\Delta)(1 - M^2)^{3/2}[1 - 4|y|(1 - M^2)^{3/2}]^{-1}, \quad (113)$$

which is clearly positive if (111) is satisfied.

This treatment, being of mean-field type, gives  $\beta = \frac{1}{2}$  as expected, as may be seen from

$$M \propto (y^2 - y_c^2)^{1/2} \sim (y - y_c)^{1/2}, \quad (114)$$

where we have taken the mean-field estimate  $y_c = \frac{1}{4}$  from (90) and identified  $\Delta \propto \ln T$  from (65). In the case  $M = 0$ , (113) agrees with (92) to first order.

It is possible to continue this treatment to higher orders in perturbation theory. At second order, the contribution to the ground-state energy is

$$\delta E^{(2)} = x^2 \sum_{\lambda} \frac{\langle \Psi_0 | V | \lambda \rangle \langle \lambda | V | \Psi_0 \rangle}{\epsilon_0 - \epsilon_{\lambda}}. \quad (115)$$

Possible intermediate states  $|\lambda\rangle$  are

(a) 'one particle',

$$\begin{aligned} |\lambda_1\rangle &= L^{-1/2} \sum_m |\psi_2(m)\rangle \prod_{m'} |\psi_1(m')\rangle, & \Delta > 0, \\ \text{or} \quad L^{-1/2} \sum_m |\psi_1(m)\rangle \prod_{m'} |\psi_2(m')\rangle, & \Delta < 0, \end{aligned} \quad (116)$$

with  $\epsilon_0 - \epsilon_{\lambda_1} = \mp \Delta \sec \theta$ ;

(b) 'two particle', either (i)

$$\begin{aligned} |\lambda_2\rangle &= L^{-1/2} \sum_m |\psi_2(m)\rangle |\psi_2(m+1)\rangle \prod_{m'} |\psi_1(m')\rangle, & \Delta > 0, \\ \text{or} \quad L^{-1/2} \sum_m |\psi_1(m)\rangle |\psi_1(m+1)\rangle \prod_{m'} |\psi_2(m')\rangle, & \Delta < 0, \end{aligned} \quad (117)$$

with  $\epsilon_0 - \epsilon_{\lambda_2} = \mp 2\Delta \sec \theta$ ,

or (ii)

$$\begin{aligned} |\lambda_3\rangle &= L^{-1/2} \sum_m |p^{\beta}(m)\rangle |p^{\beta}(m+1)\rangle \prod_{m'} |\psi_1(m')\rangle, & \Delta > 0, \\ \text{or} \quad L^{-1/2} \sum_m |p^{\beta}(m)\rangle |p^{\beta}(m+1)\rangle \prod_{m'} |\psi_2(m')\rangle, & \Delta < 0, \end{aligned} \quad (118)$$

$$\epsilon_0 - \epsilon_{\lambda_3} = -\Delta(1 \pm \sec \theta).$$

We have

$$\begin{aligned} \langle \Psi_0 | V | \lambda_1 \rangle &= \pm 2^2 L^{1/2} \sin \frac{1}{2}\theta \cos \frac{1}{2}\theta (\cos^2 \frac{1}{2}\theta - \sin^2 \frac{1}{2}\theta) \\ &= \pm 2L^{1/2} \sin \theta \cos \theta, \end{aligned} \quad (119)$$

using (107) and

$$\langle \psi_2(m) | n^{\alpha}(m) | \psi_1(m) \rangle = \delta_{\alpha 1} (\cos^2 \frac{1}{2}\theta - \sin^2 \frac{1}{2}\theta). \quad (120)$$

Similarly

$$\langle \Psi_0 | V | \lambda_2 \rangle = L^{1/2} \cos^2 \theta, \quad (121)$$

and

$$\langle \Psi_0 | V | \lambda_3 \rangle = L^{1/2} \cos^2 \frac{1}{2}\theta, \quad \Delta > 0,$$

or

$$L^{1/2} \sin^2 \frac{1}{2}\theta, \quad \Delta < 0. \quad (122)$$

Hence, from equations (115)–(122) we have

$$\begin{aligned} \delta E^{(2)} &= -\frac{x^2 L}{2\Delta} \left( 8 \cos^3 \theta \sin^2 \theta + \cos^5 \theta + 2(n-1) \frac{\cos^4 \frac{1}{2}\theta}{1 + \sec \theta} \right) \\ &= +(x^2 L/4\Delta)(1 + \cos \theta - 16 \cos^2 \theta + 14 \cos^4 \theta) \cos \theta \quad \text{for } n = 0, \Delta > 0, \end{aligned} \tag{123}$$

or

$$\delta E^{(2)} = (x^2 L/4\Delta)(-1 + \cos \theta + 16 \cos^2 \theta - 14 \cos^4 \theta) \cos \theta \quad \text{for } n = 0, \Delta < 0. \tag{124}$$

We note that  $\delta E^{(2)}$  of (123) vanishes for  $\theta = 0$ , in agreement with the mass-gap calculation of § 4. Thus we have

$$\begin{aligned} F &= \frac{1}{2}\Delta[1 \mp \sec \theta - 2y \sin^2 \theta + \frac{1}{2}y^2(\pm 1 + \cos \theta \mp 16 \cos^2 \theta \pm 14 \cos^4 \theta) \cos \theta], \\ M &= \pm \sin \theta [1 \pm 4y \cos^3 \theta + \frac{1}{2}y^2(1 \pm 2 \cos \theta - 48 \cos^2 \theta + 70 \cos^4 \theta) \cos^2 \theta], \\ \Gamma &= \frac{1}{2}\Delta[1 \mp \cos \theta - 2y \sin^2 \theta (1 - 2 \cos^2 \theta) \\ &\quad + \frac{1}{2}y^2(\pm 2 + 3 \cos \theta \mp 65 \cos^2 \theta \mp 2 \cos^3 \theta \bullet 132 \cos^4 \theta \mp 70 \cos^6 \theta)]. \end{aligned} \tag{125}$$

After much tedious algebra,  $\cos \theta$  can be eliminated in favour of  $M$  to give

$$\begin{aligned} \Gamma &= \frac{1}{2}\Delta[1 \mp (1 - M^2)^{1/2} - 2yM^2 \\ &\quad \pm \frac{1}{2}y^2(1 - M^2)^{1/2}[2 \pm (1 - M^2)^{1/2} - (1 - M^2)(3 - 2M^2 + 14M^4)]], \end{aligned} \tag{126}$$

and the equation of state

$$\begin{aligned} h/M &= \pm \frac{1}{2}\Delta\{(1 - M^2)^{-1/2} \mp 4y - \frac{1}{2}y^2[2(1 - M^2)^{-1/2} \\ &\quad \pm 2 + (1 - M^2)^{1/2}(-13 + 66M^2 - 98M^4)]\}. \end{aligned} \tag{127}$$

Differentiation again gives a well behaved susceptibility. In the limit  $M \rightarrow 0, \Delta > 0$ , we recover

$$\chi = \partial M / \partial h|_{h \rightarrow 0} = (2/\Delta)(1 + 4y + 12\frac{1}{2}y^2),$$

which agrees to second order with equation (92).

In the next section we relate some of these expressions to polymer variables.

### 7. Polymer variables: the osmotic pressure

To make contact with polymer variables, we use the relations (29)–(31) and the first-order expression for the effective potential  $\Gamma$  from equation (110):

$$\Gamma = \frac{1}{2}\Delta[1 \mp (1 - M^2)^{1/2}] - xM^2.$$

We modify (29) to

$$c = \partial \Gamma / \partial \Delta, \tag{128}$$

using the identification of  $\Delta = -\ln K_x$  from (65). Then

$$c = \frac{1}{2}[1 \mp (1 - M^2)^{1/2}] \quad \text{or} \quad M^2 = 4c(1 - c), \quad (129)$$

and

$$c/N = \frac{1}{2}M \partial\Gamma/\partial M = \pm \frac{1}{2}M^2 [\frac{1}{2}\Delta(1 - M^2)^{-1/2} \mp 2x],$$

i.e.

$$\pm \frac{\Delta}{2(1 - M^2)^{1/2}} = \frac{1}{2N(1 - c)} + 2x, \quad (130)$$

and so for the osmotic pressure  $\pi$  we obtain

$$\begin{aligned} \frac{\pi}{k_B T} &= M \frac{\partial\Gamma}{\partial M} - \Gamma = \pm \frac{\Delta}{2(1 - M^2)^{1/2}} [1 \mp (1 - M^2)^{1/2}] - xM^2 \\ &= [1/2N(1 - c) + 2x]2c - 4xc(1 - c) \end{aligned}$$

i.e.

$$\pi/k_B T = c/N(1 - c) + 4xc^2. \quad (131)$$

This expression is of van der Waals type, and if expanded for small  $c$  gives a virial expansion. We note that for  $c > \frac{1}{2}$  we take the +ve sign in (129), which corresponds to  $\Delta < 0$ . Thus, although  $\Delta = 0$  is the critical point of the  $d = 1$  model, the corresponding value of  $c = \frac{1}{2}$  plays no special role in equation (131). Also, (131) is derived for no special value of  $h$ ; in particular, we do not require  $h \rightarrow 0$ . In the limit of large  $N$  we recover the mean-field result (Daoud *et al* 1975) that

$$\pi/k_B T \sim c^2. \quad (132)$$

If the second-order expression for  $\Gamma$  (equation (126)) is used, we remark that higher powers of  $N$  and  $c$  appear.

## 8. Discussion

We began by showing that, in the limit  $n \rightarrow 0$  of the usual Ginzburg–Landau–Wilson field theory, the longitudinal susceptibility is driven negative by the Goldstone modes. Despite this, the theory as applied to semi-dilute polymer solutions (des Cloizeaux 1975, Daoud *et al* 1975, Schäfer and Witten 1977, Moore 1977) appeared to give reasonably good agreement with experiments. All these calculations have not included the effect of the transverse modes, yet, as we showed in § 2, virtually the whole of the semi-dilute regime is affected by the negative susceptibility. The alternative calculational procedure presented here is free from Goldstone mode problems, and  $\chi_L$  remains positive, as can be shown by explicit computation to  $O(y^2)$  from equation (127). The modes are not absent from our calculations, since they stem from the  $(n - 1)$   $p$ -levels close to the ground-state level. To check this,  $\chi_T = \int_{-\infty}^{\infty} dz G_T(z)$  may be calculated, using the expression (69) for  $G_T(z)$  with  $\alpha \neq 1$  within the perturbation expansion of § 6, and order by order this matches the expansion of  $M/h$  (cf equations (111), (127)).

We do not believe that the scaling forms proposed for  $\pi(c)$  etc (Daoud *et al* 1975, des Cloizeaux 1975) will be changed by the problems caused by negative susceptibilities. This is because the argument for the scaling forms rests on assertions as to what happens on the two important length scales in the problem (namely, the polymer size and the screening length). Provided the resolution of the negative susceptibility problem does not require the introduction of a third length scale (and we do not think it does), then the scaling results should remain valid.

The series expansions for the inverse correlation length and susceptibility of §§ 4 and 5 complement the strong coupling expansions of Hamer *et al* (1979) for the O(2), O(3) and O(4) models, and when taken to higher order might yield better estimates for  $\nu$  and  $\gamma$  of the self-avoiding walk than have previously been obtained by exact enumeration of short walks. This is currently being investigated (D J Elderfield, private communication).

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