Dynamics of a one-dimensional "glass" model: Ergodicity and nonexponential relaxation

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We study numerically the dynamical behavior of a chain of classical particles with competing and anharmonic interactions. Although this model possesses a complex potential-energy landscape with exponentially many metastable configurations, we find ergodic behavior at all temperatures we investigated. Ergodicity is tested with respect to several correlation functions of pseudospins, the spins describing the configurational degrees of freedom of the chain. The time dependence of the autocorrelation function is consistent with a stretched exponential for intermediate times with exponents between 0.6 and 0.75. The corresponding relaxation times fit very well with an Arrhenius law. Within a transition-state approach, it is shown that the relaxation dynamics can be described by a kinetic Ising model. The consequence of this result on the autocorrelation function and the central peak is discussed.

I. INTRODUCTION

Although the notion of ergodicity is one of the cornerstones of statistical mechanics, the systems having rigorously been proven to be ergodic are few and most of them have only a small number of degrees of freedom. This unpleasant state reflects the fact that it is almost always very difficult to prove or disprove analytically whether a system is ergodic. Therefore a lot of work has been done to test ergodicity numerically.

The seminal work for a many-particle system was done in the 1950s by Fermi, Pasta, and Ulam (FPU) (see Ref. 1). They numerically integrated the equations of motion for a chain of classical particles with anharmonic nearest-neighbor interactions. To their surprise they found the system *not* to behave in an ergodic manner at all, despite the presence of anharmonicities. Although a large amount of effort has been invested since then, it seems to be very difficult to decide whether this breaking of ergodicity is true, or perhaps merely an artifact of not having extended the simulations to sufficiently long times.[2-5] Thus this question is not yet settled. In this respect it is instructive to keep in mind a theorem by Nekhoroshev.[6] This theorem states that a solution of a nonintegrable system with Hamiltonian H does not deviate from the solution of the integrable system by more than $O(\epsilon^{\alpha})$ for all times less than $O(\exp(1/\epsilon^{\beta}))$, provided H satisfies some technical conditions. Here ϵ is a measure of the nonintegrability and α and β are model-dependent constants. Thus, for systems with weak nonintegrabilities (as, e.g., the FPU model at low energies), this can lead to very large times within which it is very difficult to decide whether or not the system behaves ergodically.[7] Very recently Pettini and Landolfi gave strong evidence that, for the FPU model and a ϕ^4 model, such a divergence as predicted by Nekhoroshev really exists.[8] But although other systems besides the FPU model have also been studied with respect to ergodicity,[9,10] no clear picture has emerged as of today.

Ergodicity itself is just the lowest level in the hierarchy of statistical behavior of dynamical systems.[11] Mixing is the next higher level and means that a correlation function $\langle A(t)B(0)\rangle - \langle A\rangle\langle B\rangle$ goes to zero for $t\to\infty$. These two properties were also used recently to describe the glass transition.[12,13] It is speculated that at the glass transition temperature the undercooled liquid freezes into a nonergodic state with density fluctuations relaxing to a nonzero value. This interpretation has been strongly supported by the mode-coupling theory (see, e.g., Refs. 14 and 15). For a review of this theory the reader is referred to Ref. 16.

Besides the ergodic behavior, the time dependence of the relaxation functions is also of interest. For most disordered materials a nonexponential relaxation (non-Debye relaxation) is found,[13,17,18] and very often a relaxation function $\phi(t)$ can be fitted by a Kohlrausch-Williams-Watts (KKW) law, also called "stretched exponential,"[19], i.e.,

$$\phi(t)=\exp\left[-\left[\frac{t}{\tau}\right]^{\beta}\right] \quad \text{with } 0<\beta<1 \ . \tag{1}$$

A value of β between 0.5 and 0.7 is common for structural glasses[20] and the relaxation time τ often exhibits an Arrhenius behavior near the glass transition temperature. However, the reader should notice that many data sets stemming from experiments as well as from simulations can be fitted only by a KWW law in an intermediate range (e.g., $0.99\geq\phi(t)\geq 0.01$).[20] For short times, transients resulting from microscopic time scales can lead to a different behavior, while for long times it is usually difficult to determine the correct relaxation behavior from experimental data and even more difficult from numerical simulations.

Despite the abundance of experimental systems showing non-Debye relaxation, it is not yet entirely clear what the relevant microscopic mechanisms are which lead to this behavior. But it is widely accepted that *cooperative effects* play a major role. For details the reader is referred to Refs. 20–22.

It is interesting that simple models like Glauber's one-dimensional kinetic Ising model[23] or the facilitated kinetic Ising model[24] exhibit also nonexponential relaxation. For the usual Glauber dynamics the spin autocorrelation function $C(t)$ in the region $0.1 < C(t) \leq 1$ can be fitted with the KWW law,[25] whereas for $t \to \infty$ it behaves as $C(t) \sim t^{-1/2} \exp(-t/\tau)$. There does exist another special case of the general Glauber model for which $C(t)$ is known exactly. For this case the domain walls between "up" and "down" domains can undergo only a diffusive motion and cannot be created or annihilated. The corresponding autocorrelation function for large times is also given by a KWW law with $\beta = \frac{1}{2}$.[26,27] For the Glauber model with the most general transition rates fulfilling the condition of detailed balance, the autocorrelation function is not known exactly. Various semianalytical results again show a stretched exponential behavior for times not too large,[25,28] but the significance of these fits is not clear since the considered time range t/τ is at most two orders of magnitude.

The relaxation behavior is also interesting from a different point of view. The Fourier transform $S(q,\omega)$ of the correlation function $\langle x_i(t)x_j(0)\rangle - \langle x_i\rangle^2$ [$x_i(t)$ is the position of the ith particle] for a one-dimensional harmonic chain with a symmetric double-well potential acting on each particle was investigated by several authors.[29-31] These authors found a central peak for low temperatures. Its existence is related to the occurrence of motions on a rather long-time scale associated with domain wall motion.[30]

It is the purpose of this paper to investigate these properties, i.e., ergodicity and relaxation behavior, for a one-dimensional model for disorder. This model does not exhibit a phase transition at nonzero temperature and it is unclear whether a one-dimensional system can show a real dynamical transition in the sense described by Götze.[16] However, glasslike metastable states may exist with finite but rather long lifetimes at very low temperatures. For this model, which is a chain of classical particles with anharmonic and competing interactions, we have recently studied the static behavior.[32,33] The model exhibits a complex potential-energy landscape and the main outcome has been the one-to-one correspondence (under certain conditions for the parameters of the potential) between *all* metastable configurations and *all* sequences $\sigma = \{\sigma_i\}$ of Ising spins (pseudospins) $\sigma_i = \pm 1$. This result was used to prove that the pair distribution function and the low-temperature specific heat behavior is like that of glassy systems. In this paper we will extend these investigations to dynamical properties. The fact that the vibrational (phonons) and configurational degrees of freedom (described by the Ising spins) can be separated from each other exactly for our model will turn out to be crucial. Particularly at low temperatures (compared to the minimum barrier height) the dynamics of the Ising spins becomes very slow. Besides this it can be shown that for low energies the energy hypersurface is no longer connected, and thus the system cannot be ergodic in general. However, we have analytical evidence that the total measure of the disconnected parts vanishes in the thermodynamic limit. So one can ask whether ergodic behavior still exists for low temperatures and for phase-space functions depending only on the configurational degrees of freedom. This point will be investigated for several static correlation functions of the pseudospins for which the time average and ensemble average will be computed.

The time-dependent correlation function $\langle x_i(t)x_j(0)\rangle$ for the particle displacements $x_i(t)$, which is needed to calculate the relaxation behavior, can be obtained exactly from the spin correlation function $\langle \sigma_i(t)\sigma_j(0)\rangle$. To calculate the latter we will assume that the dynamics of $\sigma_i(t)$ at low temperatures can be described by a Markovian process. This assumption leads immediately to a kinetic Ising model description from which the pseudospin correlation function can be obtained. This approach also enables us to discuss the existence of a central peak at low temperatures which is associated with the slow dynamics of the pseudospins.

Our paper is organized as follows. In Sec. II we introduce the model with its most important static properties and comment on the molecular-dynamics (MD) method used for our simulations. Section III investigates the ergodic behavior. It is shown how the ensemble average can be calculated analytically for some correlation functions of the spins. These results are compared with the time-averaged quantities following from the MD calculations. The time-dependent autocorrelation function of the spins is studied in Sec. IV as well as the exact relationship between $\langle x_i(t)x_j(0)\rangle$ and the spin correlation function $\langle \sigma_i(t)\sigma_j(0)\rangle$. It is shown how the dynamics of the pseudospins can be obtained from a kinetic Ising model, which will be used to discuss the phenomenon of the central peak. Section V contains the discussion and conclusions.

II. MODEL

The model considered in this paper is a slight modification of a model introduced and investigated earlier to describe some aspects of glasses.[32-34] Here we will repeat only those features relevant to the present work. For details the reader should consult the papers cited above.

We study a one-dimensional chain of classical, identical particles with an anharmonic on-site potential $V_1(x)$ and a harmonic nearest-neighbor interaction $V_2(x)$. Thus the total potential energy is given by[35]

$$V(\mathbf{x}) = \sum_i [V_1(x_i) + V_2(x_i + x_{i+1})], \quad \mathbf{x} = \{x_i\} \tag{2a}$$

with

$$V_1(x) = \frac{C_1}{2}\{[x - a_+ - a_-\sigma(x)]^2 - [c - a_+ - a_-\sigma(x)]^2\}, \quad C_1 > 0 \tag{2b}$$

and

$$V_2(x) = \frac{C_2}{2}(x-b)^2, \tag{2c}$$

where C_2 can be positive or negative. The function $\sigma(x)$ in (2b) is defined by

$$\sigma(x)=\mathrm{sgn}(x-c)\in\{\pm 1\} \tag{3a}$$

and

$$a_{\pm}=\tfrac{1}{2}(a_2\pm a_1)\ . \tag{3b}$$

The constants C_1, C_2, a_1, a_2, b, and c are model parameters. The anharmonic potential $V_1(x)$ consists of two parabola with the same second derivative C_1 and minima at a_1 and a_2, respectively. These two parabola are patched together at $x=c$. Hence a particle feels the anharmonicity only by crossing this point. The nondifferentiability of $V_1(x)$ at $x=c$ has no importance, as it has been shown that smoothing the cusp does not change the following static results significantly.[33]

This simple model already exhibits a complex energy landscape in configuration space with exponentially many metastable states (Fig. 1). Each valley (configuration cell) and its lowest point, the metastable configuration $\mathbf{x}(\boldsymbol{\sigma})=\{x_j(\boldsymbol{\sigma})\}$, is uniquely determined by a sequence $\boldsymbol{\sigma}=\{\sigma_i\},\sigma_i=\pm 1$ of (pseudo-) spins:

$$x_j(\boldsymbol{\sigma})=A+B\sum_{l=-\infty}^{+\infty}\eta^{|l|}\sigma_{j+l}\ , \tag{4}$$

with

$$A=\frac{(1+\eta)^2a_+-2\eta b}{(1-\eta)^2},\quad B=a_-\frac{1+\eta}{1-\eta}\ , \tag{5a}$$

$$\eta=-\gamma[1-(1-\gamma^{-2})^{1/2}],\quad \gamma=1+\frac{C_1}{2C_2}\ . \tag{5b}$$

The sequence $\boldsymbol{\sigma}$ can be chosen arbitrarily provided $|\eta|<\frac{1}{3}$ and the geometrical parameters a_1, a_2, b, and c are in a certain range.[33]

Neglecting a constant term, the energy of a metastable configuration $\mathbf{x}(\boldsymbol{\sigma})$ follows from the Ising-like expression

$$E(\boldsymbol{\sigma})=J_0\sum_{j\,(\neq k)}\eta^{|j-k|}\sigma_j\sigma_k-h\sum_j\sigma_j\ , \tag{6}$$

where the constants are defined as follows:

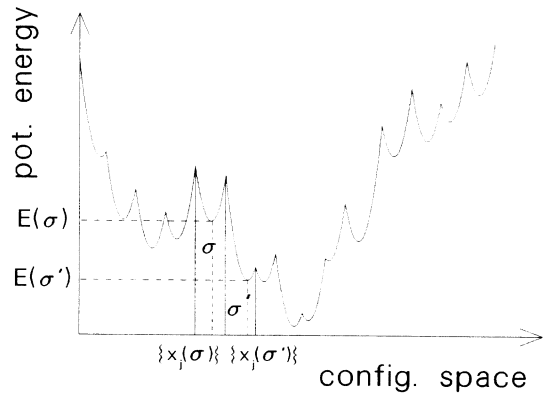

FIG. 1. Schematic representation of the potential-energy landscape. The configuration space can be decomposed into cells characterized by sequences $\boldsymbol{\sigma}$ of Ising spins. The minimum-energy configuration $\{x_j(\boldsymbol{\sigma})\}$ within a cell has energy $E(\boldsymbol{\sigma})$.

$$h=C_1a_-\frac{(1+\eta)^2a_+-(1-\eta)^2c-2\eta b}{(1-\eta)^2}=C_1a_-(A-c) \tag{7a}$$

and

$$J_0=-\frac{C_1}{2}\frac{1+\eta}{1-\eta}a_-^2<0\ . \tag{7b}$$

This one-to-one correspondence between metastable configurations and sequences of Ising spins turns out to be crucial. The configurational degrees of freedom are described by $\boldsymbol{\sigma}$. Thus transitions between two adjacent valleys are easily described by spin flips. The MD simulation shows that the configurational degrees of freedom change by *single spin flips* and not by, e.g., spin exchange. If the nth spin is flipped, the corresponding barrier height is calculated as

$$b_n(\boldsymbol{\sigma})=\frac{C_1}{2}\frac{1-\eta}{1+\eta}[x_n(\boldsymbol{\sigma})-c]^2\geq B_{\min}>0\ , \tag{8}$$

with $B_{\min}$ denoting the minimum barrier height. The difference between the energies of both minima is given by

$$\Delta_n(\boldsymbol{\sigma})=+4J_0+2C_1a_-\sigma_n[x_n(\boldsymbol{\sigma})-c]\ . \tag{9}$$

Hence each such pair of minima can be interpreted as a simple two-level system with asymmetry $\Delta_n(\boldsymbol{\sigma})$ and barrier height $b_n(\boldsymbol{\sigma})$. The transition from one minimum to one of its neighboring ones has the simple meaning that the nth particle has crossed the point $x=c$. We will see below that these two-level systems play an important role in the dynamics of the chain.

So far we have discussed the static properties of the model. The main purpose of this paper is to study its dynamics. For that reason we numerically integrated the equations of motion. Some details of the numerical simulation will now be given. As usual we have introduced scaled variables, i.e., we set $C_1=m=1$, where m is the mass of a particle. Tests with different integration schemes have shown that in our case a predictor-corrector algorithm (whose original form stems from celestial mechanics[36]) is superior to the usually applied algorithms like Verlet etc. with respect to speed (for a prescribed accuracy).

The predictor reads

$$q_{n+2}=2q_{n+1}-q_n+\frac{h^2}{12}(13\ddot{q}_{n+1}-2\ddot{q}_n+\ddot{q}_{n-1})\ , \tag{10a}$$

$$\dot{q}_{n+2}=\dot{q}_{n+1}+\frac{h}{12}(23\ddot{q}_{n+1}-16\ddot{q}_n+5\ddot{q}_{n-1})\ , \tag{10b}$$

and the corrector is given by

$$q_{n+2}=2q_{n+1}-q_n+\frac{h^2}{12}(\ddot{q}_{n+2}+10\ddot{q}_{n+1}+\ddot{q}_n)\ , \tag{11a}$$

$$\dot{q}_{n+2}=\dot{q}_{n+1}+\frac{h}{12}(5\ddot{q}_{n+2}+8\ddot{q}_{n+1}-\ddot{q}_n)\ . \tag{11b}$$

We suppose that the superiority of this integration scheme in our case is due to the nondifferentiability of

$V_1(x)$ at $x=c$, which can lead to difficulties for a simple predictor scheme.

As time step we usually chose $h=0.008$ time units [1 time unit $=(m/C_1)^{1/2}$], except for several runs with $h=0.004$ time units to test the dependence of our results on h. This step size led to a small drift in the temperature of the system of order 1% during a run. The number of particles was $N=5000$ and the longest runs were 1.8×10^7 time steps, which took about 8 h of CPU time on a CRAY XMP. Since a typical time scale of our system is of order 2π time units, this results in more than 20 000 periods of oscillation.

To generate the equilibrated initial configurations for the system in phase space we proceeded as follows. First we generated N Gaussian distributed random numbers with mean c and width σ_1. These numbers were used for the coordinates of the particles at time zero. N further Gaussian distributed random numbers with mean zero and width σ_2 gave the initial velocity of the particles. The standard deviations σ_1 and σ_2 were chosen such that the resulting temperature (defined as usual via the mean kinetic energy) of the relaxed state was high (here and in the following we will use the terms high and low temperatures always with respect to the maximum and minimum barrier heights for single spin flips, respectively). In Sec. IV we find that for high temperatures relaxation times are short, thus it is justified to expect the system to be in an equilibrated state after a short time (e.g., after a few hundred periods of oscillation). After this time period we switched on a small damping force proportional to the velocity of the particles. Because the damping constant was very small (6×10^{-5} inverse time units), the energy of the system was decreased very slowly. Therefore one can expect the system to stay in equilibrium up to very low temperatures (this will be discussed intensively in a separate paper[37]). Consequently, we can extract from this cooling run the initial configurations in phase space corresponding to different temperatures.

III. ERGODIC BEHAVIOR

In this section we investigate the ergodic behavior of our model, i.e., we compare time averages with microcanonical ensemble averages. As the analytical calculation of the latter is very difficult, we substitute it with the canonical average which differs from it, for intensive quantities, only by $O(N^{-1/2})$. This approximation should be good for a system size as ours. The details of the following calculations can be found in Ref. 38.

First we explain how the canonical averaging can be done analytically. Due to the partition of configuration space into disjoint sectors characterized by different spin sequences, the computations of the ensemble average $\langle f\rangle_x$ of a configuration space function $f(\mathbf{x})$ can be performed as follows (the subscript x in $\langle\ \rangle_x$ stands for the variables with respect to which the average is done):

$$\langle f(\mathbf{x})\rangle_x=\frac{1}{Z_{\text{conf}}}\int d^N x f(\mathbf{x})e^{-\beta V(\mathbf{x})} \tag{12a}$$

$$=\frac{1}{Z_{\text{conf}}}\sum_{\sigma}\int_{S(\sigma)} d^N x f(\mathbf{x})e^{-\beta V(\mathbf{x})}\ , \tag{12b}$$

where

$$Z_{\text{conf}}=\int d^N x\, e^{-\beta V(\mathbf{x})}\ . \tag{12c}$$

The configuration cell $S(\sigma)$ denotes that sector of configuration space with $\sigma(x_i)=\sigma_i$ for all i, and β stands for the inverse temperature. To compute the configuration integral we expand the potential $V(\mathbf{x})$ for every sequence σ around the local minimum $\mathbf{x}(\sigma)$ defined by that sequence. Denoting the deviations from $\mathbf{x}(\sigma)$ by $\mathbf{y}$ we get with (2)

$$\langle f(\mathbf{x})\rangle_x=\frac{1}{Z_{\text{conf}}}\sum_{\sigma}e^{-\beta E(\sigma)}\int_{S'(\sigma)}d^N y f(\mathbf{x}(\sigma)+\mathbf{y})\exp\left[-\frac{\beta}{2}\sum_i[(C_1+2C_2)y_i^2+2C_2y_iy_{i+1}]\right]\ , \tag{13}$$

with

$$S'(\sigma)=\bigotimes_i s_i(\sigma)\ ,$$
$$s_i(\sigma)\equiv\begin{cases}[-\infty,c-x_i(\sigma)], & \sigma_i=-1\\ [c-x_i(\sigma),+\infty], & \sigma_i=+1\ .\end{cases} \tag{14}$$

Here we made use of the Ising expression for the potential energy at $\mathbf{x}(\sigma)$ [see Eq. (6)]. Note that expression (13) is still exact due to the piecewise harmonicity of the potential.

If $k_BT\ll B_{\min}$ (the minimal barrier height) only small deviations $\mathbf{y}$ will contribute to the integral. Expanding $\mathbf{f}(\mathbf{x}(\sigma)+\mathbf{y})$ with respect to $\mathbf{y}$, one obtains, in leading order,

$$\langle f(\mathbf{x})\rangle_x\cong\sum_{\sigma}f(\mathbf{x}(\sigma))\rho_0(\sigma)\equiv\langle f(\mathbf{x}(\sigma))\rangle_\sigma\ , \tag{15}$$

with

$$\rho_0(\sigma)=\frac{1}{Z_0}e^{-\beta E(\sigma)},\quad Z_0=\sum_{\sigma}e^{-\beta E(\sigma)}\ . \tag{16}$$

This demonstrates that the statistical mechanics for the chain at low temperatures is reduced to that of the Ising model (6). The ensemble average of phase-space functions $f(\mathbf{x},\mathbf{p})$ can be obtained similarly.

If f depends only on the configurational degrees of freedom, i.e.,

$$f(\mathbf{x})\equiv g(\sigma(x_1),\sigma(x_2),\ldots,\sigma(x_N))\ , \tag{17}$$

the averaging is even simpler. From (13) we get

$$\langle f(\mathbf{x})\rangle_x=\sum_{\sigma}g(\sigma)\rho(\sigma)\equiv\langle g(\sigma)\rangle_\sigma\ , \tag{18}$$

with the reduced distribution function

$$\rho(\sigma)=\frac{e^{-\beta E(\sigma)}}{Z_{\text{conf}}}\int_{S'(\sigma)} d^N y \exp\left[-\frac{\beta}{2}\sum_i [(C_1+2C_2)y_i^2 + 2C_2 y_i y_{i+1}]\right], \tag{19}$$

which can be rewritten as

$$\rho(\sigma)=\frac{1}{Z_{\text{eff}}}e^{-\beta H_{\text{eff}}(\sigma)},\quad Z_{\text{eff}}=\sum_\sigma e^{-\beta H_{\text{eff}}(\sigma)}, \tag{20}$$

with an effective spin Hamiltonian $H_{\text{eff}}(\sigma)$. We stress that this result is still exact.

As the integral in Eq. (19) cannot be computed exactly (due to the domain of integration), we proceed as follows. The integral can be interpreted as averaging of $\exp(-\beta C_2 \sum_i y_i y_{i+1})$ over a weight proportional to

$$\exp\left[-\frac{\beta(C_1+2C_2)}{2}\sum_i y_i^2\right]. \tag{21}$$

A cumulant expansion yields after simple but lengthy calculations,

$$\rho(\sigma)=Z_{\text{eff}}^{-1}e^{-\beta E(\sigma)}\exp\left[\sum_i \ln I_i - C_2\beta\sum_i w_i w_{i+1} + \frac{C_2^2\beta^2}{2}\sum_i (u_i u_{i+1}-w_i^2 w_{i+1}^2+2w_{i-1}u_i w_{i+1}-2w_{i-1}w_i^2 w_{i+1})\right]+O((\beta C_2)^3). \tag{22}$$

The dependence of I_i, w_i, and u_i on T and σ has been suppressed. These quantities are defined as follows:

$$I_i(T,\sigma)=\left[\frac{\pi}{2\beta(C_1+2C_2)}\right]^{1/2}[1-\sigma_i \text{erf}\delta], \tag{23a}$$

$$w_i(T,\sigma)=\left[\frac{2}{\pi\beta(C_1+2C_2)}\right]^{1/2}\frac{\sigma_i e^{-\delta^2}}{1-\sigma_i \text{erf}\delta}, \tag{23b}$$

$$u_i(T,\sigma)=\frac{1-\sigma_i \text{erf}\delta+2\sigma_i\pi^{-1/2}\delta e^{-\delta^2}}{\beta(C_1+2C_2)(1-\sigma_i \text{erf}\delta)}, \tag{23c}$$

with

$$\delta(T,\sigma)=\left[\frac{\beta}{2}(C_1+2C_2)\right]^{1/2}[c-x_i(\sigma)], \tag{23d}$$

and $\text{erf}(x)$ denotes the error function, the occurrence of which originates from the domain of integration.

The exponent in Eq. (22) is an effective spin Hamiltonian which is still rather complex. By expanding it up to order η and including some terms of order η^2 we find the approximate effective spin Hamiltonian

$$H_{\text{eff}}(T,\sigma)\cong h(T,\eta)\sum_i \sigma_i + J_1(T,\eta)\sum_i \sigma_i\sigma_{i+1} + J_2(T,\eta)\sum_i \sigma_i\sigma_{i+2} + J_{11}(T,\eta)\sum_i \sigma_{i-1}\sigma_i\sigma_{i+1}. \tag{24}$$

The η and T dependence of the coupling constants is complicated and can be found in Ref. 38. Taking higher orders of η into account leads to third- and higher-nearest-neighbor interactions as well as to multispin interactions. Of course, one has

$$\lim_{T\to 0} H_{\text{eff}}(T,\sigma)\equiv E(\sigma), \tag{25}$$

i.e., the multispin interactions become important only for $k_B T \gg B_{\min}$. For the calculation of the canonical averages of functions $g(\sigma(x_1),\ldots,\sigma(x_N))$ we have used $\rho(\sigma)$ with H_{eff} given by Eq. (24).

As is well known, the partition function for a one-dimensional spin system with finite-range interactions can be computed by the transfer matrix method. The correlation functions can then be obtained by differentiating the largest eigenvalue λ_M of the transfer matrix with respect to their conjugate field. For instance the magnetization is given by

$$\langle\sigma_i\rangle=\frac{1}{\lambda_M}\frac{\partial\lambda_M}{\partial[\beta h(T,\eta)]}. \tag{26}$$

Although it is in principle possible to compute the derivative of λ_M for a 4×4 matrix analytically, it is absolutely impractical even with the aid of an algebra program such as MACSYMA, due to its complicated form. Therefore we proceeded in the following way. We computed (using MACSYMA) the characteristic polynomial of the transfer matrix and transformed it into the form

$$P(\lambda)=\lambda^4+A\lambda^3+B\lambda^2+C\lambda+D=0, \tag{27}$$

with coefficients A, B, C, and D, which depend on the coupling constants in Eq. (24). $P(\lambda)$ differentiated with respect to $\beta h(T,\eta)$ yields $\partial\lambda_M/\partial[\beta h(T,\eta)]$ as a function of λ_M and the various derivatives $\partial A/\partial[\beta h(T,\eta)]$, $\partial B/\partial[\beta h(T,\eta)]$, etc. These derivatives can also be obtained without difficulties with the aid of MACSYMA. Using these and λ_M (which was calculated numerically), the magnetization is obtained immediately. The nearest- and next-nearest-neighbor correlation functions and the three-spin correlation function $\langle\sigma_{i-1}\sigma_i\sigma_{i+1}\rangle$ can be calculated similarly. Note that an analogous calculation is still possible for more general spin Hamiltonians having a larger transfer matrix and defying an analytical determination of its eigenvalues.

The results for the ensemble average of the various correlation functions determined in this way are valid for

all temperatures as long as C_2 (or η) is not too large (e.g., $\eta \leq 0.15$). This is due to the fact that for high temperatures $C_2\beta$ is small, thus ensuring rapid convergence of the cumulant expansion. For low temperatures the temperature-dependent part of the coupling constants of H_{eff} converges to zero. Thus the expression in large parentheses in Eq. (22) is a good approximation to the temperature-dependent part of H_{eff} for all temperatures. If in addition $|\eta|$ is small, we are allowed to neglect all terms higher than the leading order in η in the exponent of (22).

Let us finally mention that the nth nearest-neighbor correlation $\langle \sigma(x_l)\sigma(x_{l+n})\rangle_x$ can be calculated exactly for $T=\infty$.[38] For instance, for the nearest-neighbor correlation function one obtains

$$\langle \sigma(x_l)\sigma(x_{l+1})\rangle_x (T=\infty) = \frac{2}{\pi(1-\eta^2)^{1/2}} \arctan \frac{\eta}{(1-\eta^2)^{1/2}} , \quad (28)$$

which is different from zero, whereas $\langle \sigma(x_l)\rangle_x (T=\infty)=0$. At first glance it might be surprising that even at infinite temperature there are correlations between neighboring particles of the chain. This is an artifact of our model because the force between adjacent particles increases unboundedly with distance. Therefore at high temperatures, where nearest-neighbor distances are large, the correlations remain finite (this effect can be also observed in a purely harmonic chain). Of course, such behavior is absent in more realistic potentials such as, e.g., the Lennard-Jones potential.

We now discuss how time averages were computed. We define the particle average $f^*(\mathbf{x})$ of a function $f(\mathbf{x})=g(\sigma(\mathbf{x}))$ depending only on R neighboring configurational degrees of freedom as follows:

$$f^*(\mathbf{x}) = \frac{1}{N-R} \sum_{i=1}^{N-R} g(\sigma_i, \sigma_{i+1}, \ldots, \sigma_{i+R}) \equiv g^*(\boldsymbol{\sigma}) . \quad (29)$$

To compute the time average $\bar{f}$ of $f^*(x)$ we periodically extracted the spin configurations $\boldsymbol{\sigma}(t)$ from the MD simulation with a period of L time units ($5 \leq L \leq 25$ depending on temperature) and obtained $\bar{f}$ from

$$\bar{f}(\mathbf{z}(0),N,L,M,K) = \frac{1}{M-K} \sum_{\nu=K}^{M-1} g^*(\boldsymbol{\sigma}(\nu L)) , \quad (30)$$

with $\mathbf{z}(0)$ denoting the initial point in phase space for the simulation, M the total number of stored configurations, and K the number of discarded configurations at the beginning of the run. It was necessary to discard these configurations because the initial configurations obtained as described in Sec. II were not quite equilibrated for *low* temperatures (see also Ref. 37). For ergodic systems $\bar{f}$ will generally not depend on the initial point $\mathbf{z}(0)$, and K for a given total energy if M is large enough.

Since M is finite for our simulation, $\bar{f}$ has a certain error, which were computed as follows. We made a partition of the data sets into several consecutive subsets of equal time length which were much larger than the relaxation time (see Sec. IV) at the corresponding temperature. We computed the time average within each of these sets and determined the standard deviation for the whole run from these averages.

The temperature T is obtained from the mean kinetic energy by

$$k_B T = \frac{m}{N} \sum_{i=1}^{N} \overline{\dot{x}_i^2} , \quad (31)$$

and throughout this paper it is given in units of $7.25 \times 10^2 C_1$ (kg/sec^2) K.

Since the potential-energy landscape has exponentially many local minima and barriers, the exploration of configuration space will progress slowly at low temperatures $k_B T \ll B_{\min}$. On the other hand, the motion will be almost unhindered for $k_B T \gg B_{\max}$. These two different behaviors are illustrated in Fig. 2 where the magnetization $\sigma^*(t)$ of the system is plotted as a function of time for two different temperatures. For the higher temperature [Fig. 2(a)] the data points show almost no structure (apart from the short-time fluctuations also present at low temperature). For the lower temperature the function shows a sometimes erratic behavior with typical time scales of the order of 10^3 time units. This feature expresses the slow exploration of the spin space by the system and its sudden entrance into regions characterized by different magnetizations. This irregular behavior makes the determination of time-averaged quantities difficult at low temperatures since long runs must be made to get reasonable statistics. Therefore the available computer time sets a lower limit to the temperatures for

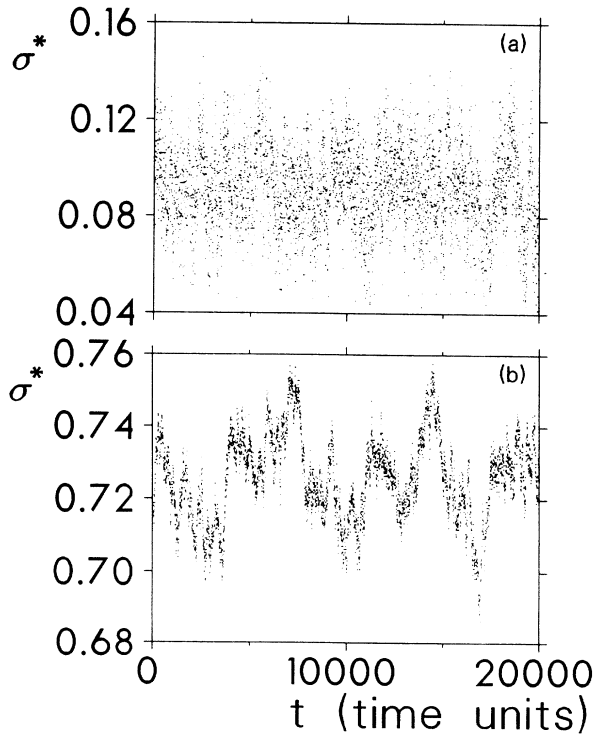

FIG. 2. Particle-averaged magnetization $\sigma^*(t)$ as a function of time for two different temperatures. $C_2=-0.07$, $a_+=5.009$, $a_-=0.201$, $b=11.698$, $c=4.672$, $h/2\eta|J_0|=0.532$, $B_{\min}=0.0144$, $B_{\max}=0.0355$. (a) $T=0.0358$, (b) $T=0.00710$.

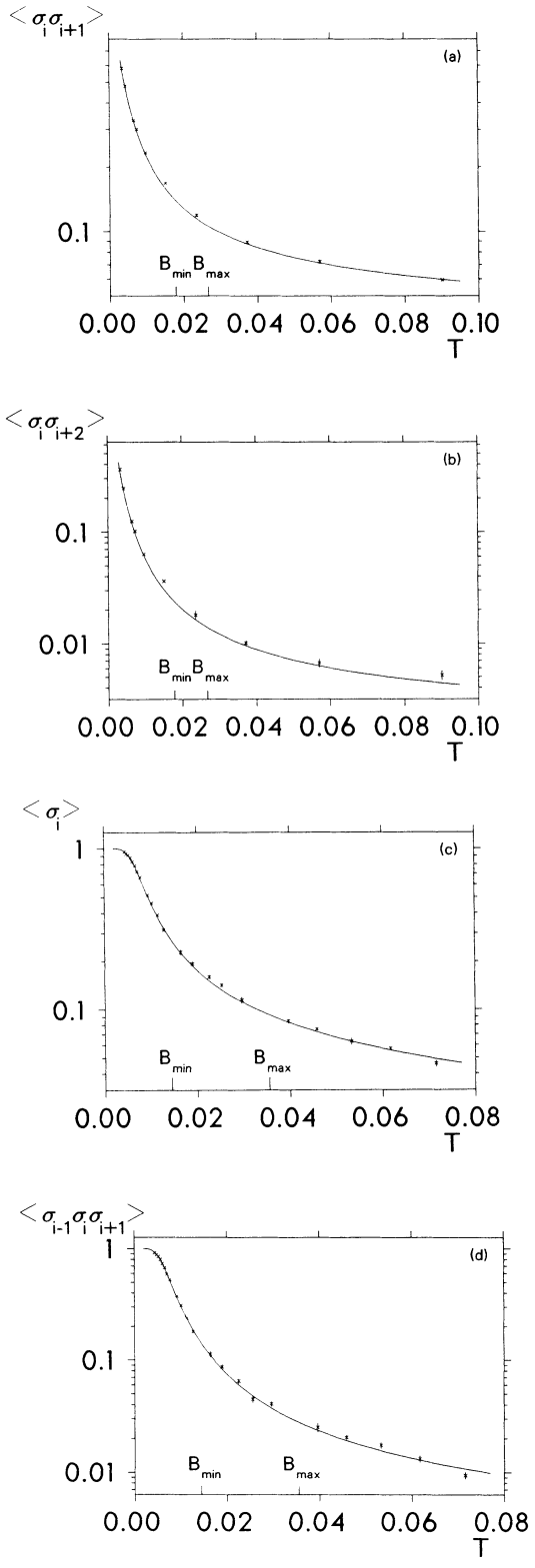

FIG. 3. Comparison between time average (crosses) and ensemble average (solid line) for different correlation functions for (a) and (b) $h=0$ and (c) and (d) $h\neq 0$. $B_{\min}$ and $B_{\max}$ are the minimal and maximal barrier heights for single spin flips, respectively. (a) and (b) $C_2=-0.044$, $a_+=5.0$, $a_-=0.2$, $b=11.7$, $c=4.818\,446\,602$, $\eta\cong 0.048$. (c) and (d) Parameters as in Fig. 2.

which the equivalence of time average and ensemble average can be tested.

Figure 3 presents the results for the magnetization, nearest- and next-nearest-neighbor spin correlation function and for a three-spin correlation function. The magnetization and the three-spin correlation function were calculated for a system with parameters such that the "magnetic field" h is nonzero (otherwise these averages are zero), whereas for the two other correlation functions $h=0$ was chosen. The simulations extended from 15 000 time units for high temperatures to 140 000 time units for low ones. The vertical bars in the figure stand for the errors of the data. Note that we considered temperatures well below and well above the minimum and maximum barriers, respectively.

It is clear from this figure that the agreement between time averages and ensemble averages is very good for all configuration-space functions and all temperatures we considered. Similar results were also found for several other parameter values of the potential. This shows that our system seems to be ergodic with respect to the phase-space functions discussed here, despite the complex potential-energy landscape.

IV. RELAXATION BEHAVIOR

Besides the time-independent quantities considered in the preceding section, also time-dependent correlation functions can be investigated to test whether a system behaves ergodically or not. If all correlation functions $\langle A(t)B(0)\rangle-\langle A\rangle\langle B\rangle$ decay to zero for $t\to\infty$, the system is called mixing, and it is known that this implies ergodicity (see, e.g., Ref. 11). Correlation functions of most disordered systems decay nonexponentially[13] and very often their relaxation functions can be described by a KWW law [Eq. (1)]. Thus, for our model we expect nonexponential relaxation too. The goal of this section is to test this supposition.

One of the most obvious correlation functions is $\langle x_n(t)x_0(0)\rangle-\langle x_n\rangle^2$. It is an interesting aspect of our model that it can be related exactly to correlation functions of the configurational degrees of freedom.

Consider the following time-dependent correlation functions:

$$S_n(t)=\langle x_n(t)x_0(0)\rangle-\langle x_n\rangle^2\,, \tag{32a}$$

$$R_n(t)=\langle \sigma(x_n(t))x_0(0)\rangle-\langle \sigma(x_n)\rangle\langle x_n\rangle\,, \tag{32b}$$

$$C_n(t)=\langle \sigma(x_n(t))\sigma(x_0(0))\rangle-\langle \sigma(x_n)\rangle^2\,, \tag{32c}$$

where $\langle\ \rangle$ denotes canonical averaging over the initial conditions in phase space. Using the equations of motion for $x_n(t)$ [note that the equation for $\ddot{x}_n(t)$ contains $\sigma(x_n(t))$ *linearly*] we find

$$\ddot{S}_n(t)=\frac{1}{m}[-C_1S_n-C_2(2S_n+S_{n-1}+S_{n+1})+C_1a_-R_n]\,, \tag{33a}$$

$$\ddot{R}_n(t)=\frac{1}{m}[-C_1R_n-C_2(2R_n+R_{n-1}+R_{n+1})+C_1a_-C_n]\,. \tag{33b}$$

In the derivation of these equations an inhomogeneous term proportional to

$$-\langle x_n\rangle(C_1+4C_2)+C_1a_-\langle\sigma(x_n)\rangle+C_1a_++2C_2b \quad (34)$$

occurs, which can be shown to vanish identically. Performing a Fourier transformation with respect to n, a Laplace transformation with respect to time, and noting that $\langle\dot{x}_n(0)x_0(0)\rangle=0$, we get

$$\hat{S}(q,z)=i\sum_n\int_0^\infty dt\, e^{-i(qn-zt)}S_n(t), \quad \mathrm{Im}z>0 \quad (35)$$

$$=-\frac{z}{z^2-\omega_q^2}S(q,t=0)+\frac{z}{(z^2-\omega_q^2)^2}\frac{C_1a_-}{m}R(q,t=0)+\left[\frac{C_1a_-}{m}\right]\frac{\hat{C}(q,z)}{(z^2-\omega_q^2)^2}, \quad (36)$$

where we have introduced the phonon frequency

$$\omega_q^2=\frac{1}{m}(C_1+2C_2+2C_2\cos q). \quad (37)$$

Thus, besides the static quantities $S(q,t=0)$ and $R(q,t=0)$, only the time-dependent spin correlation function is required to determine $\hat{S}(q,z)$. The static quantities can be calculated as shown in Sec. III, and therefore we now concentrate on the determination of $\hat{C}(q,z)$.

The starting point is the observation from our simulations that the spin configurations change by *single spin flips*. At low temperatures a particle will oscillate for a long time in one part of its local double-well potential, and transitions between both wells (i.e., crossing the point $x=c$) will be rare. Because of the coupling of the particle to its neighbors (acting as a heat bath), we can assume these transitions to be essentially uncorrelated from the previous ones, and also independent from the transitions of the other particles, i.e., we assume Markovian behavior. If $p(\boldsymbol{\sigma},t)$ denotes the probability to find the system in configuration cell $S(\boldsymbol{\sigma})$ at time t, then $p(\boldsymbol{\sigma},t)$ is a solution of the master equation

$$\dot{p}(\boldsymbol{\sigma},t)=-\sum_i w_i(\ldots,\sigma_i,\ldots)p(\ldots,\sigma_i,\ldots,t)+\sum_i w_i(\ldots,-\sigma_i,\ldots)p(\ldots,-\sigma_i,\ldots,t), \quad (38)$$

where $w_i(\boldsymbol{\sigma})$ is the transition rate for the spin flip $\sigma_i\to-\sigma_i$. We stress that these assumptions, which are not fulfilled for *high* temperatures, eliminate two essential properties occurring in the mode-coupling theory: nonlinearities and memory effects.[14–16] These two properties seem to be crucial within this theory to obtain breaking of ergodicity. However, since our system seems to be ergodic, our ansatz, resembling more the facilitated kinetic Ising model,[24] should nevertheless be reasonable.

If the time the system needs to relax within a configuration cell is much smaller than the mean sojourn time within the cell, which will be true for low temperatures, we may use transition state theory to determine the transition rates. We find[38]

$$w_i(\boldsymbol{\sigma})=\alpha_0\exp[-\beta b_i(\boldsymbol{\sigma})], \quad \alpha_0=\frac{C_1+4C_2}{m}, \quad (39)$$

with the barriers b_i from Eq. (8). Note that the reduction of the original Hamiltonian dynamics to a kinetic model was already discussed qualitatively by Zwanzig[39] and that our model makes it possible to do this reduction explicitly. We also would like to mention that such kinetic equations have been used to discuss vitrification (see, e.g., Ref. 40).

If we approximate $x_i(\boldsymbol{\sigma})$ by $A+B[\sigma_i+\eta(\sigma_{i-1}+\sigma_{i+1})]$, which is reasonable for $|\eta|\ll1$, we obtain from Eqs. (8) and (39)

$$w_i(\boldsymbol{\sigma})=\alpha_0 e^{\beta(J_0+h^2/4J_0)}[\cosh(\beta h)-\sigma_i\sinh(\beta h)]\times[\cosh^2(\beta h\eta)-(\sigma_{i-1}+\sigma_{i+1})\sinh(\beta h\eta)\cosh(\beta h\eta)+\sigma_{i-1}\sigma_{i+1}\sinh^2(\beta h\eta)]\times[\cosh^2K+\sigma_{i-1}\sigma_{i+1}\sinh^2K]\left[1-\frac{\sigma_i}{2}(\sigma_{i-1}+\sigma_{i+1})\tanh(2K)\right], \quad (40)$$

with $K=2\beta|J_0|\eta$.

The rest of this section will deal only with the case $h=0$ for which we find the more familiar expression

$$w_i(\boldsymbol{\sigma})=\alpha_0 e^{\beta J_0}(\cosh^2K)(1+\delta\sigma_{i-1}\sigma_{i+1})\times[1-\tfrac{1}{2}\sigma_i(\sigma_{i+1}+\sigma_{i-1})\tanh 2K], \quad (41)$$

with $\delta=\tanh^2K$. The transition rates (41) agree with the most general transition rates for Glauber's one-dimensional kinetic Ising model with nearest-neighbor coupling constant $-2|J_0|\eta$. The parameter δ is fully determined by the temperature and the coupling constants C_1 and C_2 of the particles. Using these transition rates the equations for the n-spin correlation functions are easily derived. From their solutions $C(q,t)$ and $\hat{C}(q,z)$ can be obtained, in principle. Unfortunately, the solutions are only known for $\delta=0$. Let us therefore assume $\delta=0$ for the moment. From Glauber's result it follows that

$$\hat{C}(q,z)=\frac{1-\tanh^2K}{1+\tanh^2K-2\tanh K\cos q}\times\frac{1}{\alpha_0[1-\tanh 2K\cos q]-iz}. \quad (42)$$

Using the relation $S(q,\omega)=\lim_{\epsilon\to0}2\,\mathrm{Im}\hat{S}(q,\omega+i\epsilon)$ we

find for $S(q,\omega)$ a contribution proportional to

$$\frac{1}{(\omega^2-\omega_q^2)^2(\omega^2+\alpha_0^2[1-\tanh 2K\cos q]^2)} . \tag{43}$$

Note that ω_q^2 is positive for all q. The first factor in the denominator gives rise to the phonon peak. The singularity in (43) is due to the lack of anharmonicities within a configuration cell excluding phonon-phonon interactions. The second factor is of Lorentzian type and leads to a central peak. As expected, its height increases and its width becomes narrower with decreasing temperature. The origin of such central peaks was the subject of many investigations in connection with displacive transitions.[29-31] It was recognized that for pure samples the peak was due to the slow motion of domain walls leading to a very slow relaxation. For the Ising description of the configurational degrees of freedom of our model the wall picture emerges in an obvious way (see also Ref. 37). For $\delta\neq 0$ we expect a similar behavior for $S(q,\omega)$.

We now proceed to the second main topic of our paper, the relaxation of the correlation functions. As argued above, we can restrict ourselves to the correlation functions between pseudospins. Only the autocorrelation function $C_0(t)$ will be investigated. Let us first discuss the existing analytical results for $C_0(t)$ for a one-dimensional kinetic Ising model. For transition rates as in Eq. (41) with $\delta=-1$ Skinner found, by means of a continuum approximation, a KWW law with exponent $\beta=\frac{1}{2}$ for $C_0(t)=\langle\sigma_i(0)\sigma_l(t)\rangle$.[26] Due to the continuum approximation, this result is valid only for *low* temperatures. However, recently Spohn has proved rigorously that for *large* times the result is true for *all* temperatures.[27] Budimir and Skinner[25] computed $\hat{C}_0(z)$ by means of a continued-fraction expansion, and used this to compute $C_0(t)$ numerically. This was done for $\delta=\pm 1$ and various temperatures. They found that $C_0(t)$ could be fitted well by a stretched exponential for $C_0(t)$ in the range $1\geq C_0(t)\geq 0.1$ with a temperature-dependent exponent β. In particular, they also fitted the exact result for $\delta=0$ by a KWW law and the fit was quite good, although it is known that it cannot be exact, at least for large t.

A disadvantage of the continued-fraction expansion, as it was done by Budimir and Skinner, is that it fails to converge at low temperatures and for long times. This drawback was partially avoided by Bauer, Schulten, and Nadler.[28] They used a generalized moment expansion and inverted the matrix containing the transition rates numerically. The advantage of this procedure is twofold: first, it can also be applied to cases where the transition rates include more complicated terms, e.g., $\sigma_{i-2}\sigma_i\sigma_{i+1}$; and second, the calculations are valid for all times and all temperatures as long as the correlation lengths are smaller than the (finite) system size. Therefore this approach should in principle enable us to determine $C_0(t)$ even in those cases where $\eta\not\ll 1$, i.e., where the transition rates cannot be approximated by (41). Bauer, Schulten, and Nadler found that $C_0(t)$ can be very well approximated by a KWW law for times not too large for all δ values they investigated. Finally, it should be mentioned that the facilitated kinetic Ising model, a modification of Glauber's model, exhibits a KWW law[24] too.

So far we may conclude that the autocorrelation function for one-dimensional kinetic Ising models may follow a KWW law for certain time regimes. If our chain of particles is a reasonable realization of a kinetic Ising model with transition rates (41), we expect $C_0(t)$ to exhibit KWW law too. Since in our case $\delta(T)$ is temperature dependent, i.e., it is not a free parameter, a quantitative comparison with the results of Refs. 25 and 28 is not possible. We should also keep in mind that the assumption of Markovian behavior is invalid for high temperatures, thus the kinetic Ising model approach is doubtful. However, we have seen in Sec. III that strong cooperative effects exist for $T\rightarrow\infty$, which prevent some of the static spin correlation functions from vanishing. From the general discussion in the Introduction concerning the possible mechanisms leading to a KWW behavior, we therefore expect a stretched exponential even at high temperatures, independent of Markovian or non-Markovian behavior.

To calculate the relaxation function $C_0(t)$ numerically, we proceeded analogously as in Eqs. (29) and (30), and write

$$C_0(t)=C_0(kL)$$
$$=\frac{1}{(M-k)}\frac{1}{N}\sum_{l=0}^{M-k-1}\sum_{i=1}^{N}\sigma_i(lL)\sigma_l((l+k)L) . \tag{44}$$

Apart from the particle average we also average over time. The time averaging is only effective if the correlation time τ is much smaller than ML, the total simulation time, since otherwise the configurations are still correlated. Our investigations for 5000 particles have shown that the total simulation time has to be at least 100 times the correlation time τ to get a reasonable statistics for $C_0(t)\geq 10^{-2}$. This fact and the available computer resources set the limit for the lowest attainable temperature for these calculations as τ increases very fast with decreasing temperature.

We also point out that for this kind of calculations it is crucial to control the temperature. The integration scheme we used increases or decreases (depending on the parameters of the potential and the total energy) the temperature in the course of time very slowly. In principle it could be that, due to the time average performed for the computation of $C_0(t)$ [cf. Eq. (44)], we just sum over several exponential functions with different relaxation times due to a slowly varying temperature. It is well known that such a superposition can lead to a stretched exponential behavior.[13,21] We have excluded this possibility by repeating the calculations with halved step size (leading to a smaller drift in the temperature) and still found the same results for $C_0(t)$. Thus a simulation with fixed temperature as proposed, e.g., by Nosé[41] seems not to be necessary in our case.

The numerical results for $C_0(t)$ are given in Figs. 4 and 5 in a logarithmic-linear representation to demonstrate the nonexponential relaxation. Figure 4 shows $C_0(t)$ in

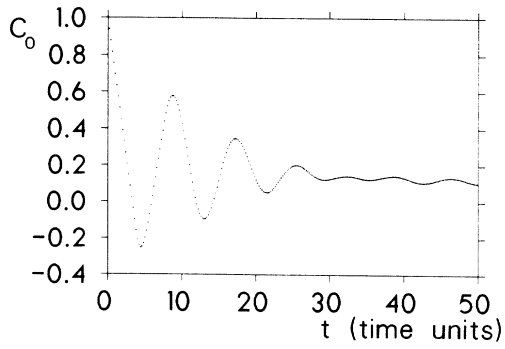

FIG. 4. Autocorrelation function $C_0(t)$ vs time t for high temperature $T=0.0904$. The oscillations stem from the oscillation of the particles in their on-site potential. Parameters as in Fig. 3(a).

the case of high temperatures. The oscillations of the curve reflect the oscillations of the particles in their on-site potential. For this time and temperature region the Markovian ansatz for the master equation is clearly not justified as the particles have a memory due to their almost periodic motion. For larger times $C_0(t)$ ceases to oscillate and turns into a relaxation behavior which sometimes can be well fitted by a KWW law . For other

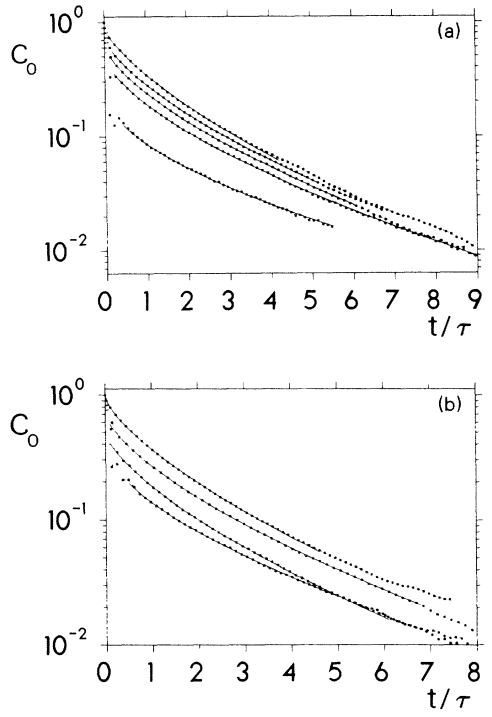

FIG. 5. Autocorrelation function $C_0(t)$ for various temperatures as a function of scaled time t/τ. The solid lines represent the fit with the KWW law. (a) Parameters: $C_2=-0.032$, $a_+=5.0$, $a_-=0.2$, $c=4.875\,229\,358$, $b=11.7$, $\eta\cong 0.034$. Temperatures from top to bottom: 0.0110, 0.0204, 0.0275, 0.0370, 0.0918. (b) Parameters: $C_2=-0.044$, $a_+=5.0$, $a_-=0.2$, $c=4.818\,446\,602$, $b=11.7$, $\eta\simeq 0.048$. Temperatures from top to bottom: 0.0097, 0.0232, 0.0365, 0.0569.

parameter values and high temperatures we found that $C_0(t)$ decays so fast that no reasonable fit was possible.

For intermediate temperatures $C_0(t)$ drops rather quickly to a value between 0.2 and 0.9. Thereafter the function converges to zero in a way that can be well described by a KWW law. For low temperatures one finds $C_0(t)$ to behave as a stretched exponential from the very beginning.

It is clear that the relative error of $C_0(t)$ increases for growing t, as the magnitude of $C_0(t)$ decreases. Thus the curves begin to become bumpy at large times. To determine the maximum time $t_{\max}$ up to which a given curve is reliably determined numerically, we have divided the data of the spin configurations into two subsets of equal length in time and calculated $C_0(t)$ for both sets. The time interval $[0,t_{\max}]$ over which the two curves coincided within a few percent was considered to be sound and was used for the fit with the KWW law. For this fit the fast transients at short times were also discarded. Therefore one has to introduce an amplitude A in the KWW law, i.e.,

$$C_0(t)=A\exp\left[-\left[\frac{t}{\tau}\right]^{\beta}\right]. \tag{45}$$

Figure 5 shows $C_0(t)$ as a function of t/τ for two different parameter sets, where the relaxation time $\tau=\tau(T)$ has been determined from the KWW fit. Also shown are the fitted stretched exponentials in those time regions we have used for the fit. One observes that the fit is very good. Thus one may conclude that $C_0(t)$ is well described by a KWW law, at least for intermediate times. For longer times this behavior can neither be excluded nor confirmed.

Fig. 6 depicts an Arrhenius plot for the relaxation time $\tau(T)$ obtained from the fits. For both parameter sets, the Arrhenius behavior over a rather large temperature range is obvious. The activation energy E_b obtained from these plots are of the order of the barrier heights for single spin flips considered previously. Note that the magnitude of this activation energy is not just given by the bare barrier heights of the two-level systems. This can be understood best for the usual Glauber model with $\delta=0$. Although no barrier is involved explicitly in this model the activation energy given by $4J$ is nonzero. To determine E_b, it is therefore necessary to calculate the spin-spin correlation functions which, however, is not feasible for $\delta\neq 0$. It is interesting to note that for most of the cases we tested ($\eta=0.034$, 0.048, 0.117, 0.277) the activation energy is larger than the minimum barrier height, but we found also one case ($\eta=0.034$) where E_b was about 30% lower than the minimum barrier height. The Arrhenius behavior shows that for high temperatures the relaxation times are short enough to ensure that the initial configurations in phase space used for our simulations were a representative of the equilibrium distribution.

Finally, Fig. 7 presents the exponent β of the KWW fits as a function of temperature. Although there is a significant scattering of the data, a clear trend that β decreases with increasing temperature can be observed. The scattering reflects the fact that β is not very well

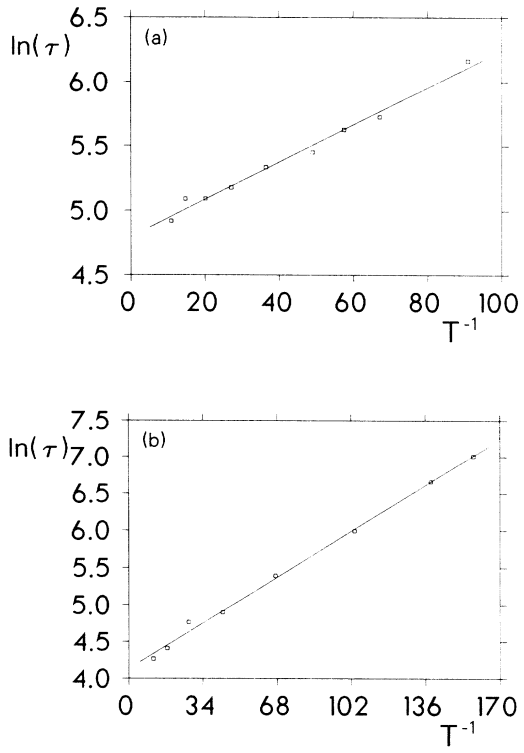

FIG. 6. ln τ (as determined from the KWW fit) vs inverse temperature. Straight line represents the best fit to the points. Parameters correspond to those in Fig. 5.

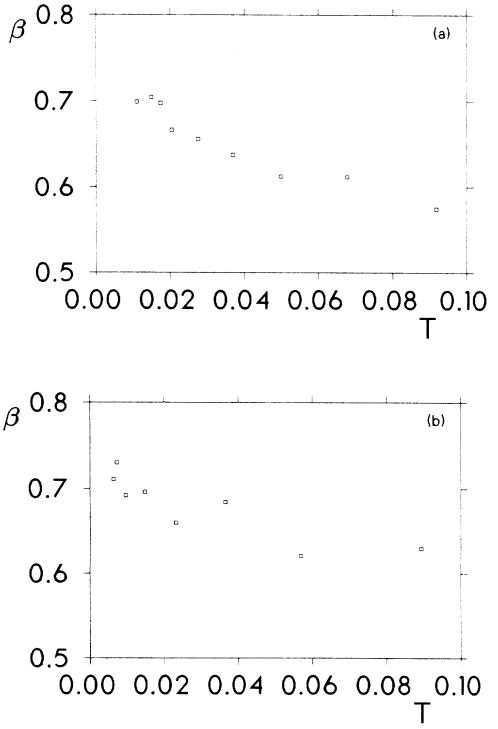

FIG. 7. Exponent β from the KWW fit vs temperature. Parameters correspond to those in Fig. 5.

determined by the fit, and a slight fluctuation in the data can lead to a noticeable change in β. The decrease of β with increasing temperature expresses the fact mentioned above, that the system becomes more cooperative for larger temperatures due to the harmonic nearest-neighbor coupling. Hence such an effect should be absent for more realistic potentials.

V. SUMMARY AND DISCUSSION

In this paper we have studied the dynamical behavior of a one-dimensional model with anharmonic and competing interactions. The potential-energy landscape of this system in configuration space has previously been shown to possess exponentially many metastable configurations. It can be shown that for low energies the energy hypersurface is no longer connected since many "valleys" of the energy landscape become isolated from the rest. Therefore the finite system cannot be ergodic in a strict sense. However, we have analytical evidence that the disconnected part of this hypersurface is of measure zero in the thermodynamic limit $N \rightarrow \infty$.

We have investigated the ergodicity of this system with respect to certain pseudospin correlation functions, where the spins describe the configurational degrees of freedom. The time averages were computed numerically. For the calculation of the canonical averages we have shown that an effective spin Hamiltonian can be deduced. This Hamiltonian contains all types of multispin interactions up to arbitrary distance, and the corresponding coupling constants are temperature dependent. This gives rise to unusual features, e.g., certain correlation functions do not vanish at high temperatures.

Our results show that, despite the complex energy landscape, time- and phase-space averages agree within the error bars of the simulation, even at low temperatures where the dynamics is strongly hindered by the high barriers. Therefore there seems to be no breaking of ergodicity as reported by other authors for the FPU model,[1–3] a rotator model,[5] or a binary mixture of soft spheres.[10] It is not clear to us where this difference comes from. It might be that for certain models the time scales to find ergodicity are very large (see the work by Kantz[4] and Pettini and Landolfi[8] for the FPU model), so that computer simulations are not yet able to decide definitely this question for these models. It might also be that the initial conditions used by these authors are rather nongeneric, leading to huge transient times to find ergodicity. Ergodicity breaking in any dimension for a model similar to ours (a ϕ^4 model) was also predicted by Aksenov *et al.*[15] using a mode-coupling approximation. These authors have shown that nonergodic behavior occurs for sufficiently large coupling strength. For all the coupling strengths and phase-space functions we investigated, ergodic behavior was found. If our model is really comparable to a ϕ^4 model, this discrepancy could be explained as follows: either the coupling constants used by us are still too small, or the mode-coupling approximation with its decoupling might be unreasonable, at least for a one-dimensional model.

The second main result we found is the nonexponential relaxation of the autocorrelation function of the pseudo-

spins. On a time scale varying with temperature between about $10^{-2}\Omega$ and $10^{-4}\Omega$ [$\Omega=(C_1/m)^{1/2}$ is the microscopic frequency], this function could be fitted by a KWW law.[42] It is known that relaxation phenomena on this mesoscopic time scale play a role for the glass transition.[16] The exponent β of the KWW law decreases with increasing temperature. This is due to the harmonic interaction leading to a large cooperativity at high temperatures. The relaxation times $\tau(T)$ exhibit an Arrhenius behavior over a large temperature range.

Although the fit with the KWW law is very good, its significance is not quite obvious because the maximum range of t/τ is only about an order of magnitude. However, additional support for a KWW law follows from our description of the spin dynamics at low temperatures by a kinetic Ising model. Within a transition state theory we have found that our chain of particles is a realization of a kinetic Ising model. For such models several authors[25–28] have shown that the autocorrelation function can be described by a KWW law for intermediate or even for arbitrarily large times.

Using the kinetic Ising model with usual Glauber dynamics (i.e., $\delta=0$), we were also able to calculate $S(q,\omega)$, the Fourier transform of the correlation function $\langle x_n(t)x_0(0)\rangle-\langle x_0(0)\rangle^2$. As expected from earlier work for a similar model,[29–31] we found a central peak at low temperatures related to the slow motion of the pseudospins, which is described by the kinetic Ising model.

Summarizing we can say that we have found nonexponential relaxation which is characteristic for disordered systems. Ergodicity breaking was not found for the temperatures and parameters we investigated.

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