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# New lattice model for interacting, avoiding polymers with controlled length distribution

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**Abstract.** A new lattice spin model for many self-avoiding polymers is introduced in which the chain length distribution is fully controllable with a single generating ('magnetic') field. The model utilises spins with additional internal symmetry degrees of freedom to impose a causal connectivity of the polymer bonds on the lattice. Use of the method of random fields then produces an equivalent  $n \rightarrow 0$  limit field theory. The Flory-Huggins theory for a polymer solution emerges simply from this field theory in the mean field approximation. Polymer-polymer interactions between polymer segments on nearest-neighbour lattice are introduced into the field theory, and the low polymer volume fraction limit of the theory reduces to the Edwards type field theory for dilute through semidilute polymer solutions. A sketch is provided towards the treatment of branched polymers with fully controllable chain and branch length distributions and branching probabilities as well as a kinetic polymerisation system governed by specified propagation and termination probabilities.

## 1. Introduction

Despite the enormous advances in the development of renormalisation group methods for the calculation of *measurable* long wavelength polymer properties in dilute (Oono *et al* 1981, Oono and Freed 1982, Kholodenko and Freed 1983a, b, 1984a, Douglas and Freed 1983, 1984, Miyake and Freed 1984, Oono and Kohmoto 1983, Nemirovsky and Freed 1985) and in semidilute (Ohta and Oono 1982, Freed 1983, Nakanishi and Ohta 1983) solutions, there are a number of fundamental problems which remain totally unresolved. One of these involves the treatment of interacting polymers in concentrated solutions and blends. Here the chain conformation space renormalisation group methods and other direct renormalisation group approaches (des Cloizeaux 1981), which are so useful in dilute and semidilute solutions, become inapplicable because they are based upon the Edwards (1966) pseudopotential model of delta function polymer interactions. This model does not account for the non-zero volume occupied by the monomer units of the polymer, so there is no upper bound on the allowable polymer density as it exists for real polymers with short-range repulsive interactions between all monomers. Hence, the pseudopotential model is useful for polymer volume fractions much less than unity.

One possible route towards extending the chain space methods to higher concentrations is to appeal to universality considerations with the recognition that an upper density adds another parameter to the system, and *perhaps* this could be accomplished by introduction of the additional three-body repulsive interactions. These interactions are marginal in three dimensions, but they have been used in collapsed polymers

(Kholodenko and Freed 1984b) to introduce effectively constraints on the maximum polymer density. Whether such a model (or one with still more parameters or higher body interactions (Ptitsyn *et al* 1968)) is adequate for concentrated solutions, melts and blends remains to be tested by comparison with experiment. The chain conformational space calculations become rather tedious in this case, so it would be extremely useful to have other theoretical support for such a two- and three-body interaction model (or one with more parameters) before embarking on these lengthy calculations.

An alternative approach to concentrated polymer systems lies in the use of lattice models where the polymer monomers occupy one or more lattice sites, providing a natural upper bound to the polymer density. Lattice models have been used in conjunction with Monte Carlo methods to simulate polymer properties. The most widely employed model involves self-avoiding polymers which have an attractive interaction between non-bonded monomers (of the same or different polymers) on neighbouring lattice sites (Kremer *et al* 1981). Variation of the attractive interaction in the lattice model is equivalent to varying the strength of the excluded volume interaction and, hence, to changing the temperature in real polymer systems.

Analytical lattice models of polymers have been developed to treat only the self-avoiding walks on a lattice (de Gennes 1979). This is accomplished by introducing  $n$ -component spins  $\mathbf{S}_j$  at each site  $j$  in the lattices such that  $|\mathbf{S}_j|^2 = n$ , and in the  $n \rightarrow 0$  limit the characteristic function for the spins is exactly

$$\text{Tr}_S[\exp(i\mathbf{k} \cdot \mathbf{S}_j)] = 1 - \frac{1}{2}k^2, \quad (1.1)$$

where the  $\text{Tr}_S$  implies averaging over the spin variables. Equation (1.1) defines the probability distribution for the  $\mathbf{S}_j$ , so the  $n \rightarrow 0$  limit approach is actually unnecessary at this juncture.

This spin model, however, suffers from a number of serious deficiencies as follows: firstly, there is an uncontrollable chain length distribution inherent to the method unless the model is extended to have different spin variables for each polymer chain with a different 'magnetic field' to generate these individual chains. This drawback poses no real impediment to the evaluation of power law 'critical' exponents, but it is unsuitable for the calculation of molecular weight dependent properties which emerge in a non-power law fashion such as those associated, say, with a dilute solution of polymer type A in a melt of polymer B. This physical example also exposes a second deficiency with the existing  $n \rightarrow 0$  limit  $n$ -component model, namely, its inability of including polymer-polymer and polymer-solvent interactions as are present in the mean field Flory-Huggins theory (Flory 1953) and in the lattice models used in Monte Carlo calculations.

To our knowledge, the lattice spin models of polymers, based on (1.1), have not yet successfully been utilised to derive even the simple mean field Flory-Huggins theory. This difficulty with present models probably stems from the uncontrollable chain length distributions with the lattice spin models, a distribution that sharply contrasts to the monodisperse one in the Flory-Huggins theory. The search for improved lattice polymer models, which reduce to Flory-Huggins theory in the mean field limit, is of interest to remedy the deficiencies, noted by Flory (1953), of this mean field theory as follows. Firstly, there is the problem of the possible difference in size of monomers and solvent molecules such that one species may occupy several lattice sites. It should be possible to extend our spin models to ones where monomers occupy several sites, however, this interesting question is not addressed further here. Flory also notes the problem of introducing preferential interactions between like or unlike

polymers, and the difficulties he cites for dilute solutions appear to apply as well for blends in which one of the components is quite dilute.

Our goal here is to develop analytically tractable lattice models of polymers having controllable chain length distributions and interaction energies. This is accomplished by the introduction in § 2 of a new  $2n$ -component  $n \rightarrow 0$  limit spin model where the spins have an internal symmetry label reflecting chain connectivity through the polymerisation index of a given segment. This model has the virtue that an arbitrary chain length distribution can be generated with a *single* two-component 'magnetic field'. The spin integrations are performed by introduction of the method of random fields in § 2. A mean field treatment is shown in § 3 to reduce identically to the Flory-Huggins result apart from the elimination of immediate self-reversals present in the latter theory. A truncated version of the full field theory is transformed in § 3.2 into a latticised version of the Edwards (1966, 1975) field theory (Freed 1972) whose continuous limit forms the basis for the chain conformational space renormalisation group treatment of semidilute solutions (Ohta and Oono 1982, Freed 1983, Nakanishi and Ohta 1983). These methods and other direct renormalisation schemes (Schäfer and Witten 1980) can deal with polydispersity but *not* high concentrations.

Polymer-polymer interactions are introduced in § 4 using the model of nearest-neighbour attractions between non-bonded segments, and the relationship is established between this popular lattice model and the corresponding continuum one with two- and three-body interactions by truncation of the lattice model field theory. We show how to generalise our spin model to exactly describe interacting, self-avoiding branched polymer systems (Lubensky and Isaacson 1979) as well as ones describing equilibrium polymerisation (Wheeler and Pfeuty 1981) with specific probabilities for chain propagation, branching and termination. Lastly, we indicate how to set up the appropriate theory for interactions in a blend or a solution containing two chemically different polymers.

Our goal in this paper is the development of an exact field theory for interacting, self-avoiding polymers of specified polydispersity in concentrated solutions and the melt. We establish the connection between this theory and other lattice and continuum models commonly employed for these systems. It is expected that this new model will enable further systematic generalisations beyond the so-called improved mean field theories of Solc (1975) and Solc *et al* (1984).

## 2. The self-avoiding walk spin model and its field theory representation

It is possible to fix the length distribution of a *single* self-avoiding lattice walk by appending the usual  $n \rightarrow 0$  limit  $n$ -component spins with an *internal symmetry index*  $\alpha = 0, 1, \dots, N$  where  $N + 1$  is the polymerisation index for the chain. This symmetry index  $\alpha$  serves to establish the connectivity of the polymer chain. These generalised spins must satisfy the exclusion condition

$$\text{Tr}_S[\mathbf{S}_{i\alpha}\mathbf{S}_{i\beta}] \propto \delta_{\alpha\beta} \mathbf{1} \quad (2.1)$$

prohibiting the  $\alpha$ th monomer from occupying site  $i$  on some  $d$ -dimensional lattice if the  $\beta$ th monomer is at  $i$ . The condition (2.1) and extensions in (2.6) below serve to define the probability distribution for the spins  $\mathbf{S}_{i\alpha}$ . Their representation as  $n \rightarrow 0$  limit vectors is then reduced unnecessary until random fields are introduced in § 2.2.

Such a generalisation (2.1) is, however, insufficient for a system of *many* polymers as can be seen by the following two-chain example. Let the first chain begin at site  $b_1$  and have the first  $\alpha + 1$  monomers given by the sequence of spin variables (whose particular spatial indices are irrelevant here):

$$S_{i\alpha} S_{j_1, \alpha-1}^2 S_{k_1, \alpha-2}^2 \dots S_{b_1, 0}^2 \tag{2.2a}$$

Each of the spins except the  $\alpha$ th occurs squared such that a probability distribution like (1.1) yields *non-zero values* and the polymer has its zeroth monomer at site  $b_1 \dots$ , its  $(\alpha - 2)$ th at site  $k_1$ , etc. Let the second chain begin at site  $b_2$  but have its  $(\alpha + 1)$ th monomer *also at site  $i$*  with the spin variables

$$S_{i\alpha} S_{j_2, \alpha-1}^2 S_{k_2, \alpha-2}^2 \dots S_{b_2, 0}^2 \tag{2.2b}$$

None of the intermediate sites  $j_1, k_1, \dots, b_1, j_2, \dots, b_2$ , have pairs in common or are the same as site  $i$ ; otherwise the self-avoiding constraint is violated, so the spin average yields zero by (2.1). Hence, the combined string of spin variables in (2.2a) and (2.2b) generates through the averaging of (2.1) an unwanted connected chain with  $2(\alpha + 1)$  monomers. There are likewise strings of spin variables emanating from the other ends of the two polymers in the form

$$S_{e_1, N}^2 S_{f_1, N-1}^2 \dots S_{m, \alpha+1} \tag{2.3a}$$

$$S_{e_2, N}^2 S_{f_2, N-1}^2 \dots S_{m, \alpha+1}, \text{ etc.}, \tag{2.3b}$$

leading to a self-avoiding chain with  $2(N - \alpha)$  monomers. Hence, in this illustrative two-chain problem we have the unwanted contributions (2.2) and (2.3) in addition to the desired ones involving a pair of self-avoiding walks each with  $(N + 1)$ -segments.

### 2.1. The spin model

The above difficulty is removed by further generalisation to  $2n$ -component spins in order to have *connected walks in the internal symmetry index  $\alpha$* . Let  $S_{i\alpha}^+$  and  $S_{i\alpha}$  be *complex*  $2n$ -component spins with the real and imaginary parts  $R_{i\alpha}$  and  $I_{i\alpha}$ , respectively, defined by

$$R_{j\alpha} = 2^{-1/2} (S_{j\alpha} + S_{j\alpha}^+) \tag{2.4a}$$

$$I_{j\alpha} = 2^{-1/2} (S_{j\alpha} - S_{j\alpha}^+) / i \tag{2.4b}$$

and each being *independent* spin vectors satisfying

$$|R_{j\alpha}|^2 = |I_{j\alpha}|^2 = n. \tag{2.5}$$

In the  $n \rightarrow 0$  limit the joint characteristic function for such a  $2n$ -component spin system is a straightforward generalisation of the  $n$ -component case without symmetry index (de Gennes 1979). The expression

$$\text{Tr}_S[\exp(i\mathbf{k} \cdot S_{j\alpha}^+ + i\mathbf{k}^* \cdot S_{m\beta})] = 1 - \mathbf{k} \cdot \mathbf{k}^* \delta_{\alpha, \beta} \delta_{j, m} \tag{2.6}$$

*defines* the only non-zero spin averages. The  $n \rightarrow 0$  limit representation is unnecessary given the definition (2.6), but in transforming to random fields in § 2.2, this  $n \rightarrow 0$  limit approach becomes useful. Equation (2.6) also introduces the condition that spins on different spatial sites are independent random variables as in the original  $n$ -component spin model.

Given the above spin variables, the string of spin variables replacing (2.2) for the two-chain problem becomes, as proven below,

$$\mathbf{S}_{i\alpha}^+ (\mathbf{S}_{j_1, \alpha-1} \mathbf{S}_{j_1, \alpha-1}^+) (\mathbf{S}_{k_1, \alpha-2} \mathbf{S}_{k_1, \alpha-2}^+) \dots (\mathbf{S}_{b_1, 0} \mathbf{S}_{b_1, 0}^+) \quad (2.7a)$$

$$\mathbf{S}_{i\alpha}^+ (\mathbf{S}_{j_2, \alpha-1} \mathbf{S}_{j_2, \alpha-1}^+) (\mathbf{S}_{k_2, \alpha-2} \mathbf{S}_{k_2, \alpha-2}^+) \dots (\mathbf{S}_{b_2, 0} \mathbf{S}_{b_2, 0}^+). \quad (2.7b)$$

Since we have

$$\text{Tr}_S[(\mathbf{S}_{i\alpha}^+)^2] = \text{Tr}_S[(\mathbf{S}_{i\alpha})^2] = 0, \quad (2.8)$$

the strings involving the product of (2.7a) with (2.7b) are not permitted. Only those strings survive the spin averaging of (2.6) in which there are self-avoiding chains of exactly  $N$  bonds, so the two chains retain their integrity *without the need for different spin variables for each chain individually*. The same situation is readily shown to follow for the many-chain case from (2.9) below.

Using these  $2n$ -component  $n \rightarrow 0$  limit chains, the grand partition function for polymers with a probability distribution  $P_N$  for the polymerisation index  $N$  for the chains is given by

$$Z = \text{Tr}_S \left[ \exp \left( K \sum_{\langle ij \rangle} \sum_{\alpha=0}^{\infty} \mathbf{S}_{i, \alpha+1}^+ \cdot \mathbf{S}_{j, \alpha} + \sum_i (\mathbf{H} \cdot \mathbf{S}_{i0}^+ + \mathbf{H}^+ \cdot \mathbf{S}_{i, N} P_N) \right) \right], \quad (2.9)$$

where the symbol  $\langle ij \rangle$  means  $i$  and  $j$  are nearest-neighbour sites. The properties of the probability distribution defined by (2.6) imply that (2.9) may be re-expressed in the expanded form of

$$Z = \text{Tr}_S \left( \prod_{\langle ij \rangle} \prod_{\alpha=1}^{\infty} (1 + K \mathbf{S}_{i, \alpha+1}^+ \cdot \mathbf{S}_{j, \alpha}) \prod_m (1 + \mathbf{H} \cdot \mathbf{S}_{m, 0}^+ + \mathbf{H}^+ \cdot \mathbf{S}_{m, N} P_N) \right). \quad (2.9a)$$

Note that in order to introduce the chain length distribution, equation (2.9a) has the product on  $\alpha$  run to infinity. Hence, (2.9a) generates strings with all possible numbers of polymers of varying lengths. The term in  $\mathbf{S}_{i, \alpha+1}^+ \cdot \mathbf{S}_{j, \alpha}$  introduces a connected bond between nearest-neighbour sites  $i$  and  $j$  with weight  $K$  while that in  $\mathbf{H}$  begins the chain with a monomer at site  $m$ , and  $\mathbf{H}^+$  ends the  $N$ th one at some other site  $m$ . Since the factor of  $\mathbf{H}^+$  in (2.6a) finishes the chain, a contribution to (2.9a) with  $n_1$  polymers of length  $N_1$ ,  $n_2$  with  $N_2$ , etc, is multiplied by the factor  $(P_{N_1})^{n_1} (P_{N_2})^{n_2}$  to provide the proper chain length probability distribution. The analogue of the parameter  $K$  in the previous spin model is used to specify the average number of monomer units whose ratio with the average number of chains yields the average chain length. Our model completely controls the chain length distribution, making the parameter  $K$  unnecessary, so it may be set equal to unity. There are further generalisations, such as to the equilibrium polymerisation problem, where it is useful to retain  $K$  as it provides the model with desired flexibility. Thus,  $K$  is maintained in the subsequent discussion with the recognition that for (2.9)  $K$  is just unity.

The condition (2.6) precludes differently labelled monomers (in  $\alpha$ ) from occupying the same lattice sites. Note that the use of these spin variables removes the annoyance of single-site walks which are present in the standard spin model (Gujrati 1981). The partition function (2.9) naturally leads upon expansion to the quoted strings of spin variables as in either (2.7a) or (2.7b). The  $n_p$  polymer partition function is simply

obtained from (2.9) as

$$Z_{n_p} = \frac{1}{(n_p)!} \frac{\partial^{n_p}}{\partial(\mathbf{H} \cdot \mathbf{H}^\dagger)^{n_p}} Z \Big|_{\mathbf{H} = \mathbf{H}^\dagger = 0}. \tag{2.10}$$

The sum over  $i$  in (2.9) or the product over  $m$  in (2.9a) implies that (2.10) contains a sum over all possible sites for the chain beginnings and ends, corresponding to their equal *a priori* probability of being anywhere in the  $d$ -space lattice.

Equation (2.9) also describes the partition function for a kinetic equilibrium polymerisation problem where  $K$  is the probability for addition of a segment to an already existing chain, and  $P_N$  is the chain termination probability. The chain fugacity is  $\mathbf{H} \cdot \mathbf{H}^\dagger$ . This kinetic polymerisation model is subject only to the self-avoiding chain constraints; no inclusion of diffusion of monomers or their initial spatial distribution is incorporated. Nevertheless, it should prove useful for further study because it generalises previous approaches (Wheeler and Pfeuty 1981) to introduce a controllable chain length distribution. Note also that the propagation term  $K$  can be made  $\alpha$  dependent and  $K_\alpha$  be taken underneath the sum over  $\alpha$ .

### 2.2. Introduction of random fields

For simplicity, we proceed with the monodisperse distribution  $P_{N_0} = \delta_{N, N_0}$ , since the polydisperse case is readily reintroduced in the final equations below. For each site  $i$  and symmetry index  $\alpha = 0, 1, \dots, N - 1$  we introduce a pair of  $2n$ -component complex random fields  $\phi_{i\alpha}^\dagger$  and  $\phi_{i\alpha}$  along with the identity

$$\begin{aligned} &\exp\left(K \sum_{\langle ij \rangle} S_{i,\alpha+1} \cdot S_{j\alpha}\right) \\ &= \left(\prod_i \int d\phi_{i\alpha}^\dagger d\phi_{i\alpha}\right) \exp\left(\sum_i (S_{i,\alpha+1}^\dagger \cdot \phi_{i\alpha} + S_{i\alpha} \cdot \phi_{i\alpha}^\dagger) \right. \\ &\quad \left. - \sum_{ij} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha}\right) \left[\left(\prod_i \int d\phi_{i\alpha}^\dagger d\phi_{i\alpha}\right) \exp\left(-\sum_{ij} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha}\right)\right]^{-1} \end{aligned} \tag{2.11}$$

where the matrix  $V_{ij}$  is found to be given by (Smith 1983)

$$V_{ij} = \sum_{\mathbf{k}} \exp[i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] [N_\ell K f(\mathbf{k})]^{-1} \tag{2.12}$$

where the sum is over all wave vectors  $\mathbf{k}$  in the first Brillouin zone,  $\mathbf{r}_i$  designates the position vector to lattice site  $i$ ,  $N_\ell$  is the number of sites in the lattice,  $f(\mathbf{k})$  is the nearest-neighbour lattice structure factor

$$f(\mathbf{k}) = \sum_{\mathbf{a}_1} \exp(i\mathbf{k} \cdot \mathbf{a}_1), \tag{2.13}$$

and the  $\{\mathbf{a}_1\}$  are the set of  $z$  lattice vectors to nearest-neighbour sites. It is only in (2.11) that we utilise the  $n \rightarrow 0$  limit realisation of the probability distribution (2.6). Other realisations of this spin averaging imply corresponding different properties of the  $\phi_{i\alpha}^\dagger$  and  $\phi_{i\alpha}$ .

Now introduce (2.11) into (2.9) for each  $\alpha$ , leading to the representation in exponential form of

$$Z = \text{Tr}_S \left[ \int \delta\phi \delta\phi^\dagger \exp \left( \sum_{\alpha=0}^{N-1} \sum_i [\mathbf{S}_{i,\alpha+1}^\dagger \cdot \phi_{i\alpha} + \mathbf{S}_{i\alpha} \cdot \phi_{i\alpha}] \right. \right. \\ \left. \left. + \sum_i (\mathbf{H} \cdot \mathbf{S}_{i0}^\dagger + \mathbf{H}^\dagger \cdot \mathbf{S}_{i,N}) - \sum_{ij} \sum_{\alpha=0}^{N-1} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} \right) \right] \\ \times \left[ \int \delta\phi \delta\phi^\dagger \exp \left( - \sum_{ij} \sum_{\alpha=0}^{N-1} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} \right) \right]^{-1}, \quad (2.14)$$

where  $\delta\phi^\dagger \delta\phi$  is defined by

$$\delta\phi^\dagger \delta\phi = \prod_i \prod_{\alpha=0}^{N-1} d\phi_{i\alpha}^\dagger d\phi_{i\alpha}. \quad (2.15)$$

Note that the sum over  $\alpha$  in (2.14) only runs up to  $N - 1$ .

The spin dependent portion of (2.14) is readily evaluated using (2.6) to give

$$\text{Tr}_S \exp \left( \sum_i \sum_{\alpha=0}^{N-1} (\mathbf{S}_{i,\alpha+1}^\dagger \cdot \phi_{i\alpha} + \mathbf{S}_{i\alpha} \cdot \phi_{i\alpha}^\dagger) + \sum_i (\mathbf{H}^\dagger \cdot \mathbf{S}_{i,N} + \mathbf{H} \cdot \mathbf{S}_{i0}^\dagger) \right) \equiv \prod_i (1 + X_i) \quad (2.16)$$

where the spin-integration rules (2.6) yield

$$X_i = X_i(\phi_{i\alpha}, \phi_{i\alpha}^\dagger, \mathbf{H}, \mathbf{H}^\dagger) = \mathbf{H} \cdot \phi_{i0}^\dagger + \sum_{\alpha=1}^{N-1} \phi_{i\alpha}^\dagger \cdot \phi_{i\alpha-1} + \mathbf{H}^\dagger \cdot \phi_{i,N-1}. \quad (2.17)$$

The expansion of the product in (2.16) gives terms containing  $M$ -factors of the  $X$ 's, associated with the sites occupied by the polymers, along with  $N_\ell - M$  factors of unity from the sites with solvent molecule occupancy. Expanding out the  $X_i$  using (2.17) implies that when the initial segment  $\alpha = 0$  is at  $i$ , then  $X_i$  contributes a factor of  $\mathbf{H} \cdot \phi_{i0}^\dagger$ , while it gives  $\phi_{i\alpha}^\dagger \cdot \phi_{i\alpha-1}$  for intermediate  $\alpha = 1, \dots, N - 1$ , with  $\mathbf{H}^\dagger \cdot \phi_{i,N-1}$  for the last  $\alpha = N$  segment.

Introduction of (2.16) into (2.14) provides the full field theory for self-avoiding chains with polymerisation index  $N + 1$  as

$$Z = \int \delta\phi \delta\phi^\dagger \prod_i (1 + X_i) \exp \left( - \sum_{\alpha=0}^{N-1} \sum_{ij} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} \right) \\ \times \left[ \int \delta\phi^\dagger \delta\phi \exp \left( \sum_{\alpha=0}^{N-1} \sum_{ij} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} \right) \right]^{-1}. \quad (2.18)$$

The appropriate generalisation to a distribution  $P_N$  of chain lengths involves letting the upper summation index of  $\alpha$  be unbounded and replacing  $X_i$  in (2.18) by

$$X_i \rightarrow \mathbf{H} \cdot \phi_{i0}^\dagger + \sum_{\alpha=1}^{\infty} \phi_{i\alpha}^\dagger \cdot \phi_{i,\alpha-1} + \sum_{N=1}^{\infty} P_N \mathbf{H}^\dagger \cdot \phi_{i,N-1}. \quad (2.19)$$

The field theory (2.18) provides the obvious definition of the 'order parameter' (Edwards and Freed 1970a, de Gennes 1979).

The introduction of polymer-solvent or polymer-polymer interactions within the lattice spin formalism of § 2.1 appears to be impossible because a pair of spins  $\mathbf{S}_{i\alpha}^\dagger$  and  $\mathbf{S}_{i\alpha}$  must appear in order that a site  $i$  be occupied by a monomer. Interactions of this monomer at  $i$  with other monomers or with solvent molecules would appear to

require introduction of additional factors of  $S_{i\alpha}^+$  and  $S_{i\alpha}$  for each such interaction. (There are a total of  $z - 2$  possible if only nearest-neighbour interactions are considered.) However, the spin averaging procedure, which makes the chains self-avoiding, precludes the possibility of non-vanishing terms with these additional factors of spins for lattice sites occupied by polymers. It is, however, possible to introduce these interactions with the field theory representation (2.18) because of the physical interpretation of the factor  $\prod_i(1 + X_i)$  in (2.16). Before introducing these interactions in § 4, we turn to a mean field evaluation of (2.16) to verify that it produces the well known Flory-Huggins result (Flory 1953) and, hence, that this field theory provides the basis for systematically investigating corrections to Flory-Huggins theory for concentrated polymer solutions, melts, blends, etc. In addition, we transform an approximate version of (2.16) into a lattice version of the Edwards field theory (Edwards 1966, 1975) for semidilute polymer solutions.

### 3. Reduction to Flory-Huggins mean field and Edwards field theory

#### 3.1. Mean field solution

The simple Flory-Huggins theory applies to a monodisperse solution of polymers in solution, so we extract out of (2.18) this contribution according to (2.10). The lattice spin model does not include polymer-solvent interactions, but a mean field description of these added interactions is identical to that of the Flory-Huggins theory, so we concentrate there on the derivation of the entropic part of the Flory-Huggins theory from a mean field treatment of (2.18) with (2.10). The conversion to a lattice form of the Edwards field theory in § 2.2 below and the introduction of interactions in § 4 demonstrate that interaction energies are properly incorporated, while the generalisation of the entropic portion to polydisperse distributions and polymer mixtures follows analogously.

In mean field approximation the  $\phi_{i\alpha}$  must become identical, independent of site  $i$  and internal index  $\alpha$ . When represented in terms of Fourier transforms on the lattice through the transformations

$$\begin{aligned}\phi_{j\alpha} &= \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}_j) \phi_{\mathbf{k}\alpha} \\ \phi_{j\alpha}^+ &= \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \phi_{\mathbf{k}\alpha}^+\end{aligned}$$

the mean field  $\phi_{0\alpha}$  is just the  $\mathbf{k} = 0$  Fourier component. (It is also the  $\kappa = 0$  component with respect to transforms with respect to  $\alpha$ .) Each chain begins with a factor  $\mathbf{H} \cdot \phi_{i_0}^+$  and ends with a  $\mathbf{H}^+ \cdot \phi_{i_N}$ , so if  $\mathbf{H}$  and  $\mathbf{H}^+$  are taken along the 1-direction in  $n$ -space, the mean field  $\phi$  and  $\phi^+$  likewise lies along this direction. Hence, vector symbols on  $\phi$  are dropped as is the  $\mathbf{k} = 0$  spatial Fourier component index. The Flory-Huggins theory considers  $n_p$  polymer chains with polymerisation index  $N + 1$ , so we likewise treat this case.

It is useful to begin by taking a set of different mean fields  $\phi_\alpha^+$  and  $\phi_\alpha$  for each  $\alpha$  before setting them equal to common values  $\phi^+$  and  $\phi$ , respectively. Then the mean field approximation to (2.16) is written as

$$\prod_i (1 + X_i) \xrightarrow[\text{field}]{\text{mean}} (1 + X)^{N_c} \quad (3.1)$$

where  $N_\ell$  is the total number of lattice sites. Below in (3.3) a subscript  $s$  is placed on unity on the left side of (3.1) to aid in counting. Our mean field representation of  $X$  of (2.17) becomes

$$X = H\phi_0^\dagger + \sum_{\alpha=1}^{N-1} \phi_\alpha^\dagger \phi_{\alpha-1} + H^\dagger \phi_{N-1}. \quad (3.2)$$

Insertion of (3.2) into (3.1) and use of the multinomial theorem results in the expression

$$(3.1) = \sum'_{\{m_\alpha\}} \frac{N_\ell!}{[(N_\ell - \sum_{\alpha=0}^N m_\alpha)!] \prod_{\alpha=0}^N m_\alpha!} 1_s^{N_\ell - \sum_{\alpha} m_\alpha} (H\phi_0^\dagger)^{m_0} \\ \times \prod_{\alpha=1}^{N-1} (\phi_\alpha^\dagger \phi_{\alpha-1})^{m_\alpha} (H^\dagger \phi_{N-1})^{m_N} \quad (3.3)$$

where the summation requires  $\sum_{\alpha} m_\alpha \leq N_\ell$ . However, chain connectivity implies that if we begin  $m_0$  polymer chains with  $m_0$  factors of  $\phi_0^\dagger$  from the  $\alpha = 0$  beginning monomers, there must likewise be  $m_0$  monomers with  $\alpha = 1, \dots, N$ . Hence, chain connectivity requires that

$$m_0 = m_1 = m_2 = \dots = m_N, \quad (3.4)$$

reducing (3.1) to the single sum

$$(3.1) \rightarrow \sum'_{m_0} \frac{N_\ell!}{[(N_\ell - (N+1)m_0)!] (m_0!)^{N+1}} (HH^\dagger)^{m_0} \prod_{\alpha=0}^{N-1} (\phi_\alpha^\dagger \phi_\alpha)^{m_0}. \quad (3.5)$$

It is convenient to replace  $N+1$  by  $N$  to compare with Flory-Huggins theory. Use of the definition (2.10) along with (3.5) and setting  $\phi_\alpha^\dagger \phi_\alpha$  to be independent of  $\alpha$  gives the mean field approximation as

$$Z_{n_p}^{MF} = \frac{N_\ell! \iint d\phi^\dagger d\phi (\phi^\dagger \phi)^{n_p(N-1)} \exp[-N_\ell(N-1)\phi^\dagger \phi / Kz]}{[(N_\ell - Nn_p)!] (n_p!)^N \iint d\phi^\dagger d\phi \exp[-N_\ell(N-1)\phi^\dagger \phi / Kz]} \quad (3.6)$$

Since  $\phi$  and  $\phi^\dagger$  are  $k=0$  fields, there is but a single integration over  $\phi$  and  $\phi^\dagger$ . The exponential factor arises from the mean field approximation to the exponential in (2.18) as follows. The use of (2.12) and retention of only the  $k=0$  portion yields the factor of  $z$ , and the sums over sites and  $\alpha$  yield the overall  $N_\ell(N-1)$  factor.

Changing variables to the real and imaginary parts

$$\phi_r = 2^{-1/2}(\phi + \phi^\dagger), \quad \phi_i = 2^{-1/2}(\phi - i\phi^\dagger)/i \quad (3.7a, b)$$

implies  $\iint d\phi^\dagger d\phi \rightarrow \int_{-\infty}^{\infty} d\phi_r \int_{-\infty}^{\infty} d\phi_i$ , and the integrals in (3.6) are readily evaluated to give

$$Z_{n_p}^{MF} = \frac{(N_\ell)!}{[(N_\ell - Nn_p)!] (n_p!)^N} \left( \frac{zK}{N_\ell N} \right)^{n_p(N-1)} [(n_p(N-1))!]. \quad (3.8)$$

The mean field entropy  $S_{n_p}^{MF}$  is defined by

$$S_{n_p}^{MF} = k_B \ln Z_{n_p}^{MF} \quad (3.9)$$

with  $k_B$  Boltzmann's constant. Hence, use of Stirling's approximation for the factors  $(n_p!)^N$  and  $[(n_p(N-1))!]$  only and setting  $K=1$  as discussed in § 2, converts (3.8) and (3.9) into

$$k_B^{-1} S_{n_p}^{MF} = \ln[(N_\ell)!] - \ln[(n_p)!] - \ln[(N_\ell - Nn_p)!] + n_p(N-1) \ln(z/N_\ell). \quad (3.10)$$

To calculate the entropy of mixing from (3.10) it is necessary to subtract the entropy of the polymer melt obtained from (3.10) by setting  $N_\ell \rightarrow N n_p$  to give

$$S_{n_p, \text{melt}}^{\text{MF}} / k_B = \ln[(n_p N)!] - \ln[(n_p)!] + n_p N \ln(z / n_p N). \tag{3.10a}$$

The difference between (3.10) and (3.10a) provides the entropy of mixing  $\Delta S_{n_p}^{\text{MF}}$ . Upon use of Stirling's approximation and the definition of the polymer volume fraction  $\psi = n_p N / N_\ell$ , this entropy of mixing is converted to the form

$$\Delta S_{n_p}^{\text{MF}} / k_B N_\ell = -(\psi / N) \ln \psi - (1 - \psi) \ln(1 - \psi) \tag{3.10b}$$

which is just the standard Flory-Huggins entropy expression. Note the important role played in the passage from (3.5) to (3.6) of the sequential monomer index  $\alpha$  and the monodispersity which are inaccessible to the standard spin model. The Flory-Huggins total entropy corresponds to (3.10) with Stirling's approximation and with the replacement of  $z$  by  $z - 1$  to eliminate immediate self reversals which the field theoretic mean field approximation retains. Hence, the deviations of the  $\phi_{i\alpha}$  and  $\phi_{i\alpha}^\dagger$  from common values for all  $i$  and  $\alpha$  provide the entropic corrections to Flory-Huggins theory due to correlations within and between chains. (Note that the customary use of saddle point approximations to (3.6) for defining the mean field would just generate the leading Stirling's approximation. In addition, it is possible to pursue the calculation with a different mean field  $\phi_\alpha$  for each  $\alpha$ . This procedure is more lengthy but automatically enforces the constraint (3.4) upon integration over  $\phi_\alpha$  and  $\phi_\alpha^\dagger$ . The  $2N$ -dimensional  $d\phi_\alpha d\phi_\alpha^\dagger$  integrals yield (3.10b) also. The above single  $(\phi, \phi^\dagger)$  mean field approach is presented because of its greater simplicity.)

### 3.2. Conversion to Edwards field theory

In the dilute and semidilute regions the polymer volume fraction  $\psi_p = n_p N / N_\ell$  is very small, and passage to a continuum limit in the field theory (2.18) is permissible. Hence, this limit should yield the same theory as in the continuum model apart from irrelevant contributions. We now verify that the leading  $\phi^4$  contribution to (2.18) is equivalent to a lattice version of the Edwards continuum field theory for the polymer excluded volume in dilute through semidilute solutions. The only difference appears because (2.18) is only applicable in the self-avoiding walk (good solvent) limit, so the quartic coupling constant is a pure number and not a variable as in the continuum theory. However, when the nearest-neighbour attractive interactions are appended in § 4, the  $\phi^4$  coupling constant then becomes a variable parameter.

We begin by applying (2.10) to the field theory (2.18) to extract  $Z_{n_p}$ . The  $\partial/\partial(\mathbf{H} \cdot \mathbf{H}^\dagger)$  operation acts only on the  $\prod_i (1 + X_i)$  portion of (2.18), so we work first on this factor to get

$$\partial^{n_p} \left( \prod_i (1 + X_i) \right) / \partial(\mathbf{H} \mathbf{H}^\dagger)^{n_p} = \sum_{i_b, i_e} \prod_{i_b, i_e} \phi_{i_b, 0}^{(1)\dagger} \phi_{i_e, N-1}^{(1)} \prod_{j \notin \{i_b, i_e\}} (1 + X'_j), \tag{3.11}$$

where the beginning lattice sites  $i_b$  and the chain ending ones  $i_e$  are all distinct from each other, and sums run over all possible  $i_b$  and  $i_e$  on the whole lattice. The quantity  $X'_i$  is just the remaining portion of  $X_i$  of (2.17) from the interior monomers,

$$X'_i = \sum_{\alpha=1}^{N-1} \phi_{i\alpha}^\dagger \cdot \phi_{i, \alpha-1}. \tag{3.12}$$

As noted above, both  $\mathbf{H}$  and  $\mathbf{H}^\dagger$  are taken to lie along the 1-direction in  $n$ -space, so the  $\phi_{i_b,0}^{(1)\dagger}$  and  $\phi_{i_e,N}^{(1)}$  are likewise the components in this direction.

Exponentiating the product in  $X'_i$  and expanding through quadratic in the  $X'_i$  yields

$$\prod_{i \in (i_b, i_e)} (1 + X'_i) = \exp\left(\sum_{i \in (i_b, i_e)} [X'_i - \frac{1}{2}(X'_i)^2 + O(X_i'^3)]\right). \tag{3.13}$$

In the continuum limit the restriction  $i \notin (i_b, i_e)$  can be ignored, so we drop it below. Alternatively, we can exponentiate and expand the full  $X_i$  without first extracting the chain end terms. That would yield contributions from  $\mathbf{H}$  and  $\mathbf{H}^\dagger$  in  $-\frac{1}{2}X_i^2$  of the form  $\mathbf{H} \cdot \phi_{i,0}^\dagger \sum_{\alpha=1}^{N-1} \phi_{i\alpha}^\dagger \cdot \phi_{i\alpha-1}$  and  $(\mathbf{H} \cdot \phi_{i\alpha}^\dagger)^2$ , etc (Smith 1983). The Edwards field theory would then follow by neglect of the higher than linear terms  $\mathbf{H} \cdot \phi_{i,0}^\dagger$  and  $\mathbf{H}^\dagger \cdot \phi_{i,N-1}$ .

Now introduce the one-component field  $\psi_i$  and use the identity

$$\exp[-(X'_j)^2/2] = \int_{-\infty}^{\infty} d\psi_j \exp(iX'_j\psi_j - \psi_j^2/2) \left(\int_{-\infty}^{\infty} d\psi_j \exp(-\psi_j^2/2)\right)^{-1}, \tag{3.14}$$

to give the approximation

$$\begin{aligned} Z_{n_p} = & \int \delta\psi \int \delta\phi \delta\phi^\dagger \sum_{i_b, i_e} \prod_{i_b, i_e} \phi_{i_b,0}^{(1)\dagger} \phi_{i_e,N-1}^{(1)} \exp\left(\sum_j \sum_{\alpha=1}^{N-1} \phi_{j\alpha}^\dagger \cdot \phi_{j\alpha-1} - \sum_{ij} \sum_{\alpha=0}^{N-1} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} \right. \\ & \left. + i \sum_j \sum_{\alpha=1}^{N-1} \psi_j \phi_{j\alpha}^\dagger \cdot \phi_{j,\alpha-1} - \frac{1}{2} \sum_j \psi_j^2\right) \\ & \times \left[ \int \delta\phi \delta\phi^\dagger \delta\psi \exp\left(-\sum_j \sum_{\alpha=0}^{N-1} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha} - \frac{1}{2} \sum_j \psi_j^2\right) \right]^{-1} \end{aligned} \tag{3.15}$$

where the summation constraints in (2.12) and (3.13) are ignored.

The  $\phi$ -field integration is a Gaussian one, producing  $n_p$  factors of the lattice Green's function

$$\begin{aligned} G(i_b, i_e, N; \psi) = & \int \delta\phi \delta\phi^\dagger \phi_{i_b}^{(1)\dagger} \phi_{i_e}^{(1)} \exp\left(\sum_j \sum_{\alpha=1}^{N-1} (\phi_{j\alpha}^\dagger \cdot \phi_{j\alpha-1})(1 + i\psi_j) \right. \\ & \left. - \sum_j \sum_{\alpha=0}^{N-1} V_{ij} \phi_{i\alpha}^\dagger \cdot \phi_{j\alpha}\right). \end{aligned} \tag{3.16}$$

The normalisation factor in  $\phi^\dagger \cdot \phi$  from (3.15) vanishes in the  $n \rightarrow 0$  limit, so it has been omitted in (3.16).

In the long wavelength limit for centrosymmetric lattices  $f(\mathbf{k})$  of (2.13) behaves as  $z - \frac{1}{2} \sum_{a_1} (\mathbf{k} \cdot \mathbf{a}_1)^2 + O(k^4)$ , so to order  $k^2$  (2.12) contains

$$[f(\mathbf{k})]^{-1} = z^{-1} \left(1 + (2z)^{-1} \sum_I (\mathbf{k} \cdot \mathbf{a}_I)^2\right) \tag{3.17}$$

which in isotropic lattices may be written in the form  $z^{-1} + (\frac{1}{2})^2 \ell_{\text{eff}}^2 k^2$  with  $\ell_{\text{eff}}$  an effective step length. The term in  $\phi_{j\alpha}^\dagger \cdot \phi_{j,\alpha-1}$  can be rewritten as

$$\phi_{j\alpha}^\dagger \cdot \phi_{j,\alpha-1} = \phi_{j\alpha}^\dagger \cdot \phi_{j\alpha} - (\phi_{j\alpha}^\dagger \cdot \phi_{j\alpha} - \phi_{j\alpha}^\dagger \cdot \phi_{j,\alpha-1}) \tag{3.18}$$

which in the continuum limit becomes

$$\phi_{j\alpha}^\dagger \cdot \phi_{j,\alpha-1} \rightarrow \phi_{j\alpha}^\dagger \cdot \phi_{j\alpha} - \phi_{j\alpha}^\dagger \cdot (\partial/\partial\alpha) \phi_{j\alpha}. \tag{3.19}$$

The  $(X'_j)^2$  term with (3.19) would contain  $\phi_{j\alpha}^\dagger \cdot \phi_{j\alpha} \phi_{j\alpha}^\dagger \cdot (\partial/\partial\alpha) \phi_{j\alpha}$ , etc, but these are

dropped here as becoming irrelevant in the dilute and semidilute solution limits. Further use of (3.17) and (3.19) and passage to the continuum limit converts (3.16) to

$$G(i_b, i_e, N; \psi) = \int \delta\phi \delta\phi^\dagger \phi^{(1)\dagger}(i_b, N) \phi^{(1)}(i_e, 0) \times \exp\left(-\int d\mathbf{r} \int_0^N d\alpha \phi(\mathbf{r}, \alpha) [\partial/\partial\alpha - \frac{1}{2}\ell_{\text{eff}}^2 \nabla_r^2 + i\psi(\mathbf{r})] \phi(\mathbf{r}, \alpha)\right), \quad (3.20)$$

corresponding to the chain space form given previously by Edwards and Freed (1970a, b, c, Freed 1972) and used in the Edwards field theory (Edwards 1966, 1975, Ohta and Oono 1982, Freed 1983).

The summation over  $i_b$  and  $i_e$ , reflecting all possible positions for the chain ends, just becomes an integration of (3.20) over the chain ends which we designate as  $Q(N, \psi)$ . Reintroducing the chain length distribution enables (3.15) to be written generally as

$$Z_{n_p} = \int \delta\psi \prod_{\lambda=1}^{n_p} Q(N_\lambda, \psi) \exp\left(-\frac{1}{2} \int d\mathbf{r} \psi^2(\mathbf{r})\right) / \int \delta\psi \exp\left(-\frac{1}{2} \int d\mathbf{r} \psi^2(\mathbf{r})\right) \quad (3.21)$$

$$= \int \delta\psi \exp\left(n_p \langle \ln Q(N, \psi) \rangle_N - \frac{1}{2} \int d\mathbf{r} \psi^2(\mathbf{r})\right) / \int \delta\psi \exp\left(-\frac{1}{2} \int d\mathbf{r} \psi^2(\mathbf{r})\right), \quad (3.21a)$$

where the  $\langle \rangle_N$  designates an average with the chain length distribution  $P_N$ . The lattice form (3.15) is like (3.21) with sums over lattice sites, with the full lattice  $G$  of (3.16) and constraints that chain end points not coincide with each other or with lattice sites occupied by interior chain monomers. At low polymer volume fractions  $\psi_p$  this latter constraint may be neglected, but it must be retained at higher  $\psi_p$ , perhaps along with the higher body interactions. The Flory-Huggins results are obtained using the full field theory, *not* the truncated one with only two- and three-body interactions. (In passing from  $\sum_i \rightarrow \int d\mathbf{r}$  factors of lattice vector magnitudes have been omitted for notational simplicity.)

This section demonstrates that previous theories are obtained as particular limits of the lattice spin model of § 3. First of all, a mean field approximation reproduces the entropic portion of standard Flory-Huggins lattice theory for a polymer solution. At low polymer volume fractions the continuum limit yields the Edwards field theory for a set of  $n_p$  self-avoiding polymers with the chain length distribution  $P_N$ , a field theory that has been shown to work well through the semidilute region. It still remains to incorporate interaction energies into the model, and this is the generalisation to which we now turn.

#### 4. Interactions

If the nearest-neighbour polymer-solvent interaction is taken to be the zero of energy, then it suffices to include the nearest-neighbour polymer-polymer interactions. Interactions between polymers on next-nearest lattice sites can be included similarly, but these are not considered for algebraic simplicity. We employ the same model as in lattice Monte Carlo calculations, namely one involving an attractive energy  $-\epsilon$  between non-bonded monomers on neighbouring lattice sites. These interacting monomers may

belong to the same or different polymers. It is convenient to let  $-\varepsilon$  apply for all neighbouring sites, so an extra energy of  $-n_p N\varepsilon$  between sequentially bonded neighbouring sites must be removed, and this is understood to be done below at the end of the calculation.

4.1. Polymer-polymer interactions

Section 2 already notes the difficulty in describing polymer-polymer interactions by the addition of extra spin-dependent terms in the exponent of (2.9), so we consider their incorporation directly into the field theory (2.18). A contribution to  $Z_{n_p}$  from (2.18) has a product of  $\sum_{i=1}^{n_p} N_A$  factors of the  $X_i$ , one factor for each lattice sites occupied by a monomer. The nearest-neighbour interaction energy can simply be introduced by determining the number  $M$  of distinct pairs of nearest-neighbour sites occupied by polymers. Such a term is multiplied by  $\exp(M\varepsilon/k_B T)$ .

It is convenient to define an averaging process  $\langle \rangle_1$  acting on the lattice site indices of  $X_i$  to introduce this interaction energy. We have the obvious leading terms

$$\langle 1 \rangle_1 = 1, \quad \langle X_i \rangle_1 = X_i \tag{4.1a, b}$$

$$\langle X_i X_j \rangle = \begin{cases} X_i X_j, & i \text{ and } j \text{ not neighbours} \\ X_i X_j \exp(\varepsilon/k_B T), & i \text{ and } j \text{ neighbours.} \end{cases} \tag{4.1c}$$

Let  $\langle ij \rangle$  imply  $i$  and  $j$  are nearest-neighbour lattice sites, so the next member of (4.1) is

$$\langle X_i X_j X_k \rangle = \begin{cases} X_i X_j X_k, & \text{non-neighbours} \\ X_i X_j X_k \exp(\varepsilon/k_B T) & \text{for } \langle ij \rangle \text{ or } \langle ik \rangle \text{ or } \langle jk \rangle \\ X_i X_j X_k \exp(2\varepsilon/k_B T) & \text{for } \langle ij \rangle \langle jk \rangle \text{ or } \langle ij \rangle \langle ik \rangle \text{ or } \langle ik \rangle \langle jk \rangle \\ X_i X_j X_k \exp(3\varepsilon/k_B T) & \text{for } \langle ij \rangle \langle jk \rangle \langle ik \rangle = \langle ijk \rangle. \end{cases} \tag{4.1d}$$

(The last possibility in (4.1d) can arise on triangular lattices.) This situation can be depicted graphically as in the Mayer expansion for non-ideal gases.

Condition (4.1) enables us to write

$$\begin{aligned} \left\langle \prod_i (1 + X_i) \right\rangle_1 &= \left\langle \exp\left(\sum_i \ln(1 + X_i)\right) \right\rangle_1 \\ &= \exp\left[ \left\langle \exp\left(\sum_i \ln(1 + X_i)\right) \right\rangle_{c,1} - 1 \right] \end{aligned} \tag{4.2}$$

where the subscript  $c$  designates a cumulant average (Kubo 1962). The leading terms from (4.2) are then found to be

$$\begin{aligned} \exp\left( \sum_i \ln(1 + X_i) + \frac{1}{2} \sum_{\langle ij \rangle} [\ln(1 + X_i) \ln(1 + X_j)] [\exp(\varepsilon/k_B T) - 1] \right. \\ \left. + \frac{1}{6} \sum_{\langle ijk \rangle} [\ln(1 + X_i) \ln(1 + X_j) \ln(1 + X_k)] [\exp(3\varepsilon/k_B T) - 3 \exp(2\varepsilon/k_B T) + 2] + \dots \right) \end{aligned} \tag{4.3a}$$

which upon expansion to  $X^3$ , i.e., to  $\phi^6$ , gives

$$\begin{aligned} \exp\left(\sum_i (X_i - \frac{1}{2}X_i^2 + \frac{1}{3}X_i^3 + \dots) + \frac{1}{2}\sum_{\langle ij \rangle} (X_i X_j - \frac{1}{2}X_i^2 X_j - \frac{1}{2}X_i X_j^2 + \dots)\right. \\ \times [\exp(\varepsilon/k_B T) - 1] + \frac{1}{6}\sum_{\langle ijk \rangle} (X_i X_j X_k + \dots) \\ \left. \times [\exp(3\varepsilon/k_B T) - 3\exp(2\varepsilon/k_B T) + 2] + \dots\right). \end{aligned} \quad (4.3b)$$

Nearest-neighbour lattice sites are taken to coalesce in the continuum limit, so  $\sum_{\langle ij \rangle} X_i X_j$  is replaced by  $z \sum_i X_i^2$ . Hence, equation (4.3) reduces in this limit to

$$\begin{aligned} \exp\left(\sum_i X_i - \frac{1}{2}\sum_i X_i^2 [1 + z - z\exp(\varepsilon/k_B T)] + \frac{1}{6}\sum_i X_i^3 \{2 - 3z[\exp(\varepsilon/k_B T) - 1] \right. \\ \left. + zz'[\exp(\varepsilon/k_B T) - 3\exp(2\varepsilon/k_B T) + \exp(3\varepsilon/k_B T)]\} + O(X_i^4)\right) \end{aligned} \quad (4.4)$$

where  $z'$  is the number of sites  $k$  which are nearest neighbours to a pair of neighbours  $i$  and  $j$  (i.e., in  $\langle ijk \rangle$ ). Since  $X_i$  contains  $\phi_{i\alpha}^+ \cdot \phi_{i\alpha-1}$  for  $\alpha \neq 0$  or  $N$ , the terms in (4.4) correspond to a chain (i.e.,  $\alpha$ ) space version of the  $\phi^4$ - $\phi^6$  field theory utilised to describe polymers near the theta point  $T = \theta$  (Kholodenko and Freed 1983c) which occurs near the compensation point  $T_c$  where the effective quartic constant  $[1 + z - z\exp(\varepsilon/k_B T)]/2$  vanishes. This condition yields  $\varepsilon/k_B T_c = \ln(1 + z^{-1})$ .

A related but somewhat different quantity is obtained from Monte Carlo data where the parameter  $\varepsilon/k_B \theta$  is defined such that the mean square end-to-end distance is Gaussian. McCrackin *et al* (1973) find  $\varepsilon/k_B \theta$  of 0.25 on the simple cubic lattice ( $z = 6$ ) and 0.12 on a face centred cubic lattice ( $z = 12$ ). For these cases  $\varepsilon/k_B T_c$  is 0.15 and 0.08, respectively. Kremer *et al* (1981) obtain  $\varepsilon/k_B \theta$  of 0.44 on a diamond lattice ( $z = 4$ ), while  $\varepsilon/k_B T_c$  for this case is 0.22. Although  $T_c$  and  $\theta$  are physically different, the magnitudes are similar, and they parallel each other in their variation with  $z$ . Choosing our value for  $\varepsilon/k_B T_c$  leaves the remaining  $\phi^6$  term from  $X_i^0$  with an overall coefficient of  $-5/6$  as the dominant correction term. Hence, a continuum limit of the lattice theory with nearest-neighbour polymer-polymer attractive interactions likewise produces the  $\phi^4$ - $\phi^6$  type field theory in chain space that has been previously postulated as a model for polymers in the theta region (de Gennes 1979, Kholodenko and Freed 1984a). The approach, in principle, also yields the means for estimating the relative magnitude of successive higher terms for  $T < T_c$  where the polymer collapses and the higher body terms may enter. Hence, the approach in this section provides a reasonable beginning field theory for the consideration of finer details of the coil-globule transition (Kholodenko and Freed 1984b).

#### 4.2. Interactions between different polymers

Blends, solutions of two different types of polymers and copolymers contain different types of polymers with different interaction energies. Let these polymers be labelled as type A and type B. The lattice spin model of self-avoiding chains of § 2 is readily generalised to these cases by addition of the indices A and B to the spins to give the variables  $S_{i\alpha}^A, S_{i\alpha}^{+A}, S_{i\alpha}^B, S_{i\alpha}^{+B}$ , etc. As different types of monomers cannot occupy the

same lattice site, we have exclusion conditions

$$\langle S_{i\alpha}^{\dagger A} S_{i\alpha}^B \rangle = \langle S_{i\alpha}^{\dagger B} S_{i\alpha}^A \rangle = 0 \quad (4.5)$$

while retaining (2.6) if both spins have A labels or B labels, etc.

The grand partition function for polymer mixtures becomes

$$Z = \text{Tr}_S \exp \left[ \sum_{\lambda=A,B} \left( K_{\lambda} \sum_{\langle ij \rangle} \sum_{\alpha=0}^{\infty} S_{i\alpha}^{\dagger \lambda} \cdot S_{j\alpha}^{\lambda} + \sum_{i,\lambda} (H^{\lambda} \cdot S_{i0}^{\dagger \lambda} + H^{\dagger \lambda} \cdot S_{iN}^{\lambda} P_{N}^{\lambda}) \right) \right]. \quad (4.6)$$

The transformation (2.15) is applied for each  $\lambda$  by the introduction of  $\phi_{i\alpha}^{\dagger A}$  and  $\phi_{i\alpha}^A$  for polymer of type A and  $\phi_{i\alpha}^{\dagger B}$  and  $\phi_{i\alpha}^B$ , etc, if more components are present. The spin integrations analogous to (2.16) follow readily to produce the factor

$$\prod_i (1 + X_i^A + X_i^B) \quad (4.7)$$

with obvious notation and physical interpretation. The interaction average  $\langle \rangle_I$  now must be generalised to include different energies  $\varepsilon^{AA}$ ,  $\varepsilon^{AB}$  and  $\varepsilon^{BB}$ , and the details follow directly as in § 2.1, so they are omitted for brevity. The treatment of block copolymers follows similarly by use of the term  $K_{AB} \sum_{\langle ij \rangle} S_{iN_A+1}^{\dagger B} \cdot S_{jN_A}^A$  to link the blocks together.

### 5. Branched polymers, loops and generalisations

The introduction of branching into the lattice model of self-avoiding walks follows straightforwardly because of the use of an internal symmetry variable  $\alpha$  and the complex spin to produce sequential (directional in  $\alpha$  space) bonds. The classic treatment of Lubensky and Isaacson (1979) alters the standard  $n \rightarrow 0$  requirement to treat branched polymers and introduces in a rather abstract fashion a set of branching operators. These procedures are both unnecessary here, and, in addition, we can control the length distributions.

It clearly follows that a trifunctional branch is formed with the term

$$\sum_{\alpha=1}^{\infty} \sum_{\langle ik \rangle, \langle jk \rangle} (K_b \cdot S_{i0}^{\dagger}) (S_{j,\alpha+1}^{\dagger} \cdot S_{k\alpha}) Q_{\alpha}$$

or

$$\sum_{\alpha=1}^{\infty} \sum_{\langle ik \rangle, \langle jk \rangle} (K_b \cdot S_{i0}^{\dagger}) (S_{j0}^{\dagger} \cdot S_{k\alpha}) Q_{\alpha} \quad (5.1)$$

added into the exponential on (2.9). Here  $K_b$  represents a controllable branching 'probability', and  $Q_{\alpha}$  is a probability of branch occurrence after a chain has grown to  $\alpha$  bonds. This latter possibility is added for specially constructed branched systems in which the lengths of chain segments between branches can be controlled. The alternative forms in (5.1) differ in their labelling of  $\alpha$  along the newly created branch, and the latter choice would be taken if the average chain length between branches were of interest. Chains are begun again with factors of  $\sum_i H \cdot S_{i0}^{\dagger}$  and all chains and branches end with factors  $\sum_{\alpha=1}^{\infty} \sum_i P_{\alpha} H^{\dagger} \cdot S_{i\alpha}$ . Thus, a typical contribution to  $Z$  with

$n_p$  originating chains and  $M$  branches has a coefficient of  $H^{n_p} K_b^M (H^\dagger)^{n_p+M}$  and is therefore generated by

$$Z_{n_p, M} = \frac{1}{(n_p)! M!} \frac{\partial^{n_p}}{\partial H^{n_p}} \frac{\partial^M}{\partial K_b^M} \frac{\partial^{n_p+M}}{\partial (H^\dagger)^{n_p+M}} Z \Bigg|_{H=H^\dagger=K_b=0} \quad (5.2)$$

Distribution in  $n_p$  and  $M$  can also be generated by specifying  $H$ ,  $K_b$  and  $H^\dagger$ .

The model is readily generalised to include tetrafunctional and higher degrees of branching. For instance, the tetrafunctional branching vertices are produced by terms in  $S^\dagger \cdot SS^\dagger \cdot S$  with appropriate indices and summations by analogy with the network theory of Edwards and Freed (1970a, b, c) and Freed (1971). These higher functionality spin models have completely controllable chain lengths and branch length distributions as well as branching and chain termination probabilities. The standard  $n \rightarrow 0$  limit of  $n$ -component field theory, on the other hand, cannot control these length distributions. The close similarity between the two descriptions, however, enables the derivation of the corresponding field theory to be obtained quite straightforwardly as the average of the exponential of (5.1) plus any higher functionality terms with the weight factor given by (2.16). Then the average of the branching operators can be handled following Lubensky and Isaacson (1979) by the use of cumulants. The trifunctional terms on the left side of (5.1) lead to cubic terms like

$$\sum_{\alpha=1}^{\infty} Q_\alpha \sum_{(ij), (jk)} (\mathbf{K}_b \cdot \boldsymbol{\phi}_{i0}) (\boldsymbol{\phi}_{j, \alpha+1}^\dagger \cdot \boldsymbol{\phi}_{k\alpha}) \quad (5.3)$$

to be added into the exponent in the numerator of the field theory (2.18) as well as  $\phi^6$ ,  $\phi^9$ , etc. higher-order terms from higher cumulants. This field theory with the leading cumulant reduces to the form of that of Lubensky and Isaacson by following the procedure of § 3.2 to convert to the continuum limit, by introducing Laplace transforms with respect to the  $\alpha$  index and by then dropping the dependence of the fields on this transform index. The introduction of polymer-polymer interactions becomes somewhat more complicated for the branch points. No details are presented here as we plan to consider branched polymer systems more fully in a future paper.

It is also possible to introduce closed loops into the polymer system. Suppose trifunctional generating terms of the form (5.1) are included. Then the term

$$\sum_{\alpha, \beta=1} Q_{\alpha\beta} \sum_{(ij), (jk)} (\mathbf{K}_\ell \cdot \mathbf{S}_{k\beta}) (\mathbf{S}_{i, \alpha+1}^\dagger \cdot \mathbf{S}_{j\alpha}) \quad (5.4)$$

takes two chain segments at  $\alpha$  and  $\beta$  and joins them into a single chain with monomer unit index  $\alpha + 1$ . If  $\alpha$  and  $\beta$  lie on separate linear chains, then (5.4) just produces the trifunctional branch (5.1) in reverse (in order of increasing values of  $\alpha$ ). However, when the strands ending in  $\alpha$  and  $\beta$  are themselves produced through branching by (5.1), then (5.4) can lead to closed loops.

Other lattice polymer problems can be developed by further generalising the spin statistics to spin averages which differ from the form in (2.6). For instance, it is possible to introduce spin variables to describe self-avoiding polymers which have different weights for trans and gauche bonds. Such a model is of interest in the study of the glass transition (Flory 1956) and of micelle structure. The spin model produces a very complicated field theory which is left for a future work for further study.

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