

Kinetic model for a polymer in one dimension

José Arthur Martins* and Jürgen F. Stilck

Departamento de Física, Universidade Federal de Santa Catarina 88040-900 Florianópolis, Santa Catarina, Brazil

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We consider a model for a directed polymer on a one-dimensional lattice of width 2, with attractive interactions between monomers that occupy first-neighbor sites on the lattice and are not consecutive along the chain. We show that this model is equivalent to the one-dimensional Ising model with first- and second-neighbor interactions. We study the kinetic behavior of the model in the region of the phase diagram where the ground state is not frustrated, using a Glauber ansatz for the time evolution of the configurations. In order to decouple the dynamical equations, we use the pair approximation. In this approximation, we show that the dynamical exponent of the model is a function of the ratio between second- and first-neighbor interaction strengths.

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I. INTRODUCTION

Among the studies of the time evolution of statistical mechanical models, the classical work of Glauber [1] about the kinetic one-dimensional Ising model is one of the few examples where a closed solution could be obtained. On the other side, the time-dependent behavior of flexible long chain molecules (polymers) has attracted attention, from both the experimental and theoretical points of view for quite a long time, and the bead-and-spring model formulated by Rouse [2] should be mentioned in this context. The Rouse process seems to be one of the basic dynamical processes in polymer melts, besides reptation [3] and double reptation [4]. In the dynamical processes cited above, it is supposed that the configuration of the polymer chains changes in time, but no monomers are added or subtracted from the chain. An alternative theory has been proposed of chains that may break apart and reconnect [5], as happens for living polymers [6] and equilibrium polymerization [7]. Most of the models for the kinetic behavior of polymers have not been solved analytically, since they are too complex. Therefore, approximate solutions are one of the possible ways to study these models.

One may ask whether the Glauber model could be applied to describe a polymer model, in a rather simple situation. One possibility already studied in the literature is to consider a random walk in one dimension. Once a site of the lattice has been reached, there are two possibilities for the next step (left or right), and therefore a random walk may be mapped on a configuration of Ising spins, and the time evolution of such a model can be studied through a Glauber ansatz for the change of the configurations as a function of time [8]. In this paper we estab-

lish a mapping between a one-dimensional Ising model and a model for a polymer with excluded volume interactions. The polymer is modeled by a self-avoiding walk on a one-dimensional lattice of width two (see Fig. 1). Periodic boundary conditions are assumed in the transverse direction. It is supposed that a single walk crosses the whole lattice, starting from the left and ending on the right. Each monomer incorporated into the polymer will have an activity x associated with it, and we suppose the existence of an attractive interaction between monomers that are located on first-neighbor sites but are not consecutive monomers of the chain. So, to each pair of interacting monomers an energy ϵ is associated, corresponding to a Boltzmann weight $\omega = \exp[-\epsilon/k_B T]$. For attractive interactions $\omega \geq 1$.

The model we consider is a one-dimensional version of the model often used to study the collapse transition in poor solvents (SASAW: self-attracting self-avoiding walk) [9]. Actually, by solving a sequence of such models on strips of increasing widths L and using finite-size scaling methods to extrapolate the results to the two-dimensional limit $L \rightarrow \infty$, estimates for the location and exponents of the tricritical Θ point for the model on the square lattice were obtained [10]. One important difference between the SASAW model and the one we consider here is that we do not include the empty lattice configuration in our model, so that a nonpolymerized phase is excluded.

One experimental realization of the SASAW model may be found in sulfur solutions [7]. An appropriate

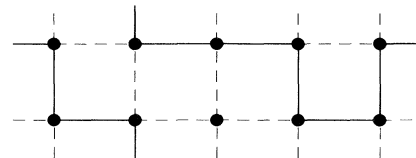


FIG. 1. A walk with 10 sites and statistical weight $x^9 \omega^2$.

*Present address: Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, 91500-970 Porto Alegre, Rio Grande do Sul, Brazil.

model for this case should consider the solvent explicitly, as was done in the equilibrium polymerization model proposed by Scott [11] and solved in the mean-field approximation [12] and on the Bethe lattice [13]. However, it was shown that a model where the solvent-monomer system is treated as an Ising lattice gas reduces to the SASAW model in an appropriate limit [14]. Therefore, the particular model we study here may be suited to describe a situation of equilibrium polymerization in a solvent when the solvent-monomer system is confined inside a thin pore. The static and dynamic properties of similar models were studied some time ago using scaling arguments [15].

For the model defined above, the proper partition function is

$$Y_N(x, \omega) = \sum_{n_p, n_b} \omega^{n_p} x^{n_b} \Gamma(n_p, n_b; N), \quad (1)$$

where n_p is the number of monomer pairs on first-neighbor sites that are not consecutive monomers along the chain, n_b is the number of bonds in the monomer, and $\Gamma(n_p, n_b; N)$ is the number of configurations of the polymer that share the same values of n_p and n_b , on a one-dimensional lattice of width 2 and a total number of sites N .

In Sec. II we calculate the partition function of the model, and show that it corresponds to a one-dimensional Ising model with first- and second-neighbor interactions (a one-dimensional version of the axial next-nearest-neighbor Ising model), which was solved some time ago [16]. In Sec. III we present the time evolution equations of the model, supposing that the evolution occurs through Glauber-like transitions of the configuration. For nonvanishing attractive interactions ϵ , which corresponds to nonvanishing second-neighbor interactions in the equivalent Ising model, we find out that the differential equations for the n -spin correlation functions are coupled, and we were not able to find an exact solution for them. For $\epsilon = 0$, Glauber's exact solution describes the kinetic behavior of the polymer model we consider. In order to decouple the equations, we use the pair approximation [17]. We then compare the stationary solution of the equations with the exact equilibrium solution of the model and calculate the dynamical critical exponent z . As might be expected, z is nonuniversal within the pair approximation, being a function of the ratio between first- and second-neighbor interaction strengths in the equivalent Ising model. Finally, we discuss the results and present our conclusions in Sec. IV.

II. EQUILIBRIUM SOLUTION AND CORRESPONDENCE WITH THE ISING MODEL

To solve the one-dimensional polymer model introduced above in equilibrium, we point out that the partition function Eq. (1) may be easily calculated through the transfer matrix method. We consider a pair of vertically aligned sites. The bonds incident on these sites (two vertical bonds and four horizontal half bonds) may

be in four different configurations, depicted in Fig. 2. The element of the transfer matrix between two states may be calculated considering the bonds of the polymer incident on each of the four sites involved, as well as the multiplicity of configurations |3) and |4). One should notice that the activity of each monomer is considered two times in successive steps of the transfer process. If the configurations of the two states are not compatible (such as configurations 1 and 2, for example), the corresponding transfer matrix element is zero. Some examples may be found in Fig. 2.

The transfer matrix is then given by

$$\mathbf{T} = \begin{pmatrix} x & 0 & \sqrt{2x^3} & 0 \\ 0 & x & 0 & \sqrt{2x^3} \\ 0 & \sqrt{2x^3} & 0 & 2\omega x^2 \\ \sqrt{2x^3} & 0 & 2\omega x^2 & 0 \end{pmatrix}, \quad (2)$$

and the partition function of the model is

$$Y_N = \text{Tr}(\mathbf{T}^{N/2}) = \lambda_1^{N/2}, \quad (3)$$

where λ_1 is the largest eigenvalue of \mathbf{T} ,

$$\lambda_1 = \frac{x[\sqrt{4\omega^2 x^2 - 4x(\omega - 2) + 1} + 2\omega x - 1]}{2}. \quad (4)$$

The model will exhibit a phase transition when the largest eigenvalue is degenerated, and we will discuss this possibility later.

Next, we show that the polymer model defined above is described by an effective one-dimensional Ising Hamiltonian. Let us associate an Ising spin $\sigma_i = \pm 1$ to each vertically aligned pair of horizontal bonds in the original lattice. Since the polymer spans the whole lattice, a

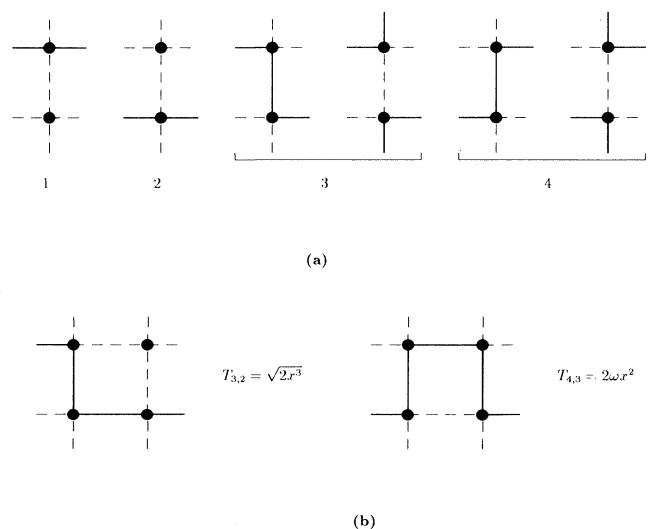


FIG. 2. (a) Configurations corresponding to the states of the transfer matrix for the polymer model. (b) Diagrams corresponding to some elements of the transfer matrix.

polymer bond will be located either on the upper or on the lower bond, and we associate the values $\sigma_i = +1$ and $\sigma_i = -1$ to these cases, respectively. Thus the locations of all horizontal polymer bonds are fixed if the values of the $N/2$ Ising spins are given. Now let us suppose that there are first- and second-neighbor interactions between the spins, defining the Hamiltonian

$$H(\sigma) = \frac{-J_1}{2} \sum_i^{N/2} (\sigma_i \sigma_{i+1} + \sigma_{i+1} \sigma_{i+2}) - J_2 \sum_i^{N/2} \sigma_i \sigma_{i+2} - J_0 \frac{N}{2}, \quad (5)$$

with periodic boundary conditions ($\sigma_{N/2+1} = \sigma_1$). The last term in the Hamiltonian, which was included to allow us to establish the correspondence between both models, is constant, thus having no influence on the thermodynamic properties.

The transfer matrix for this Ising model can be calculated defining a state by the configurations of two neighboring spins $|\sigma_i \sigma_{i+1}\rangle$; there are then four possible states, namely,

$$\begin{aligned} |1\rangle &= |++\rangle, |2\rangle = |--\rangle, \\ |3\rangle &= |+-\rangle, |4\rangle = |-+\rangle. \end{aligned} \quad (6)$$

So, the element M_{11} of the transfer matrix will be given by

$$M_{11} = \langle 1|1\rangle = \exp \left[\frac{K_1}{2} (\sigma_i \sigma_{i+1} + \sigma_{i+1} \sigma_{i+2}) + K_2 \sigma_i \sigma_{i+2} + K_0 \right], \quad (7)$$

where $K_i \equiv J_i/k_B T'$, T' being the temperature of the magnet, and $\sigma_i = \sigma_{i+1} = \sigma_{i+2} = 1$, with the result

$$M_{11} = \omega_0 \omega_1 \omega_2, \quad (8)$$

with $\omega_i \equiv \exp K_i$. M_{ij} vanishes if the common spin of states i and j does not have the same value. The transfer matrix is given by

$$\mathbf{M} = \begin{pmatrix} \omega_0 \omega_1 \omega_2 & 0 & \omega_0 \omega_2^{-1} & 0 \\ 0 & \omega_0 \omega_1 \omega_2 & 0 & \omega_0 \omega_2^{-1} \\ 0 & \omega_0 \omega_2^{-1} & 0 & \omega_0 \omega_1^{-1} \omega_2 \\ \omega_0 \omega_2^{-1} & 0 & \omega_0 \omega_1^{-1} \omega_2 & 0 \end{pmatrix}. \quad (9)$$

Comparing the transfer matrix for the polymer model Eq. (2) with the transfer matrix for the Ising model Eq. (9) we notice that they are identical if

$$\omega_1 = \frac{1}{\sqrt{2x\omega}}; \quad \omega_2 = \omega^{\frac{1}{2}}; \quad \omega_0 = x\omega^{-\frac{1}{2}} \sqrt{2x\omega}; \quad (10)$$

so that the thermodynamic properties of both models are the same if conditions in Eq. (10) are met.

In Fig. 3 the regions of different signs of the interac-

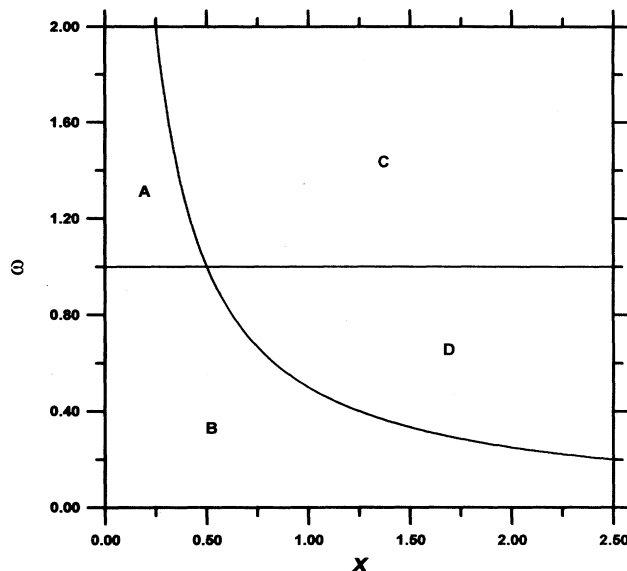


FIG. 3. Signs of the interactions J_1 and J_2 of the Ising model for different values of the parameters x and ω of the polymer. In regions A and B we have $J_1 > 0$ and in regions A and C $J_2 > 0$ in the corresponding Ising model. In regions B and D of the diagram the ground state is frustrated.

tions J_1 and J_2 in the Ising model are shown, as functions of the polymer variables x and ω . It should be stressed that we will restrict ourselves to the case where the interactions among monomers in first-neighbor sites are attractive ($\omega \geq 1$), and therefore consider $J_2 \geq 0$, which ensures that the ground state of the Ising model is not frustrated.

The correlation length ξ may be calculated through

$$\xi = [\ln(\lambda_1/\lambda_2)]^{-1}, \quad (11)$$

where λ_1 and λ_2 are the largest and second-largest eigenvalues of the transfer matrix, respectively. If we define the parameter α through $\omega_2 = \omega_1^\alpha$, so that $\alpha = J_2/J_1$ in the Ising model, we can write the correlation length as

$$\xi = \left[\ln \left(\frac{\sqrt{1-a} + 1 + \omega_1^{-2}}{\sqrt{1+b} + 1 - \omega_1^{-2}} \right) \right]^{-1}, \quad (12)$$

where

$$a \equiv 2\omega_1^{-2} - \omega_1^{-4} - 4\omega_1^{-2(2\alpha+1)},$$

and

$$b \equiv 2\omega_1^{-2} + \omega_1^{-4} - 4\omega_1^{-2(2\alpha+1)}.$$

When $T' \rightarrow 0$ we notice that

$$\xi \simeq 2\omega_1^{2(1+2|\alpha|)}. \quad (13)$$

Considering the mapping given by Eq. (10), between the equilibrium polymerization model and the Ising model, we may discuss the phase transition in the polymer model which corresponds to the transition at $T' \rightarrow 0$ in the Ising model. The nature of the transition may be ferromagnetic or antiferromagnetic, depending on the sign of J_1 . For $J_1 < 0$ and $J_2 > 0$, a para-antiferromagnetic transition occurs when $\omega_1 \rightarrow 0$ and $\omega_2 \rightarrow \infty$. In the polymer model, this corresponds to $\omega \rightarrow \infty$ and $x \neq 0$. The antiferromagnetic ground state in the Ising model corresponds to a configuration in the polymer model where every site of the lattice is incorporated into the polymer. Thus, the transition we are considering here is between two polymerized phases. It may be recalled that exact calculations on the $n \rightarrow 0$ model with two- and four-spin interactions on the square lattice, which is related to a two-dimensional version of the model we are considering, also lead to a phase diagram with two different polymerized phases and a transition between them [18].

III. TIME EVOLUTION OF THE MODEL

We now study the time evolution of the model, starting with an arbitrary configuration of the spin variables and letting it evolve to equilibrium. Thus we suppose the $N/2$ Ising spins to be stochastic variables of time $\sigma_i(t)$, $i = 1, 2, \dots, N/2$. Therefore, the configuration of the model evolves in time through the flipping of individual spins. It should be noted that the flipping of a spin corresponds to changing the horizontal bond through which the polymer chain passes, thus polymer bonds are broken and others are formed in this process and the configuration of the polymer evolves through reversible chain-scission reactions, as in the process proposed by Cates [5]. Also, since we consider that the polymer chain crosses the whole lattice, our formalism does not take into account the dynamics of the longitudinal motion of the chain in the pore [19]. The transition probabilities of individual spins are functions of the spin values, of the values of first- and second-neighbor spins, and of the temperature T' of the heat bath. Defining $w(\sigma_i)$ as the probability, per time unit, that spin i changes its value from σ_i to $-\sigma_i$, we obtain

$$\frac{dP(\sigma_1, \sigma_2, \dots, \sigma_{N/2}, t)}{dt} = - \sum_i w_i(\sigma_i) P(\sigma_1, \dots, \sigma_i, \dots, \sigma_{N/2}, t) + \sum_i w_i(-\sigma_i) P(\sigma_1, \dots, -\sigma_i, \dots, \sigma_{N/2}, t), \quad (14)$$

which is the master equation of the process.

When the system reaches equilibrium, at a given temperature T' , the probability of any configuration should be proportional to the Boltzmann factor $P(\{\sigma\}) \propto \exp[-H(\{\sigma\})/k_B T']$, where $H(\{\sigma\})$ is the Hamiltonian of the system and $\{\sigma\}$ denotes a configuration of the spins. Substitution of the Hamiltonian, Eq. (5) into Eq. (14) leads to

$$\frac{P(-\sigma_i)}{P(\sigma_i)} = \frac{1 - \sigma_i \tanh[K_1(\sigma_{i-1} + \sigma_{i+1}) + K_2(\sigma_{i-2} + \sigma_{i+2})]}{1 + \sigma_i \tanh[K_1(\sigma_{i-1} + \sigma_{i+1}) + K_2(\sigma_{i-2} + \sigma_{i+2})]}. \quad (15)$$

If all spins, with the exception of σ_i , are considered fixed, and if the stochastic model is to approach the equilibrium distribution as $t \rightarrow \infty$ (stationary state), the transition rates in Eq. (14) should obey detailed balance

$$\frac{P(-\sigma_i)}{P(\sigma_i)} = \frac{w_i(\sigma_i)}{w_i(-\sigma_i)}, \quad (16)$$

and this will be the case if we choose

$$w_i(\sigma_i) = \frac{\mu}{2} \{1 - \sigma_i \tanh[K_1(\sigma_{i-1} + \sigma_{i+1}) + K_2(\sigma_{i-2} + \sigma_{i+2})]\}. \quad (17)$$

The parameter μ fixes the time scale of the transitions.

It should be remarked that if we consider the transition rate proposed by Glauber [Eq. (115) of Ref. [1]] for the one-dimensional Ising model with interactions beyond first neighbors, we get

$$w_i(\sigma_i) = \frac{\mu}{2} \left\{ 1 - \frac{\sigma_i}{2} [\tanh K_1(\sigma_{i-1} + \sigma_{i+1}) + \tanh K_2(\sigma_{i-2} + \sigma_{i+2})] \right\}, \quad (18)$$

and this transition rate, although being linear in the spins and therefore allowing an exact solution of the time evolution of the model, does not lead to an equilibrium distribution in the stationary state [20].

The transition rate, Eq. (17), may be rewritten as

$$w_i(\sigma_i) = \frac{\mu}{2} \left\{ 1 - \frac{\sigma_i}{2} [A(\sigma_{i-1} + \sigma_{i+1}) + B(\sigma_{i-2} + \sigma_{i+2}) + C\sigma_{i-2}\sigma_{i+2}(\sigma_{i-1} + \sigma_{i+1}) + D\sigma_{i-1}\sigma_{i+1}(\sigma_{i-2} + \sigma_{i+2})] \right\}, \quad (19)$$

where

$$\begin{aligned}
A &= (\rho + \gamma + 2\eta)/4, \\
B &= (\rho - \gamma + 2\delta)/4, \\
C &= (\rho + \gamma - 2\eta)/4, \\
D &= (\rho - \gamma - 2\delta)/4,
\end{aligned} \tag{20}$$

and

$$\begin{aligned}
\rho &= \tanh(2K_1 + 2K_2), \\
\gamma &= \tanh(2K_1 - 2K_2), \\
\eta &= \tanh(2K_1), \\
\delta &= \tanh(2K_2).
\end{aligned} \tag{21}$$

We now define the mean values

$$\langle \sigma_i \sigma_j \cdots \sigma_n \rangle(t) = \sum_{\{\sigma\}} \sigma_i \sigma_j \cdots \sigma_n P(\{\sigma\}, t). \tag{22}$$

Through the master equation we can then find the evolution equations of the mean values. Let us concentrate on one- and two-spin terms, restricting the latter case to first- and second-neighbor pairs. The results for the mean values are

$$\begin{aligned}
\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \rangle &= -\langle \sigma_i \rangle + \frac{A}{2} \langle \sigma_{i-1} + \sigma_{i+1} \rangle + \frac{B}{2} \langle \sigma_{i-2} + \sigma_{i+2} \rangle \\
&\quad + \frac{C}{2} \langle \sigma_{i-2} \sigma_{i+2} (\sigma_{i-1} + \sigma_{i+1}) \rangle + \frac{D}{2} \langle \sigma_{i-1} \sigma_{i+1} (\sigma_{i-2} + \sigma_{i+2}) \rangle,
\end{aligned} \tag{23}$$

$$\begin{aligned}
\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \sigma_{i+1} \rangle &= -2 \langle \sigma_i \sigma_{i+1} \rangle + \frac{D}{2} \langle \sigma_{i-2} \sigma_{i-1} + 2 \sigma_{i-1} \sigma_{i+2} + \sigma_{i+2} \sigma_{i+3} \rangle \\
&\quad + \frac{C}{2} \langle \sigma_{i-2} \sigma_{i-1} \sigma_{i+1} \sigma_{i+2} + \sigma_{i-2} \sigma_{i+2} + \sigma_{i-1} \sigma_{i+3} + \sigma_{i-1} \sigma_i \sigma_{i+2} \sigma_{i+3} \rangle \\
&\quad + \frac{A}{2} \langle \sigma_{i-1} \sigma_{i+1} + \sigma_i \sigma_{i+2} \rangle + A + \frac{B}{2} \langle \sigma_{i-2} \sigma_{i+1} + \sigma_{i+1} \sigma_{i+2} + \sigma_{i-1} \sigma_i + \sigma_i \sigma_{i+3} \rangle,
\end{aligned} \tag{24}$$

and

$$\begin{aligned}
\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \sigma_{i+2} \rangle &= -2 \langle \sigma_i \sigma_{i+2} \rangle + \frac{D}{2} \langle \sigma_{i-2} \sigma_{i-1} \sigma_{i+1} \sigma_{i+2} + \sigma_{i-1} \sigma_{i+1} + \sigma_{i+1} \sigma_{i+3} + \sigma_i \sigma_{i+1} \sigma_{i+3} \sigma_{i+4} \rangle \\
&\quad + \frac{C}{2} \langle \sigma_{i-2} \sigma_{i-1} + \sigma_{i-2} \sigma_{i+1} + \sigma_{i+1} \sigma_{i+4} + \sigma_{i+3} \sigma_{i+4} \rangle \\
&\quad + \frac{A}{2} \langle \sigma_{i-1} \sigma_{i+2} + \sigma_{i+1} \sigma_{i+2} + \sigma_i \sigma_{i+1} + \sigma_i \sigma_{i+3} \rangle + \frac{B}{2} \langle \sigma_{i-2} \sigma_{i+2} + \sigma_i \sigma_{i+4} \rangle + B.
\end{aligned} \tag{25}$$

We notice that for $J_2 = 0$, when $A = (1/2) \tanh(2K_1) = \eta/2$, $B = C = D = 0$, the equations reduce to

$$\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \rangle = -\langle \sigma_i \rangle + \frac{\eta}{2} \langle \sigma_{i-1} + \sigma_{i+1} \rangle, \tag{26}$$

$$\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \sigma_{i+1} \rangle = -2 \langle \sigma_i \sigma_{i+1} \rangle + \frac{\eta}{2} \langle 2 + \sigma_{i-1} \sigma_{i+1} + \sigma_i \sigma_{i+2} \rangle, \tag{27}$$

and

$$\frac{1}{\mu} \frac{d}{dt} \langle \sigma_i \sigma_{i+2} \rangle = -2 \langle \sigma_i \sigma_{i+2} \rangle + \frac{\eta}{2} \langle \sigma_{i-1} \sigma_{i+2} + \sigma_{i+1} \sigma_{i+2} + \sigma_i \sigma_{i+1} + \sigma_i \sigma_{i+3} \rangle. \tag{28}$$

These equations were solved exactly by Glauber [1]. Also, as expected, similar equations are obtained when $J_1 = 0$, since in this limit the model decouples into two interpenetrating chains.

The coupling of the time evolution equations in the general case (the equation for the time evolution of the mean value of one spin has mean values of three spins in the right-hand side and so on), does not allow us to solve them by the same technique used by Glauber for the $J_2 = 0$ case. To find approximate solutions, we define two sublattices 1 and 2 in such a way that first-neighbor spins belong to different sublattices and restrict ourselves to solutions where the mean value of *any* spin belonging

to sublattice 1 (2) is equal to m_1 (m_2), the mean value of a product of any two first-neighbor spins is equal to r_3 and the mean value of any pair of second-neighbor spins belonging to sublattice 1 (2) is equal to r_1 (r_2). If we call $P(\sigma_i^{(1)})$ the probability that the spin $\sigma_i^{(1)}$, located at a site i of sublattice 1, has the specified value, then

$$P(\sigma_i^{(1)}) = (1 + m_1 \sigma_i^{(1)})/2, \tag{29}$$

and similar expressions are found for other probabilities of one and two spins. The results are

$$P(\sigma_i^{(2)}) = (1 + m_2\sigma_i^{(2)})/2; \quad (30)$$

$$P(\sigma_i^{(1)}, \sigma_{i+1}^{(2)}) = (1 + m_1\sigma_i^{(1)} + m_2\sigma_{i+1}^{(2)} + r_3\sigma_i^{(1)}\sigma_{i+1}^{(2)})/4; \quad (31)$$

$$P(\sigma_i^{(1)}, \sigma_{i+2}^{(1)}) = (1 + m_1\sigma_i^{(1)} + m_1\sigma_{i+2}^{(1)} + r_1\sigma_i^{(1)}\sigma_{i+2}^{(1)})/4; \quad (32)$$

$$P(\sigma_i^{(2)}, \sigma_{i+2}^{(2)}) = (1 + m_2\sigma_i^{(2)} + m_2\sigma_{i+2}^{(2)} + r_2\sigma_i^{(2)}\sigma_{i+2}^{(2)})/4. \quad (33)$$

Now, using the pair approximation [17], we reduce configuration probabilities of larger clusters to the ones indicated above, decoupling the time evolution equations (23)–(25). Let us illustrate these calculations with a specific example, considering the approximate calculation of $P(\sigma_{i-2}^{(1)}, \sigma_{i-1}^{(2)}, \sigma_{i+1}^{(2)})$. Using the pair approximation, we may write $P(\sigma_{i-2}^{(1)}, \sigma_{i-1}^{(2)}, \sigma_{i+1}^{(2)}) \approx P(\sigma_{i-1}^{(2)})P(\sigma_{i+1}^{(2)}|\sigma_{i-1}^{(2)})P(\sigma_{i-2}^{(1)}|\sigma_{i-1}^{(2)})$, where $P(\sigma_i|\sigma_j)$ is the conditional probability of σ_i for a fixed value of σ_j . Using the identity $P(\sigma_i, \sigma_j) = P(\sigma_j)P(\sigma_i|\sigma_j)$, we get the result

$$P(\sigma_{i-2}^{(1)}, \sigma_{i-1}^{(2)}, \sigma_{i+1}^{(2)}) \approx \frac{P(\sigma_{i-1}^{(2)})P(\sigma_{i-2}^{(1)}, \sigma_{i+1}^{(2)})}{P(\sigma_{i-1}^{(2)})}.$$

Now this result may be applied to calculate a term that appears in Eq. (23). Writing

$$\langle \sigma_{i-2}^{(1)}\sigma_{i-1}^{(2)}\sigma_{i+1}^{(2)} \rangle = \sum_{\{\sigma\}} \sigma_{i-2}^{(1)}\sigma_{i-1}^{(2)}\sigma_{i+1}^{(2)}P(\sigma_{i-2}^{(1)}, \sigma_{i-1}^{(2)}, \sigma_{i+1}^{(2)}),$$

and performing the sum using the approximate expression for the cluster probability, we may express the result in terms of the probabilities expressed in Eqs. (29)–(33). The result is

$$\langle \sigma_{i-2}^{(1)}\sigma_{i-1}^{(2)}\sigma_{i+1}^{(2)} \rangle \approx \frac{r_2(m_2r_3 - m_1) - m_2(r_3 - m_1m_2)}{m_2^2 - 1}. \quad (34)$$

Performing similar approximations on the other mean values of products of spins appearing in Eqs. (23)–(25) we finally get the following dynamical equations

$$\frac{1}{\mu} \frac{d}{dt} m_1 = -m_1 + Am_2 + Bm_1 + Cm_1r_3 + D \left(\frac{r_2(m_2r_3 - m_1) - m_2(r_3 - m_1m_2)}{m_2^2 - 1} \right), \quad (35)$$

$$\frac{1}{\mu} \frac{d}{dt} m_2 = -m_2 + Am_1 + Bm_2 + Cm_2r_3 + D \left(\frac{r_1(m_1r_3 - m_2) - m_1(r_3 - m_1m_2)}{m_1^2 - 1} \right), \quad (36)$$

$$\begin{aligned} \frac{1}{\mu} \frac{d}{dt} r_1 = & -2r_1 + \frac{D}{2} \left[2r_2 - \frac{2m_1^2(m_2^2 - r_2) - 4r_3m_1m_2(m_2^2 - r_2) - 2r_3^2(m_2^2(r_2 - 2) + 1)}{(1 - m_2^2)^2} \right] \\ & + \frac{A + C}{2} \left[2r_3 + \frac{m_2m_1 + r_2r_3 - m_2^2r_3 - m_1m_2r_2}{1 - m_2^2} + \frac{m_2m_1 + r_1r_3 - m_2^2r_3 - m_1m_2r_2}{1 - m_1^2} \right] \\ & + \frac{B}{2} \left[\frac{2m_1^2 + 2r_1^2 - 4r_1m_1^2}{1 - m_1^2} \right] + B, \end{aligned} \quad (37)$$

$$\begin{aligned} \frac{1}{\mu} \frac{d}{dt} r_2 = & -2r_2 + \frac{D}{2} \left[2r_1 - \frac{2m_2^2(m_1^2 - r_1) - 4r_3m_1m_2(m_1^2 - r_1) - 2r_3^2[m_1^2(r_1 - 2) + 1]}{(1 - m_1^2)^2} \right] \\ & + \frac{A + C}{2} \left[2r_3 + \frac{m_2m_1 + r_1r_3 - m_2^2r_3 - m_1m_2r_1}{1 - m_1^2} + \frac{m_2m_1 + r_2r_3 - m_2^2r_3 - m_1m_2r_1}{1 - m_2^2} \right] \\ & + \frac{B}{2} \left[\frac{2m_2^2 + 2r_2^2 - 4r_2m_2^2}{1 - m_2^2} \right] + B, \end{aligned} \quad (38)$$

$$\begin{aligned} \frac{1}{\mu} \frac{d}{dt} r_3 = & -2r_3 + \frac{D}{2} \left[2r_3 + \frac{m_2m_1 + r_2r_3 - m_2^2r_3 - m_1m_2r_2}{1 - m_2^2} + \frac{m_2m_1 + r_1r_3 - m_2^2r_3 - m_1m_2r_1}{1 - m_1^2} \right] \\ & + \frac{C}{2} \left[\frac{m_1^2 + r_1^2 - 2r_1m_1^2}{1 - m_1^2} - \frac{m_2^2(m_1^2 - r_1) - 2r_3m_1m_2(m_1^2 - r_1) - r_3^2[m_1^2(r_1 - 2) + 1]}{(1 - m_1^2)^2} \right] \\ & + \frac{m_2^2 + r_2^2 - 2r_2m_2^2}{1 - m_2^2} - \frac{m_1^2(m_2^2 - r_2) - 2r_3m_1m_2(m_2^2 - r_2) - r_3^2[m_2^2(r_2 - 2) + 1]}{(1 - m_2^2)^2} \\ & + \frac{B}{2} \left[2r_3 + \frac{m_1m_2 + r_2r_3 - m_2^2r_3 - m_1m_2r_2}{1 - m_1^2} + \frac{m_1m_2 + r_1r_3 - m_2^2r_3 - m_1m_2r_1}{1 - m_1^2} \right] \\ & + \frac{A}{2}(r_1 + r_2) + A. \end{aligned} \quad (39)$$

The solution of these coupled equations for given initial values of m_1 , m_2 , r_1 , r_2 , and r_3 determines the time evolution of the densities, within the pair approximation. Let us consider the steady state at $t \rightarrow \infty$, where all time derivatives in Eqs. (35)–(39) vanish. As expected, we obtain from Eqs. (35) and (36) that $m_1^* = \lim_{t \rightarrow \infty} m_1(t) = 0$ and $m_2^* = 0$ in this state. Using this result in the remaining three equations we find that $r_1^* = r_2^*$ and

$$-2r_2^* + D[r_2^* + (r_3^*)^2] + (A + C)(r_3^* + r_2^*r_3^*) + B[1 + (r_2^*)^2] = 0; \quad (40)$$

$$-2r_3^* + (B + D)(r_3^* + r_2^*r_3^*) + C[(r_2^*)^2 + (r_3^*)^2] + A(1 + r_2^*) = 0. \quad (41)$$

The numerical solution of this pair of equations for r_2 and r_3 may be compared with the exact expression for the correlations found by Stephenson [16]. One example of this comparison is shown in Fig. 4. It should be stressed that for $\alpha = 0$ the correlations obtained through Eqs. (40) and (41) are exact.

The dynamical critical exponent z is defined in the vicinity of the critical temperature $T_c = 0$ through the relation

$$\tau \approx A\xi^z, \quad (42)$$

where A is a constant and τ is the relaxation time that characterizes the evolution of the system towards equilibrium. For the one-dimensional Ising model with first-neighbor interactions only it was shown that $z = 2$. Some generalizations of this model, such as a model with alternating first-neighbor interactions J_1 and J_2 , may present a value for z that is a function of the ratio J_1/J_2 , and therefore nonuniversal behavior of the dynamical critical exponent is observed [21]. So, we studied the value of z as a function of α , for small values of the second-neighbor interaction, that is, for $\alpha \approx 0$. We consider Eqs. (35)–(39) and linearize them in the deviations of $m_{1,2}$ and $r_{1,2,3}$ from their steady-state values, that is, $\delta m_{1,2}(t) = m_{1,2}(t)$ and $\delta r_{1,2,3}(t) = r_{1,2,3}(t) - r_{1,2,3}^*$. The result for the sublattice magnetizations is

$$\frac{1}{\mu} \frac{d}{dt} \delta m_{1,2} = (B - 1 + Cr_3^* + Dr_{2,1}^*) \delta m_{1,2} + (A - Dr_{2,1}^*r_3^* + Dr_3^*) \delta m_{2,1}, \quad (43)$$

and up to first order in the deviations of the steady-state values the equations for the magnetizations do not depend on $\delta r_{1,2,3}$. Defining the relaxation time τ through

$$\delta m_{1,2} = A_{1,2} \exp(-t/\tau),$$

we may substitute this expression into Eq. (43) and find that there is a nontrivial solution if we choose

$$\frac{1}{\mu\tau} = 1 - A - B - Cr_3^* + D(r_2^*r_3^* - r_2^* - r_3^*). \quad (44)$$

Proceeding with the calculation up to first order in α we notice that

$$\begin{aligned} A &\simeq \tanh(2K_1), \\ B &\simeq [2 - \tanh^2(2K_1)]K_1\alpha, \\ C &\simeq 0, \\ D &\simeq -k_1 \tanh^2(2K_1)\alpha, \end{aligned}$$

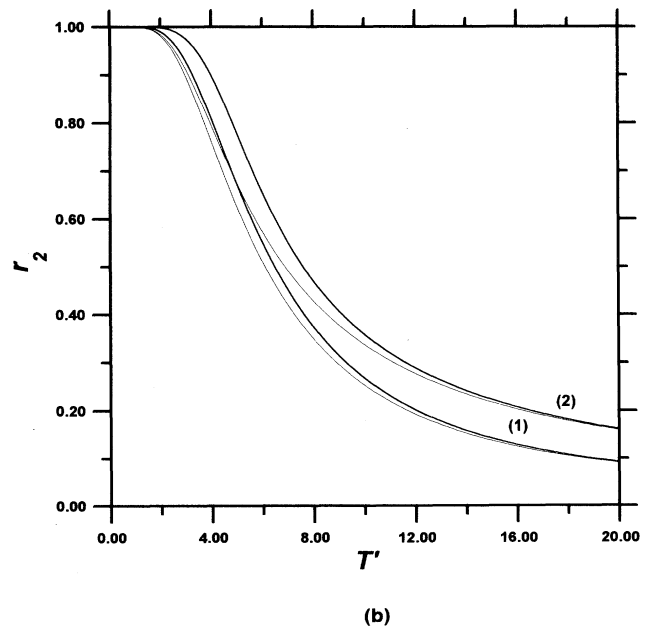
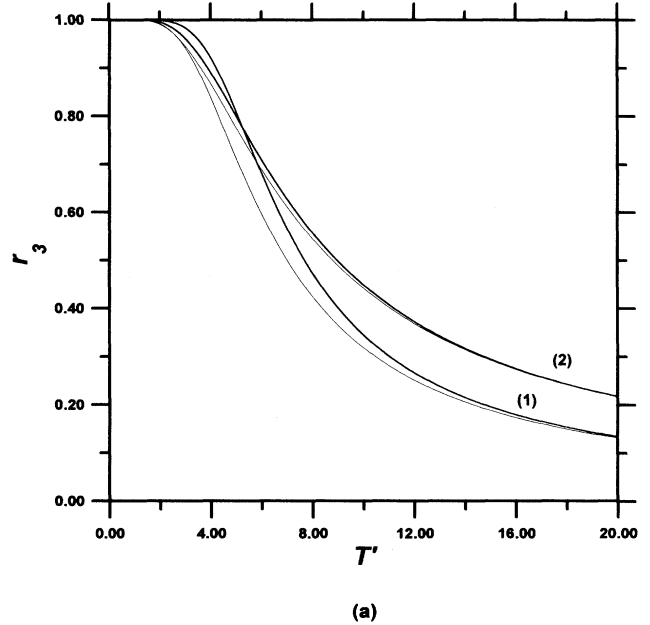


FIG. 4. (a) First- and (b) second-neighbor correlations as functions of $T' \equiv k_B T/J_1$ for $\alpha = 0.25$ (1) and $\alpha = 1.5$ (2). Exact results (thick lines) and results obtained through the pair approximation (thin lines) are shown.

so that only the zeroth-order terms in α are needed for the pair correlations

$$\begin{aligned} r_2^* &\simeq \tanh^2 K_1, \\ r_3^* &\simeq \tanh K_1. \end{aligned}$$

So we can calculate $\mu\tau$ to first order in α . Since for the calculation of the dynamical exponent all we need is the behavior of the relaxation time τ in the vicinity of $T' = T'_c = 0$ we expand the hyperbolic tangents above and get

$$\mu\tau \simeq (1 + 8K_1\alpha) \frac{\omega_1^{-4}}{2}. \quad (45)$$

Finally, recalling the asymptotic expression for the correlation length from Eq. (13), as well as the definition of the dynamical critical exponent z in Eq. (42), we conclude that

$$z = 2 + 4|\alpha|; \quad (46)$$

so that, at least within the pair approximation used to decouple the time evolution equations, the dynamical exponent is a function of the ratio α between first- and second-neighbor interactions.

IV. CONCLUSION

It should be stressed that the phase transition in the original polymer model that corresponds to the transition at $T' \rightarrow 0$ in the corresponding one-dimensional Ising model has no relation to the usual equilibrium polymerization transition, which is a first-order transition in one-dimensional lattices [22]. The equilibrium polymerization transition occurs between a nonpolymerized phase and a polymerized phase, whereas in the transi-

tion we are considering here no non-polymerized phase is present. The paramagnetic state of the Ising model corresponds to a disordered state of the polymer, in the sense that the bonds of the polymer are not ordered with respect of the two possibilities (upper or lower bond) of their configuration at each horizontal step. The ferromagnetic or antiferromagnetic ground states correspond to ordered configurations of the polymer also. In particular, as was indicated above, the para-antiferromagnetic transition in the Ising model may be physically understood in the polymer model as an effect of the attractive interactions between the monomers.

The dependence of the dynamical critical exponent z upon the details of the Hamiltonian is not surprising. It seems that the universality of this exponent is much weaker than the one observed usually for the static critical exponents. It may be recalled that a one-dimensional kinetic Ising model with *alternating* interaction strengths J_1 and J_2 is exactly solvable and its dynamical critical exponent is a function of the ratio J_2/J_1 [21].

Finally, the calculations presented here could be generalized for a directed polymer model on a lattice with arbitrary width L . In this case the corresponding magnetic model should be related to a L -state Potts model. The two-dimensional static model of directed polymers, corresponding to $L \rightarrow \infty$ is exactly solvable [23], but the corresponding kinetic model seems to be much harder to handle.

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