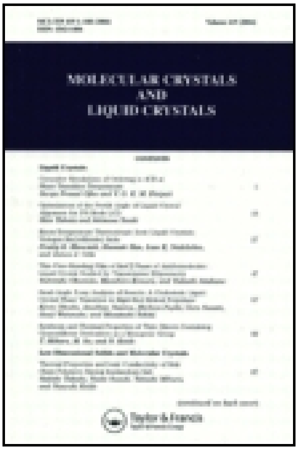

Molecular Crystals and Liquid Crystals

Polymer Solution Model with Anisotropic Phase

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POLYMER SOLUTION MODEL WITH ANISOTROPIC PHASE

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We investigate a lattice self-avoiding walk model with directive (hydrogen bond like) interactions between chain segments and isotropic interactions between monomers and solvent molecules. The model, meant to describe a polymer in the dilute solution regime, is investigated in the framework of the Bethe approximation. Directive interactions produce, in addition to the ordinary Θ collapse, a first order transition to an anisotropic (structured) phase. The interplay with solvent interactions modifies the nature of the isotropic phase, which can be either swollen or collapsed. Such an interplay may be an important ingredient for the formation of ordered structures in biopolymers. The relationship with previously investigated self-avoiding walk models is also discussed.

Keywords: self-avoiding walk; hydrogen bonding; polymer folding; anisotropic phase; secondary structure

INTRODUCTION

A polymer in a good solvent is usually described as a Self-Avoiding Walk (SAW) on a lattice, i.e. a random walk which is forbidden to visit lattice sites more than once [1–3]. A short range interaction between non-consecutively visited sites is also generally considered in order to model affinity between monomers (for instance Vander Waals forces). Such intra-molecular interaction causes the well known Θ collapse from a swollen coil at high temperature to a compact globule at low temperature [4,5]. The degree of affinity between monomers and solvent molecules (solvophilicity) can also be mapped onto an effective monomer-monomer interaction [6,7], affecting the collapse temperature.

In a large number of real polymers (in particular biopolymers) the most relevant contribution to intra-molecular interactions is related to hydrogen (H) bonds. They are extremely directive in nature, and are thought to play a fundamental role in the formation of protein secondary structures [8]. In the framework of lattice SAW models H bonding has been described reducing the number of configurations in which neighbor chain sections can interact [9–12], giving rise to a competition between energy gain and entropy cost of forming H bonds. At low temperature such models predict a dense anisotropic phase in which all chain segments (except a vanishing fraction) are aligned to a particular direction. This phase is supposed to mimick an ordered ("secondary") structure. In this kind of models it is not possible to vary the intensity of monomer-solvent interactions by tuning the monomer-monomer interaction energy, because, unlike in the Θ model [4,5], the latter parameter describes a configuration dependent interaction, while monomer-solvent interactions can be reasonably assumed to be independent of chain configurations. This may be a drawback because also the solvent properties are thought to play an important role in the folding of polymers [7,13,14], and hence they should be taken into account.

In this paper we consider a particular model with configuration-dependent monomer-monomer interactions, known as interacting bond model [11]. This model, which assigns an attractive energy to parallel chain segments on opposite square edges (on the 2d square lattice or on the 3d simple cubic lattice), has been already investigated in both cases [11,12]. Here we study the model on the simple cubic lattice, introducing explicitly also monomer-solvent interactions that are independent of chain configurations. We investigate how the phase behavior depends on the intensity of monomer-solvent interactions, both for the repulsive (solvophobic) and the attractive (solvophilic) case, pointing out the interplay between directive and isotropic interactions.

We make use of the Bethe approximation, a classical tool of the statistical mechanics of lattice systems [15,16], that has been shown to give qualitatively good results also for polymer models [17,18]. By the way Reference 12, compared to 11, seems to suggest that the Bethe approximation can introduce artifacts in the 2d case, but they might be actually ascribed to low dimensionality.

THE MODEL AND THE BETHE APPROXIMATION

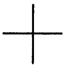
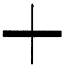
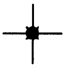
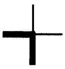
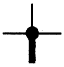
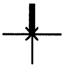
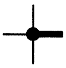
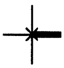
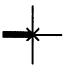
We model the polymer as a SAW on a simple cubic lattice. Sites visited by the walk represent monomers, empty sites represent clusters of solvent molecules. Parallel chain segments on an elementary square of the lattice interact with an attractive energy $\varepsilon < 0$. Monomers interact also with nearest neighbor (NN) solvent with an energy γ, that may be either repulsive (solvophobic, $\gamma > 0$) or attractive (solvophilic, $\gamma < 0$). A chemical potential contribution μ is associated to each monomer.

In the framework of the grand-canonical ensemble the state of the system can be described by specifying, for each lattice site, the occupation number $n = 0, 1$ (i.e. whether the site is empty or visited), and, in the latter case, the local chain configuration (i.e. the directions of two chain segments towards the previous and the next monomer). One can then introduce a suitable site state variable k, according for instance to the mapping defined in Table 1. It is thus possible to analyze the lattice polymer system as a Potts-like model in which, to preserve connectivity, site state variables have to satisfy certain constraints. In particular, if A and B are NN sites, and the configurational state of A is linked (resp. not linked) to B, then also the state of B must be linked (resp. not linked) to A. The Bethe approximation, taking into account pair correlations exactly [15,16], is able to impose such constraints. The self-avoiding condition is guaranteed by the set of site configurations (Table 1), which does not include self-crossing. The absence of closed loops is apparently not guaranteed, but this fact is irrelevant to equilibrium thermodynamics, because the Bethe approximation coincides with the exact solution on the interior of a Cayley tree (Bethe lattice) [19], on which loops are forbidden in principle.

According to the Bethe approximation, in the hypothesis of translational invariance, the grand-potential per site ω can be written as [12]

$$\beta\omega = \sum_{a=1}^{3}\sum_{k=0}^{15}\sum_{k'=0}^{15} p_{k,k'}^{(a)}\left[\beta\tilde{h}_{k,k'}^{(a)} + \log p_{k,k'}^{(a)}\right] - 5\sum_{k=0}^{15} p_k \log p_k, \tag{1}$$

TABLE 1 Correspondence Between Local Chain Configurations and Values of the Site State Variable k: • (resp. X) Denotes a Chain Segment Along the Positive (resp. negative) z Direction. Notice that $k = 0$ Corresponds to Empty site and $k > 0$ to visited site

								
k	0	1	2	3	4	5	6	7
								
k	8	9	10	11	12	13	14	15

where as usual $\beta = 1/KT$ (being K the Boltzmann constant and T the absolute temperature), $a =$ is an axis label (1, 2, 3 meaning respectively x, y, z), $p_{k,k'}^{(a)}$ is a pair probability distribution (the probability that two NN sites along the a-axis are respectively in the k, k' states), and p_k is the site probability distribution (the probability that a site is in the k state). Finally

$$\tilde{h}_{k,k'}^{(a)} = h_{k,k'}^{(a)} - \frac{\mu}{6}(n_k + n_{k'}), \tag{2}$$

where $h_{k,k'}^{(a)}$ represent pair interaction energies along the a-axis and n_k are occupation numbers ($n_k = 0$ if $k = 0$ and $n_k = 1$ otherwise). Normalization to the coordination number 6 avoids multiple counting. In Table 2 we report for example the pair energies $h_{k,k'}^{(1)}$. Let us notice that, in Table 2, k states have been divided into two subsets so that in the former subset k is ***not linked*** to k', while in the latter subset k is ***linked*** to k' along the x axis (see Table 1). The same has been done for k' with respect to k. Thus, when k is linked to k' but k' is not linked to k (lower left submatrix), or vice versa (upper right submatrix), the connectivity constraint is violated, and infinite energy penalties are assigned, that is $h_{k,k'}^{(1)} = \infty$. Such terms can be treated numerically as vanishing Boltzmann weights. Moreover, when k is linked to $k'$and also k' is linked to k (lower right submatrix), no interaction is present, whence $h_{k,k'}^{(1)} = 0$. Finally, when k is not linked to k' and k' is not linked to k (upper left submatrix), different interactions are possible: $h_{k,k'}^{(1)} = \gamma$ between

TABLE 2 Pair Interaction Energies $h_{k,k'}^{(1)}$. It is Understood that k' Follows k Along the x axis. Notice that $h_{k,k'}^{(2)}$ and $h_{k,k'}^{(3)}$ can be Determined by Means of Eq. (5) (See the Text)

k' k	0	2	3	8	9	10	11	4	7	12	13	1	5	6	14	15
0	0	γ	γ	γ	γ	γ	γ	γ	γ	γ	γ					
2	γ	ε	0	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	0	0					
3	γ	0	ε	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	0	0	$\varepsilon/2$	$\varepsilon/2$					
8	γ	$\varepsilon/2$	$\varepsilon/2$	ε	$\varepsilon/2$	0	$\varepsilon/2$	$\varepsilon/2$	0	$\varepsilon/2$	0					
9	γ	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	ε	$\varepsilon/2$	0	0	$\varepsilon/2$	$\varepsilon/2$	0					
10	γ	$\varepsilon/2$	$\varepsilon/2$	0	$\varepsilon/2$	ε	$\varepsilon/2$	0	$\varepsilon/2$	0	$\varepsilon/2$			∞		
11	γ	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	0	$\varepsilon/2$	ε	$\varepsilon/2$	0	0	$\varepsilon/2$					
5	γ	$\varepsilon/2$	0	$\varepsilon/2$	0	0	$\varepsilon/2$	$\varepsilon/2$	0	0	0					
6	γ	$\varepsilon/2$	0	0	$\varepsilon/2$	$\varepsilon/2$	0	0	$\varepsilon/2$	0	0					
15	γ	0	$\varepsilon/2$	$\varepsilon/2$	$\varepsilon/2$	0	0	0	0	$\varepsilon/2$	0					
14	γ	0	$\varepsilon/2$	0	0	$\varepsilon/2$	$\varepsilon/2$	0	0	0	$\varepsilon/2$					
1																
4																
7						∞								0		
12																
13																

a monomer in any configuration and a site occupied by solvent (either $k = 0$ or $k' = 0$), $h^{(1)}_{k,k'} = \varepsilon/2$ between monomers with one pair of parallel half-segments, $h^{(1)}_{k,k'} = \varepsilon$ between monomers with two pairs of parallel half-segments, and $h^{(1)}_{k,k'} = 0$ either between monomers with no parallel half-segments or between two sites occupied by solvent ($k = 0$ and $k' = 0$).

Let us also notice that site and pair probability distributions (PDs) are not independent. The site PD must be obtained from the pair PDs as a marginal distribution

$$p_k = \sum_{k'=0}^{15} p^{(a)}_{k,k'} = \sum_{k'=0}^{15} p^{(a)}_{k',k}. \tag{3}$$

Moreover it must satisfy the normalization constraint

$$\sum_{k=0}^{15} p_k = 1. \tag{4}$$

In order to determine equilibrium states, we have to minimize the grand-potential with respect to the PDs, taking into account the constraints (3) and (4). Among different local minima, the stable phase is the lowest potential one. It is possible to perform the constrained minimization numerically, by means of an iterative method proposed by Kikuchi [20]. Technical details of the method applied to a polymer problem have been described elsewhere [12]. As an order parameter, we evaluate the fraction of sites visited by the walk $x = 1 - p_0$, which we shall briefly refer to as ***density*** in the following.

In our treatment the system is in principle allowed to contain an intrinsic anisotropy in the pair energy terms $h^{(a)}_{k,k'}$ (and consequently in $\tilde{h}^{(a)}_{k,k'}$), which depend on the axis label a. Such a dependence does not correspond to real anisotropic interactions, but is only related to the fact that site states are defined with respect to a fixed reference frame. If we define an operator $\mathcal{S}$ which, acting on a state variable k returns the state $\mathcal{S}k$, obtained by shifting axis labels 1, 2, 3 into 2, 3, 1 (Table 3), it turns out that

$$h^{(a+1)}_{k,k'} \equiv h^{(1)}_{\mathcal{S}^{-a}k,\mathcal{S}^{-a}k'}. \tag{5}$$

If the equilibrium state does not break isotropy, we shall obtain an equivalent relation for the pair PDs

TABLE 3 Definition of the Shift Operator $\mathcal{S} : k \mapsto \mathcal{S}k$.

k	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$\mathcal{S}k$	0	2	3	1	8	9	10	11	12	13	14	15	4	5	6	7

$$p^{(a+1)}_{\mathcal{S}^{-a}k,\mathcal{S}^{-a}k'} \equiv p^{(1)}_{k,k'}, \qquad (6)$$

and, according to (3), the following one for the site PD

$$p_{\mathcal{S}^{a}k} \equiv p_{k}. \qquad (7)$$

THE PHASE DIAGRAMS

In order to investigate the role of the solvent, we first describe in some detail the phase behavior of the bare interacting bond model ($\gamma = 0$), as a function of $\beta|\varepsilon|$ and $\beta\mu$ [12]. As shown in Figure 1(a), three different phases are present: the zero density (Z) phase, the isotropic dense (I) phase, and the anisotropic dense (A) phase. The Z phase is characterized by $x = 0$ and $\omega = 0$ (notice that ω is actually the excess grand potential with respect to pure solvent). The I phase is characterized by $0 < x < 1$ and the PDs satisfy the isotropy conditions (6) and (7). These two phases appear also in the ordinary Θ model. The A phase is anisotropic, saturated ($x = 1$), and frozen (its entropy is zero). All lattice sites, except a vanishing fraction, are occupied by chain segments aligned to a coordinate direction. The latter phase is induced by the peculiar H bond like interactions present in the model and may be considered as a rough representation of a secondary structure (for instance a stacking of β sheets [9]). The Z phase boundary, that is the transition between the Z phase and the dense phases, represents the dilute solution limit (a single chain in solution) [12]. The density x, computed in the limit of $\beta\mu$ tending to the transition from above, which denotes the chain compactness, is reported in Figure 1(b) as a function of

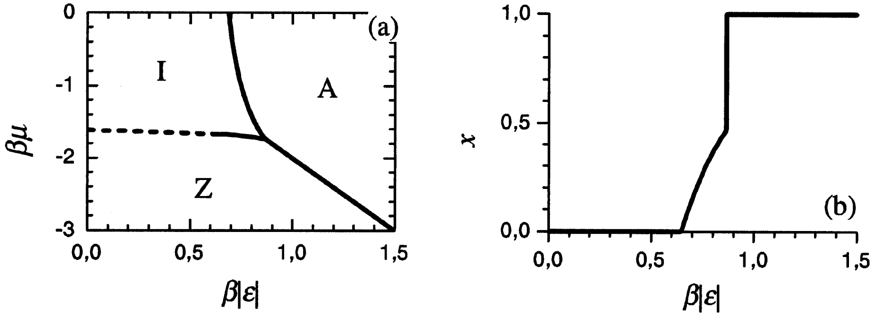


FIGURE 1 (a) Phase diagram of the bare interacting bond model ($\gamma = 0$). Solid lines denote first order transitions, dashed lines second order ones; Z, I, A denote respectively the zero density phase, the isotropic dense phase, and the anisotropic dense phase. (b) Density x as a function of the inverse temperature $\beta|\varepsilon|$ for $\gamma = 0$ in the dilute solution limit.

the inverse temperature $\beta|\varepsilon|$. In the lowest temperature region the polymer is in the frozen anisotropic (A) phase. At some temperature the system undergoes a first order transition in which the chain becomes orientationally disordered but its density does not fall down to zero. This phase may be identified with the ordinary compact globule (G) observed in the Θ model. Upon further increasing temperature, the density continuously decreases, reaching zero at an ordinary Θ point, after which the polymer is in a swollen coil (C) state.

Let us now investigate the effect of different interactions with the solvent, namely the case of solvophilic $\gamma < 0$ or solvophobic $\gamma > 0$ monomers. For $\gamma/|\varepsilon| = -0.1$ the phase behavior changes consistently. Figure 2(a) shows that the first order portion of the Z-ID transition disappears. The density plot, Figure 2(b), referred again to the dilute solution limit, shows that the polymer undergoes an abrupt first order transition from the anisotropic

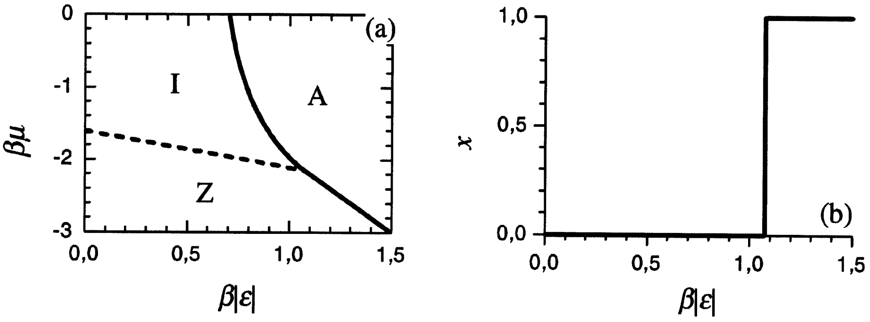


FIGURE 2 (a) Phase diagram in the solvophilic case ($\gamma|\varepsilon| = -0.1$). Lines and labels as in Figure 1. (b) as in Figure 1 for $\gamma/|\varepsilon| = -0.1$.

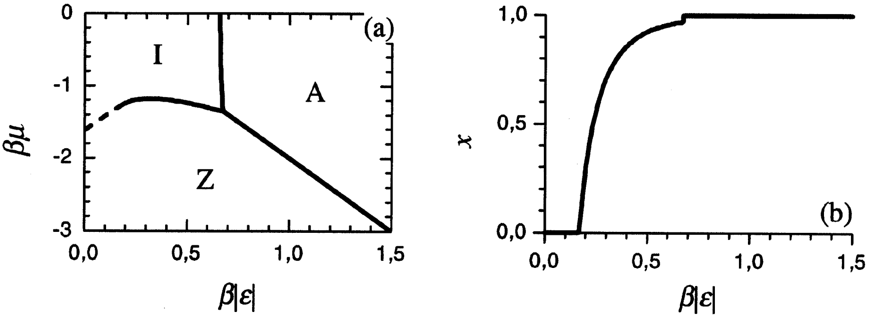


FIGURE 3 (a) Phase diagram in the solvophobic case ($\gamma/|\varepsilon| = 0.5$). Lines and labels as in previous figures. (b) as in previous figures for $\gamma/|\varepsilon| = 0.5$.

phase to the swollen coil. The solvent destabilizes the compact globule state, due to the fact that intra-molecular H bonds are not sufficiently present in a disordered, though compact, state. Hence they are easily overcome if monomers experiment even a slight attractive interaction with the solvent. For $\gamma/|\varepsilon| = 0.5$ (solvophobic interaction) the phase diagram is shown in Figure 3(a): in this case the first order portion of the Z-ID transition is amplified. The phase diagram is topologically equivalent to that observed for $\gamma = 0$, even if the Z-ID line is shifted towards higher μ values. Let us remind that the ***Helmholtz free energy per monomer*** in the dilute solution limit coincides with μ at the Z phase boundary, due to the fact that on that line the excess grand-potential per site

$$\omega = f - \mu x \tag{8}$$

(being f the Helmholtz free energy ***per site***) vanishes, whence

$$\mu = f/x. \tag{9}$$

The increased free energy of the compact globule can then be easily explained by the fact that the configurational entropy is now contrasted by the formation of monomer-solvent contacts, that is by an increased solvophobic interaction. As expected the solvent stabilizes the compact phases, in order to minimize monomer-solvent contacts, but the effect is more evident for the isotropic globule. Accordingly the density plot, Figure 3(b), shows that that the Θ temperature is increased more than the anisotropic-globule transition temperature. Moreover the latter transition does display a large density change, meaning that the most relevant effect is the loss of anisotropy, that is of secondary structure.

The complete phase behavior in the dilute solution limit is reported in Figure 4(a) as a function of the solvent interaction parameter $\beta\gamma$. As previously mentioned, we can observe that increasing values of γ(solvophobic interaction) have the effect of increasing both transition temperatures, but the effect is more pronounced for the Θ temperature. As a consequence, on decreasing the ratio $\gamma/|\varepsilon|$, one finds a triple point at which the isotropic globule phase disappears, and a direct anisotropic-coil transition is observed. Upon further decreasing $\gamma/|\varepsilon|$ (stronger solvophilic interaction) also the anisotropic phase eventually disappears.

DISCUSSION AND CONCLUSIONS

In this paper we have considered a lattice polymer model with a short range attractive interaction between parallel chain sections (interacting bond model), taking into account also the role of interactions with the solvent. In the dilute solution limit we have shown that the interplay between such interactions produces different phase behaviors. For the solvophobic case ($\gamma > 0$) we observe a regime in which the polymer undergoes two phase transition upon increasing temperature: from the anisotropic dense (A) phase to an isotropic compact globule (G) and then from the compact globule to the swollen coil (C). Upon decreasing γ the globule phase becomes less and less dense, and eventually disappears, giving rise to a direct A-C transition. Finally, for negative γ exceeding some threshold, also the anisotropic phase disappears.

The dilute solution phase diagram, Figure 4(a), turns out to be remarkably similar to that observed for the semi-flexible model [21–24], Figure 4(b). In the latter case an energy cost $k > 0$ assigned to polymer bending (stiffness) drives the phase behavior from that of an ordinary Θ model (with $\chi < 0$ monomer-monomer attractive energy) to an A-G-C regime to a direct A-C transition regime, as the solvophilicity does in our model. Let us notice that in the semiflexible model the structured phase is more and more stabilized by stiffness, while in our model solvophilicity does drive the system towards the direct A-C transition regime but also tends to penalize the structured phase. This is related to the fact that in the semi-flexible model k is actually the configuration dependent interaction

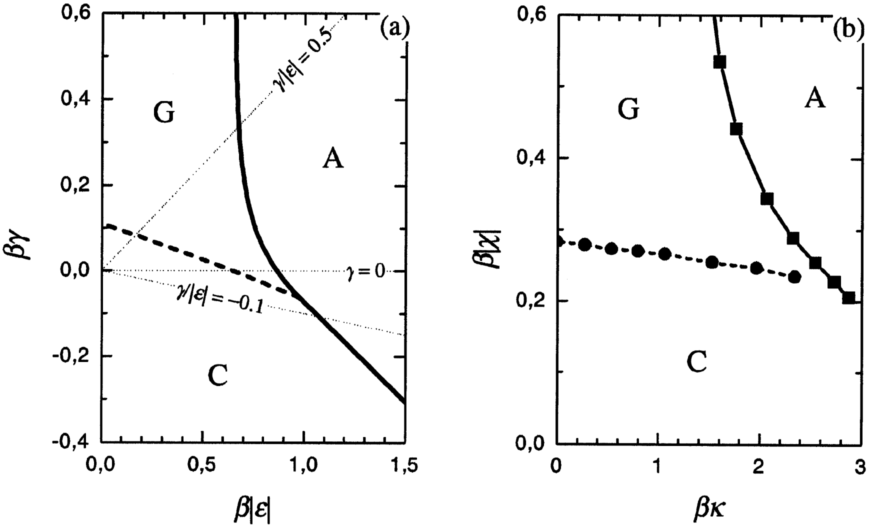


FIGURE 4 Phase diagram in the dilute solution limit for (a) the present model and (b) the semi-flexible model (data drawn from Reference [23]). Solid lines denote discontinuous transitions, dashed lines continuous (Θ) transitions; A, G, C denote respectively the anisotropic phase, the isotropic compact globule and the swollen coil.

parameter while χ is the independent one. The semi-flexible model has been proposed as a toy model for polymer folding with a secondary structure. The model we have investigated provides essentially similar phenomenology, with a different microscopic explanation of different levels of polymer stiffness, based on the competition between intra-molecular configuration dependent interactions and isotropic interactions with the solvent.

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