PHYSICAL REVIEW E VOLUME 48, NUMBER 2 AUGUST 1993

Thermodynamic behavior of chains on the Bethe lattice

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(Received 19 January 1993)

We solve models of self- and mutually avoiding M-mers placed on the Bethe lattice with additional energies that include (i) semiflexibility of the chains, (ii) attractive interactions between first neighbors, and (iii) preference for spatial orientation of bonds on the lattice. Free energies and phase diagrams are obtained and compared to earlier results when available. For the case of polymers on an anisotropic Bethe lattice with a coordination number equal to 4, we find two different polymerized phases.

PACS number(s): 05.70.$-$a, 64.60.Cn, 05.50.+q

Self- and mutually avoiding chains placed on regular lattices have been studied for quite a long time as models for a variety of experimental situations. Without attempting completeness, we may mention dimer models [1], originally proposed for studying adsorbed diatomic molecules on a solid surface [2], and infinitely long chains, which have been extensively used as models for polymers [3]. In our recent work [4], the problem of calculating the entropy of chains with M monomers (M-mers) each placed on Bethe and Husimi lattices was considered, and it was shown that this problem is exactly solvable in a variety of cases. Also, for some particular cases where exact results on regular lattices are available, the entropy calculated on Bethe and Husimi lattices turned out to be quite close to the exact values on the regular lattices with the same coordination number, indicating that calculations on cores of trees may be a good approximation for estimating properties on regular lattices.

In this paper we generalize the earlier athermal calculations [4] by associating an energy to each chain configuration on the lattice, thus studying the thermodynamic properties of chain models on the Bethe lattice in three specific cases.

(i) Semiflexible chains, where a bending energy ε is associated with each $\pi/2$ rotation (bending) of the chain (for hypercubic lattices the angle between consecutive bonds may be either 0 or $\pi/2$). This type of model has been used to study polymer melting [5].

(ii) Self- and mutually interacting chains, where an attractive interaction energy ε is included between first-neighbor monomers which are not consecutive along the same chain. Thus we consider an "M-mer lattice gas," which for the particular case of dimers ($M=2$) may describe diatomic molecules adsorbed on a surface [6]. For the case of polymers ($M\to\infty$), the interacting model has been used for studying the collapse transition [3].

(iii) Anisotropic lattices, where an additional energy ε is associated with each bond which is on a particular direction (excited state). This model may describe chains in a medium with an hydrodynamic flow, thus favoring bonds lying along a particular direction.

Let us consider the problem of placing p self- and mutually avoiding chains formed by M consecutive monomers on a lattice of N sites, so that the number of lattice sites visited by chains is $m=Mp$, and the total energy associated with each particular mode of distribution of the chains on the lattice is $E=n\varepsilon$, where n is the number of configurations with which we associate an energy ε.

In an ensemble which is grand canonical with respect to the number of chains the relevant partition function is

$$Y_{N,M}(x,\omega)=\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}x^m\omega^n\Gamma_{N,M}(m,n)\ , \tag{1}$$

where x is the activity of a monomer, ω is the Boltzmann factor associated with the configurations of energy ε [$\omega=\exp(-\varepsilon/kT)$], and $\Gamma_{N,M}(m,n)$ is the number of distinct ways to place the chains on the lattice, so that all constraints are satisfied. The sum is over all values of m and n between zero and infinity, since for values which do not satisfy the constraints (in particular, if m is not a multiple of M) we have $\Gamma_{N,M}(m,n)=0$.

The grand-canonical potential $\Phi(x,\omega)=N^{-1}\times\ln[Y_{N,M}(x,\omega)]$, in the thermodynamic limit ($N\to\infty$), is related to the adimensional free energy $\varphi(\rho,\varepsilon)$ by the Legendre transform

$$\Phi(x,\omega)=\max_\rho[\rho\ln x-\varphi(\rho,\varepsilon)]\ ,$$

where $\rho=m/N$ is the density of monomers on the lattice. We therefore have $\partial\varphi/\partial\rho=\ln x$, so that

$$\varphi(\rho,\varepsilon)=\int_0^\rho\ln[x(\rho')]d\rho'\ . \tag{2}$$

To solve the models on the Bethe lattice with arbitrary coordination number q, we proceed in a way quite similar to the earlier athermal calculation [4], defining partial partition functions associated with the subtrees and labeling them according to configuration of the root of corresponding subtree. We then obtain recursion relations between partial partition functions associated with subtrees of successive generations.

In the case of semiflexible chains, we define M partial partition functions in a way that g_1 is associated with the subtrees with empty root site, whereas g_i, $i=2,3,\dots,M$, refers to the subtrees whose root is occupied by the ith monomer of a chain. The fixed point of the recursion relations for the ratios $R_j = g_{j+1}/g_1$, $j = 1,2,\ldots,M-1$, is given by $R_j^* = \alpha^j/\sigma$, where $\sigma = 1+(q-2)\omega$ and α is the root of the equation

$$\sigma x = \alpha + \frac{(q-1)x\alpha^M}{\sigma}\left[1+\frac{(q-2)(M-2)}{2(q-1)}\right] . \quad (3)$$

In the thermodynamic limit (where the fixed point is reached), it is possible to express the density ρ of monomers on the central site of the Bethe lattice as a function of α, and the activity x may then be obtained as a function of ρ [the expression for $x(\rho)$ is similar to the one for the athermal case—Eqs. (20) and (21) of Ref. [4]—substituting the parameter $r = q-1$ by $\sigma = 1+(q-2)\omega$]. This enables us to calculate analytically the free energy through expression (2). The curves of the free energy $\varphi(\rho, \varepsilon)$ as a function of the density ρ are shown in Fig. 1. In the limit $M \to \infty$, a polymerization transition is observed, as may be seen in the diagram of ρ versus $x/(1+x)$ in Fig. 2. The critical activity is given by

$$x_c = 1/[1+(q-2)\omega] ,$$

which reduces to the known results [7] in the limits $\omega = 1$ (flexible polymers) and $\omega = 0$ (one-dimensional case).

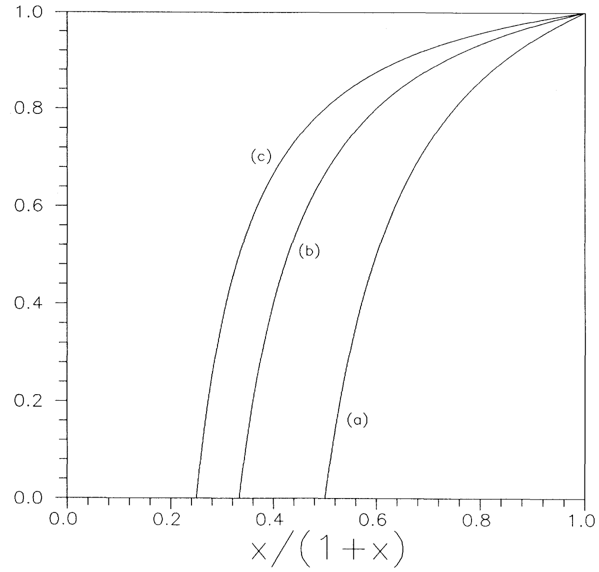

FIG. 2. Monomer density ρ as a function of the activity fraction $x/(1+x)$ for semiflexible polymers $(M \to \infty)$ on a Bethe lattice with coordination $q = 4$. (a) $\omega = 0$, (b) $\omega = 0.5$, and (c) $\omega = 1.0$.

For the case of self- and mutually interacting chains, we define $M+1$ partial partition functions, where g_0 corresponds to the subtrees with empty sites on both the root site and its first neighbor, whereas g_1 refers to the subtrees with an empty root site but a monomer present on its first-neighbor site, and g_i, $i = 1,2,\ldots,M$, are defined in a way analogous to the case of semiflexible chains. Introducing the ratios $R_0 = (g_0+g_1)/(g_0+\omega g_1)$ and $R_j = g_{j+1}/(g_0+\omega g_1)$, $j = 1,2,\ldots,M-1$, the fixed points of the recursion relations are given by $R_j^* = \alpha^j/(q-1)$ and $R_0^* = \alpha_0$, where α and α_0 are obtained from the system of equations

$$(q-1)x = \alpha\alpha_0^{q-1} + \omega x\alpha^M\left[1+\frac{(q-2)(m-2)}{2(q-1)}\right] , \quad (4a)$$

$$(q-1)x\alpha_0 = \alpha\alpha_0^{q-1} + x\alpha^M\left[1+\frac{(q-2)(M-2)}{2(q-1)}\right] . \quad (4b)$$

It is possible to obtain the activity x as a function of the monomer density ρ at the central site. Some results are shown in Fig. 3. It is apparent that the $x(\rho)$ curves are

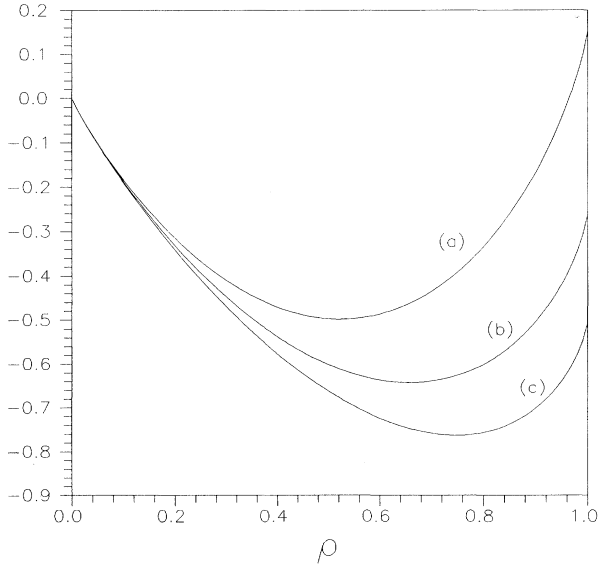

FIG. 1. Free energy φ as a function of monomer density ρ for semiflexible pentamers $(M = 5)$ on a Bethe lattice with coordination $q = 4$. (a) $\omega = 0$, (b) $\omega = 0.5$, and (c) $\omega = 1.0$, where ω is the Boltzmann factor associated with the configuration energy.

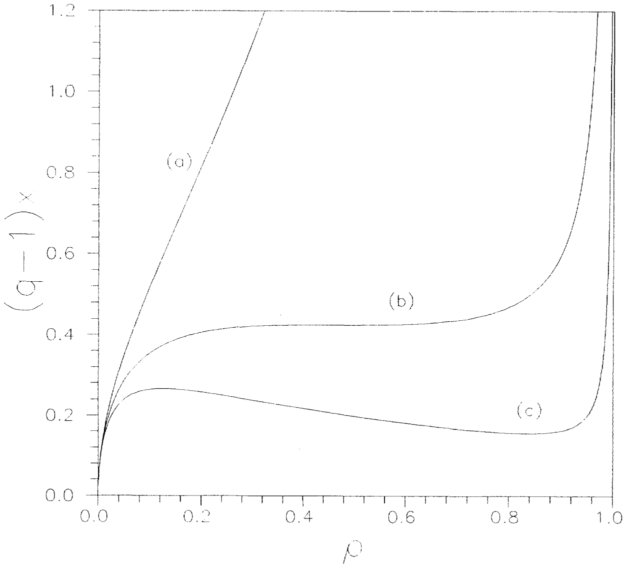

FIG. 3. Activity x as a function of the density ρ of interacting dimers $(M = 2)$ on a Bethe lattice with coordination $q = 4$. (a) $\omega = 1$, (b) $\omega = \omega_c = 2.968\,246\ldots$, and (c) $\omega = 5$.

no longer monotonic, but display a first-order transition ending at a critical point. The corresponding phase diagram may be found in Fig. 4, where the first-order line was calculated via a Maxwell construction. In the polymer limit $M \to \infty$, the results are qualitatively different, a tricritical point being found in the phase diagram, as may be seen in Fig. 5. The tricritical point in the phase diagram ω versus x, is located at

$$x_{\mathrm{TC}}=1/(q-1)\ , \quad \omega_{\mathrm{TC}}=(q-1)/(q-2)\ ,$$

and we recover earlier results on the collapse transition of polymers on the Bethe lattice [7].

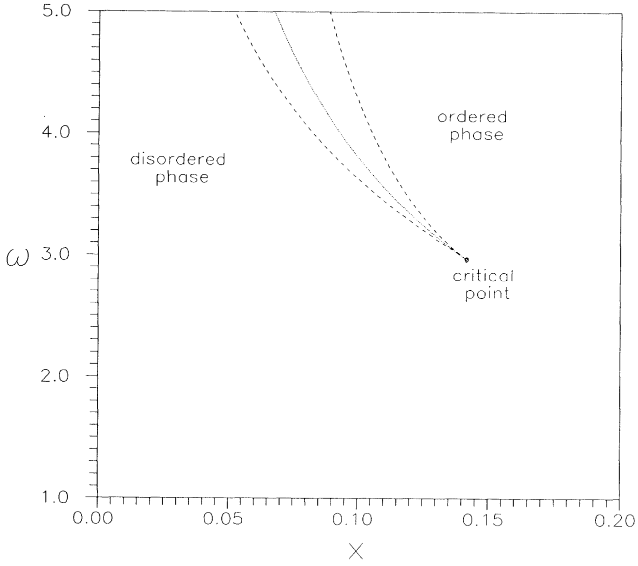

FIG. 4. Phase diagram for interacting dimers ($M=2$) on a $q=4$ Bethe lattice, showing the line of first-order transition (dotted line) and the spinodal lines (dashed lines).

The problem of M-mers on an anisotropic Bethe lattice is formulated considering that of q incident lattice bonds on each site, two correspond to excited states with an additional energy ε (type 1 bonds), and the remaining $(q-2)$ correspond to the ground state (type 2 bonds). In the case of general M, we obtained the recursion relations, but we were unable to find its fixed point analytically. We thus concentrated our attention on the particular limits of dimers ($M=2$) and polymers ($M\to\infty$), where analytic calculations were performed.

In the case of dimers, we defined four partial partition functions according to configuration of the (type 1 or type 2) root bonds of the subtrees, which may be occupied by a dimer or not. The density of dimers on type 1 bonds ρ_ε and the total density of dimers ρ are given by, respectively,

$$\rho_\varepsilon=2\omega^{1/2}\alpha\rho[2\omega^{1/2}\alpha+q-2]^{-1}\ , \tag{5a}$$

$$\rho=[2\omega^{1/2}\alpha+q-2][2\omega^{1/2}\alpha+q-2+f]^{-1}\ , \tag{5b}$$

where $f=(1-\rho)(2\omega^{1/2}\alpha+q-2)/\rho$ and α is given by

$$\alpha=\frac{-(q-2-2\omega)+[(q-2-2\omega)^2+4\omega(2-\rho)(q-2-\rho)]^{1/2}}{2\omega^{1/2}(2-\rho)}\ . \tag{6}$$

In general, the model does not present any phase transition. However, for lattices with coordination number $q=3$, in the particular limit of full coverage $\rho=1$, a phase transition is observed as may be seen in Fig. 6, where the function $\rho_\varepsilon(\omega)$ displays a discontinuity in its derivative $d\rho_\varepsilon/d\omega$ when ω assumes the critical value $\omega_c=\frac{1}{2}$. This behavior is observed also in exact calculations of the anisotropic dimer model on two-dimensional lattices with a coordination number equal to 3, such as the hexagonal lattice [1]. It may be mentioned that the critical value of ω for full-packed dimers on the Bethe lattice with $q=3$ is equal to the exact value on the hexagonal lattice.

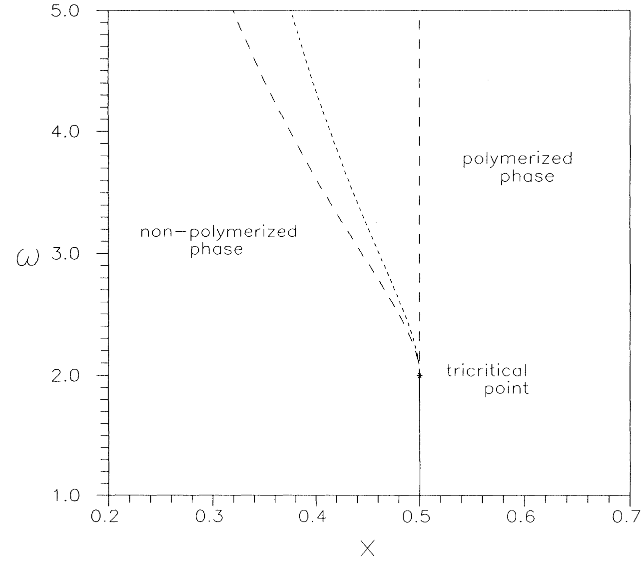

FIG. 5. Phase diagram for interacting polymers ($M\to\infty$) on a $q=3$ Bethe lattice, showing the second-order (full line) and first-order (dotted line) transition lines, as well as the spinodal lines (dashed lines).

In the case of polymers on the anisotropic Bethe lattice, we define four partial partition functions in a way similar to the preceding case of dimers. Analyzing the stability of the fixed points of the recursion relations, we find a polymerization transition at the critical activity

$$x_c=2\{(q-3+\omega)+[(q-3+\omega)+4\omega(q-1)]^{1/2}\}^{-1}\ . \tag{7}$$

The fixed points associated with the polymerized phase are given by non-negative roots of the polynomial

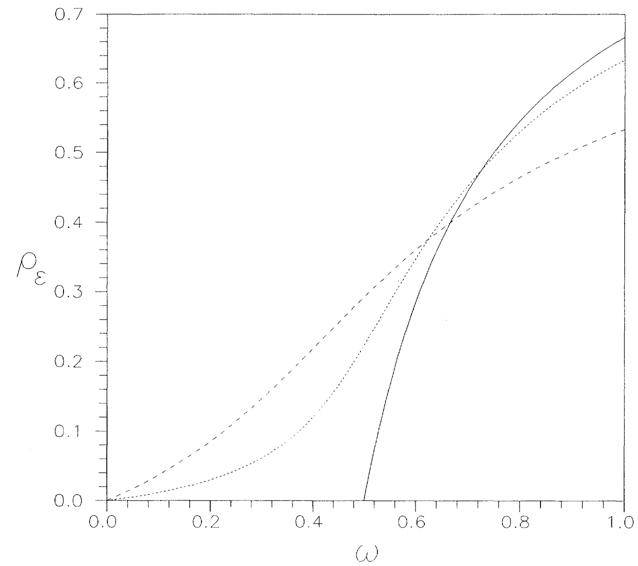

FIG. 6. Phase diagram for dimers ($M=2$) on an anisotropic Bethe lattice with $q=3$. Full line, $\rho=1$; dotted line, $\rho=0.95$; dashed line, $\rho=0.8$.

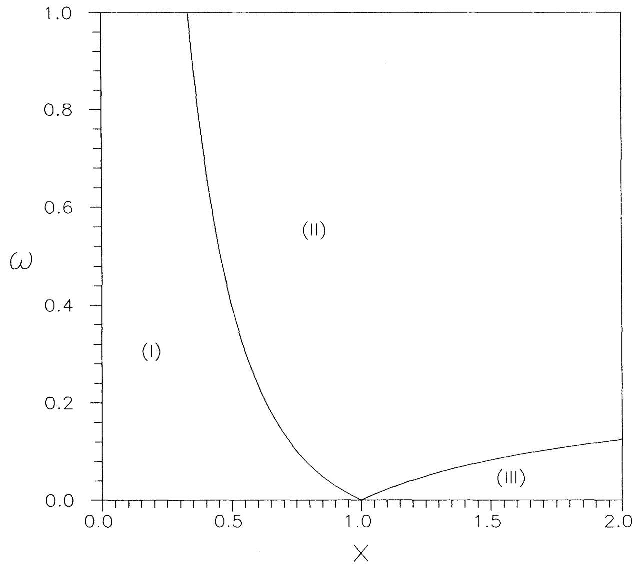

FIG. 7. Phase diagram for polymers ($M\rightarrow\infty$) on an anisotropic Bethe lattice with $q=4$. Phase I, nonpolymerized phase; phase II, usual polymerized phase; phase III, uniaxial polymerized phase.

$$P(\alpha)=\left[2\omega^{1/2}\alpha+q-3-\frac{1}{x}\right]\alpha A_1 - \left[\left[\omega-\frac{1}{x}\right]\alpha+\omega^{1/2}(q-2)\right]A_2\ , \tag{8}$$

where

$$A_1=\omega^{1/2}(q-2)\alpha+(q-2)(q-3)/2\ ,$$

$$A_2=\omega\alpha^2+2\omega^{1/2}(q-3)\alpha+(q-3)(q-4)/2\ .$$

For $q>4$, the polynomial $P(\alpha)$ admits only one nonnegative root, so that a single polymerized phase is found. When $q=4$, however, an additional root $\alpha=0$, for $\omega\neq 0$, is found in the fixed-point equation, thus signaling the appearance of another polymerized phase, where all bonds of the polymer lay on lattice bonds of type 2 (ground state). The corresponding phase diagram is given by Fig. 7, and the second-order transition line between polymerized phases is given by

$$\omega_c=\left[1-\frac{1}{x}\right]\Big/4\ .$$

In conclusion, we will make some comments on our results. The problem of semiflexible chains has attracted much attention recently [8], the main interest in these contributions being the scaling properties of semiflexible polymers. One relevant point is related to the dependence of the radius of gyration upon the molecular weight of the chain, as the flexibility of the chain is varied. Since, however, our calculations are done on the Bethe lattice, which is a lattice of infinite dimension [9], we were not able to calculate the radius of gyration directly. Nevertheless, it is worth mentioning that for infinite chains, the density $\rho(x)\simeq(x-x_c)$ for $q>2$, so that the critical exponent $\Delta_\rho=1$. Since $\Delta_\rho=1-\alpha$ and using the hyperscaling relation $d\nu=2-\alpha$ we get

$$\Delta_\rho=d\nu-1\ . \tag{9}$$

Therefore, our results, as expected, are consistent with the classical exponent $\nu=\frac{1}{2}$ for $d=4$.

The case of chains with attractive interactions between first neighbors for finite chains corresponds to a lattice gas of M-mers, a generalization of the Ising lattice gas which is recovered when $M=1$. As M is increased, the critical values of ω and x decrease and increase, respectively, and in the polymer limit $M\rightarrow\infty$ the critical point turns into a tricritical point.

Finally, for chains on an anisotropic lattice the appearance of two distinct polymerized phases when $q=4$ was quite surprising for us. One may ask if something similar happens on the square lattice or if in this case the Bethe-lattice solution of the model is qualitatively different from the behavior found on regular lattices. We are presently investigating this point.

We acknowledge partial financial support by the Brazilian agencies CNPq and CAPES.

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