# Kinetic-Ising-model description of Newtonian dynamics: A one-dimensional example

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We show that the Newtonian dynamics of a chain of particles with an anharmonic on-site potential and harmonic nearest-neighbor interactions can be described by a one-dimensional kinetic Ising model with most general Glauber transition rates, provided the temperature is low enough compared to the minimum barrier height. The transition rates are calculated by use of the transition-state theory. At higher temperatures, memory effects occur which invalidate this kinetic description. These memory effects are due to the appearance of dynamically correlated clusters of particles performing periodic oscillations over a certain time scale.

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## I. INTRODUCTION

The microscopic dynamical behavior of a system with a macroscopic number of degrees of freedom is an extremely difficult problem to be solved analytically. Of course, the goal cannot be to solve the Newtonian equation of motion for all the phase-space coordinates, since such detailed information is not generally important for the physical properties of a macroscopic system. Therefore one has to single out the most relevant quantities and their time dependence. The *projection formalism* by Zwanzig [1] and Mori [2] allows one to eliminate all the irrelevant degrees of freedom and leads to a generalized Langevin equation for the *slow* (relevant) variables, including memory effects and fluctuating forces (see, e.g., Forster [3]). The choice of the slow variables is based on physical intuition and experience, and is not always obvious from the very beginning.

In this paper we will not use this formalism but will apply the transition-state theory in order to reduce the Newtonian dynamics to a kinetic one. In contrast to some special cases, where a kinetic equation such as the Boltzmann or Vlasov equation can be rigorously derived from the original Newtonian dynamics (for a review see Spohn [4]), our approach is approximate, and it is only valid at low enough temperatures. The starting point is a classical $N$-particle system with some interactions. In our case it is a one-dimensional model with anharmonic and competing interactions, but it could be a system with any other potential energy, such as a Lennard-Jones potential, as well. Neither is the restriction to one dimension essential. For any such classical system it is believed that in general the potential-energy landscape in the configuration space consists of exponentially many metastable configurations (see, e.g., [5]). Each metastable configuration is a local minima of a configuration cell $S$, and the configuration space can be decomposed into a set of $M$ disjoined configuration cells $S_i$, $i=1,2,\ldots,M$.

Since we will assume Newtonian dynamics, which is autonomous, the total energy $E$ is conserved. Hence the system can only explore that part of configuration space for which $V(\underline{x})\leq E$. Here, $\underline{x}=(\vec{x}_1,\ldots,\vec{x}_N)$ describes a point in the $N$-particle configuration space, and $V(\underline{x})$ is the potential energy. If the system is ergodic, a trajectory $\underline{x}(t)$ may spend a certain time in the configuration cells which are compatible with $V(\underline{x})\leq E$. The mean lifetime within a cell $S_i$ will increase if the total energy $E$, or equivalently the temperature $T$, becomes lower. When the temperature is small enough compared to the relevant barrier heights, the microscopic motion from one cell to one of its neighboring cells may be described by a stochastic motion from one cell to another. Since for low temperatures the lifetime within a cell $S_i$ is rather large, the system will lose its *memory* after a transition to $S_j$, before performing the next transition $S_j\rightarrow S_k$. Accordingly, we assume that the stochastic motion within the allowed configuration space is *Markovian* and that it can be described by a *master equation:*

$$\dot{P}(S_i,t)=-\sum_j W(S_i\rightarrow S_j)P(S_i,t)+\sum_j W(S_j\rightarrow S_i)P(S_j,t)\ , \tag{1}$$

where $P(S_i,t)$ denotes the probability to be in $S_i$ at time $t$. The transition rate $W(S_i\rightarrow S_j)$ for a transition from cell $S_i$ to $S_j$ still has to be determined. This will be done below by use of the transition-state theory.

We think that such a description might also be suitable for the dynamics of glassy structures at temperatures below the calorimetric glass transition temperature $T_g$, since an amorphous structure corresponds to one of the metastable configurations and local rearrangements of the atoms correspond to transitions between two different configuration cells (see also Brawer [6] for similar considerations). These rearrangements contribute to the structural relaxation. Below, but near $T_g$, it could be that *memory effects* have to be taken into account, similar

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to the recent mode-coupling approach to the glass transition starting from the liquid side of a glass (for reviews the reader may consult Götze [7], Götze and Sjögren [8], Schilling [9]).

Using a projector on the cells $S_i$, Zwanzig [10] has already suggested a more formal way to reduce the Newtonian dynamics to a master equation. In his general approach, a memory kernel appears, which is simplified by a Markov approximation. The result is a master equation like (1) with an expression for the transition rates still involving the Liouvillian of the microscopic dynamics. In order to improve our master-equation approach, and in particular to account for memory effects, one has to follow Zwanzig's treatment, but without Markov approximation.

In the next section we will present our model, which allows one to calculate details of the potential-energy landscape exactly. Section III describes how to calculate the transition rates in the framework of the transition-state theory. The numerical procedure for the calculation of a distinct time-dependent correlation function $C(t)$ is given in Sec. IV, and Sec. V demonstrates how $C(t)$ can be calculated from the master-equation approach, also containing a comparison of both results for $C(t)$. In Sec. VI, we summarize and conclude our results.

## II. MODEL

In this section we briefly describe the model we will use. For more details the reader may consult Reichert and Schilling [11] and Schilling [12].

We consider a one-dimensional chain of $N$ classical, identical particles with an anharmonic on-site potential $V_1(x)$ and a harmonic nearest-neighbor interaction $V_2(x)$. The total potential energy is given by

$$V(\{x_i\})=\sum_{i=1}^{N}[V_1(x_i)+V_2(x_{i+1}-x_i)]\ , \tag{2a}$$

with

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

and

$$V_2(x)=\frac{C_2}{2}(x-b)^2,\quad C_2>0 \text{ or } C_2<0\ , \tag{2c}$$

where

$$\sigma(x)=\mathrm{sgn}(x-c)\in\{\pm1\},\quad a_\pm=\tfrac{1}{2}(a_2\pm a_1)\ , \tag{2d}$$

and $x_i$ is the displacement of the $i$th particle. We choose $V_1(x)$ to be piecewise parabolic with the same second derivative $C_1$ except for $x=c$, where both parabola are patched together. $a_1,a_2$ are the positions of the parabola minima. The function $\sigma(x)$ causes the particles to feel the anharmonicity of $V_1(x)$ only when crossing the position $x=c$. All the constants $C_1$, $C_2$, $a_1$, $a_2$, and $C$ are model parameters (see Fig. 1). One can prove that *all* metastable configurations of the *infinite* chain are given

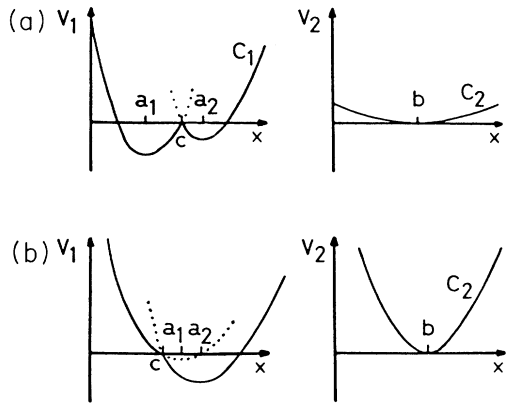


FIG. 1. Nearest- and next-nearest-neighbor potential (a) double-well-like and (b) single-well-like potential.

by

$$x_n(\boldsymbol{\sigma})=A+B\left[\sigma_n+\sum_{i=1}^{\infty}\eta^i[\sigma_{n-i}+\sigma_{n+i}]\right]\ , \tag{3a}$$

with

$$A=\frac{(1+\eta)^2a_+-2\eta b}{(1-\eta)^2},\quad B=a_-\frac{1+\eta}{1-\eta} \tag{3b}$$

and

$$\eta=-\gamma(1-\sqrt{1-\gamma^{-2}})\ \text{ with }\ \gamma=1+\frac{C_1}{2C_2}\ . \tag{3c}$$

For this to be true it is *necessary* that $|\eta|<\frac{1}{3}$. This result means that each configuration $\{x_n(\boldsymbol{\sigma})\}$ is uniquely determined by a sequence $\boldsymbol{\sigma}=\{\sigma_j\}$, $\sigma_j=\pm1$, of (pseudo-) Ising spins, i.e., there exists a one-to-one correspondence between the metastable configurations $\{x_n\}$ and the sequences $\boldsymbol{\sigma}$ of pseudospins. The energy of such a configuration, up to a constant, is given by the Ising-like expression

$$E(\boldsymbol{\sigma})=J_0\sum_{\substack{n,m\\ n\neq m}}\eta^{|n-m|}\sigma_n\sigma_m-h\sum_n\sigma_n\ , \tag{4a}$$

with

$$h=C_1a_-\frac{(1+\eta)^2a_+-(1-\eta)^2c-2\eta b}{(1-\eta)^2} =C_1a_-(A-c) \tag{4b}$$

and

$$J_0=-\frac{C_1}{2}\frac{1+n}{1-\eta}a_-^2<0\ . \tag{4c}$$

A schematic representation of these results is shown in Fig. 2. The configuration space can uniquely be decomposed into *cells* $S(\boldsymbol{\sigma})$ characterized by $\sigma$. The minimum within a cell represents the metastable configuration $\{x_n(\boldsymbol{\sigma})\}$ and its energy is given by $E(\boldsymbol{\sigma})$.

Transitions between different configurations are most

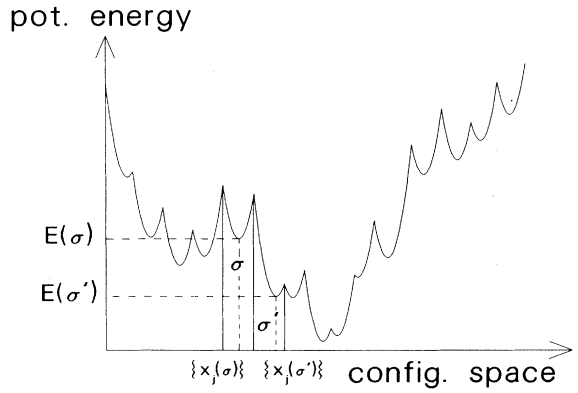


FIG. 2. Schematic representation of the potential-energy landscape for the potential energy [Eq. (2)]. The configuration space can be decomposed into cells characterized by sequences $\sigma$ of Ising spins.

simply described by spin flips. Flipping the $n$th spin corresponds to crossing the point $c$ by the $n$th particle. The barrier height for such a flip can easily be calculated. One obtains

$$b_n(\sigma)=\frac{C_1}{2}\frac{1-\eta}{1+\eta}[x_n(\sigma)-c]^2 . \tag{5}$$

The energy difference between both minima is given by [11]

$$\Delta_n(\sigma)=-J_0-2C_1 a_- \sigma_n[x_n(\sigma)-c] . \tag{6}$$

## III. KINETIC DESCRIPTION

One of the most interesting quantities to study the dynamics of the chain of particles is the time-dependent correlation function $S_n(t)=\langle x_n(t)x_0(0)\rangle-\langle x_n\rangle^2$. $\langle\ \rangle$ denotes the canonical average over the initial conditions in the $N$-particle phase space. It is a crucial aspect of our model that $S_n(t)$ can be exactly related to the correlation function of the configurational degrees of freedom, i.e., to the dynamics of the pseudospins [13]. This is due to the fact that the vibrational (phonons) and the configurational degrees of freedom (described by the Ising spins) can be separated from each other. Accordingly, we can consider the spin-correlation function $C_n(t)=\langle\sigma_n(t)\sigma_0(0)\rangle-\langle\sigma_n\rangle^2$ to study the relaxation behavior of the system. For simplicity we restrict ourselves to the autocorrelation function $C(t)\equiv C_0(t)=\langle\sigma_n(t)\sigma_n(0)\rangle-\langle\sigma_n\rangle^2$, which does not depend on $n$. In the following we choose the model parameters in such a way that $h=0$ [cf. Eq. (4b)]. Hence $\langle\sigma_n\rangle=0$ at nonzero temperature due to the one-dimensionality of our model.

At low temperatures (compared to the minimum barrier height) a particle will oscillate for a long time around one of the local minima in the configuration space. This means that transitions between different local minima (i.e., crossing the point $x=c$) become very rare, compared to the frequency of oscillation. We assume these transitions to be *uncorrelated* to previous ones and independent from the transitions of other particles, i.e., the spin configurations change only by *single spin flips*. If these assumptions are fulfilled we can describe the dynamics of $\sigma_i(t)$ at low temperatures by a *Markovian* process. With $p(\sigma,t)$ the probability to find the system in the configuration cell $S(\sigma)$ at time $t$, $p(\sigma,t)$ is the solution of the master equation:

$$\dot{p}(\sigma;t)=-\sum_i W_i(\ldots,\sigma_i,\ldots)p(\ldots,\sigma_i,\ldots;t)+\sum_i W_i(\ldots,-\sigma_i,\ldots)p(\ldots,-\sigma_i,\ldots;t) , \tag{7}$$

where $W_i(\sigma)$ is the transition rate for a single spin flip $\sigma_i\rightarrow-\sigma_i$, provided all other spins remain unchanged. Thus the original microscopic (Newtonian) dynamics has been reduced to a kinetic Ising model, and the microscopic details are condensed to the transition rates $W_i(\sigma)$. $W_i(\sigma)$ follows from

$$W_i(\sigma)=\lim_{\Delta t\rightarrow 0}\frac{W_i(\sigma,\Delta t)}{\Delta t p(\sigma)} , \tag{8}$$

with $W_i(\sigma,\Delta t)$ the probability that the $i$th spin flips in the time interval $[t,t+\Delta t]$ and $p(\sigma)$ is the canonical distribution function for the pseudospin configurations $\sigma$, which is given by

$$p(\sigma)=\frac{1}{Z}\int_{-\infty}^{\infty}\prod_i dp_i\int_{S(\sigma)}\prod_i dx_i\exp\left[-\beta\left[\sum_i\frac{p_i^2}{2m}+V(\{x_j\})\right]\right] , \tag{9}$$

where

$$S(\sigma)\equiv\otimes S_{\sigma_i},\quad S_{\sigma_i}\equiv\begin{cases}[-\infty,c], & \sigma_i=-1\\ [c+\infty], & \sigma_i=+1 .\end{cases} \tag{10}$$

$\beta=1/kT$, $m$ is the mass of the particles, and $Z$ is the partition function. The $p_i$ integration in Eq. (9) is easily performed. The remaining configurational part has been calculated by Tschöp [14]. In a low-temperature and small-$\eta$ expansion one obtains in leading order

$$p(\sigma)\cong\frac{1}{Z_\sigma}e^{-\beta H_{\text{eff}}(\sigma,T)} , \tag{11a}$$

with

$$Z_\sigma = \mathrm{Tr} e^{-\beta H_{\mathrm{eff}}(\sigma,T)} \tag{11b}$$

and an *effective, temperature-dependent* Hamiltonian

$$H_{\mathrm{eff}}(\sigma,T) = E(\sigma) + \frac{1}{\beta}\sum_{j=1}^{N} I_j(\sigma,T) , \tag{11c}$$

where

$$I_j(\sigma,T) = -\frac{2}{\sqrt{\pi}} B (a^2-b^2)^{1/4} e^{B^2(a^2-b^2)^{1/2}} \eta \sigma_j (\sigma_{j-1}+\sigma_{j+1}) , \tag{11d}$$

$$a = \frac{\beta}{2}(C_1+2C_2), \quad b = \beta C_2 . \tag{11e}$$

Note that $H_{\mathrm{eff}}(\sigma,T)$ converges to $E(\sigma)$ for $T \to 0$.

For the computation of $W_i(\sigma,\Delta t)$ we apply the transition-state theory (see, e.g., Hänggi, Talkner, and Borkovec [15]). Since the on-site potential $V_1$ does *not* have a quadratic maximum but a cusp, the particles have *finite* momenta when crossing the cusp at $x=c$. Therefore the $i$th spin can only flip in the interval $[t, t+\Delta t]$, if the following conditions for the displacement $x_i$ and the conjugate momentum $p_i$ hold:

$$\begin{aligned} &\{c-(1/m)p_i(t)\Delta t < x_i(t) < c,\ p_i(t) > 0\} \Longleftrightarrow \sigma_i = -1 \to \sigma_i = +1 , \\ &\{c < x_i(t) < c+(1/m)p_i(t)\Delta t,\ p_i(t) < 0\} \Longleftrightarrow \sigma_i = +1 \to \sigma_i = -1 . \end{aligned} \tag{12}$$

Then, we get for $W_i(\sigma,\Delta t)$:

$$\begin{aligned} W_i(\sigma,\Delta t) = \frac{1}{Z}\int_{-\infty}^{\infty} \prod_{j(\neq i)} dp_j \exp\left[-\beta \sum_{j(\neq i)} \frac{p_j^2}{2m}\right] \\ \times \int_{S(\sigma)} \prod_{j(\neq i)} dx_j \left\{ \frac{1+\sigma_i}{2} \int_{-\infty}^{0} dp_i \exp\left[-\beta\frac{p_i^2}{2m}\right] \int_{c}^{c+p_i\Delta t/m} dx_i e^{-\beta V(\{x_j\})} \right. \\ \left. + \frac{1-\sigma_i}{2} \int_{0}^{\infty} dp_i \exp\left[-\beta\frac{p_i^2}{2m}\right] \int_{c-p_i\Delta t/m}^{c} dx_i e^{-\beta V(\{x_j\})} \right\} . \end{aligned} \tag{13a}$$

For $\Delta t \to 0$ the $x_i$ integration and $p_j$ integration ($j \neq i$) is easily performed, leading to

$$W_i(\sigma,\Delta t) = \frac{\Delta t}{m}\frac{1}{Z}\left[\frac{2\pi m}{\beta}\right]^{(N-1)/2} \int_0^\infty dp_i p_i e^{-\beta p_i^2/2m} \int_{S_i(\sigma)} \prod_{j(\neq i)} dx_j e^{-\beta V_i(\{x_j\}_{j\neq i}, x_i = c)} . \tag{13b}$$

The right-hand side of Eq. (13b) is rather similar to the right-hand side of Eq. (9), but with the main difference that the $i$th particle is taken at $x_i = c$, the transition state. $S_i(\sigma)$ is the configuration cell under the constraint that $x_i = c$. $W_i(\sigma,\Delta t)$ can also be calculated in a low-temperature and small-$\eta$ expansion. Substituting this result and Eq. (11) into Eq. (8), one obtains [13,14]

$$\begin{aligned} W_i(\sigma) \cong \alpha(T)[1+\delta(T)\sigma_{i-1}\sigma_{i+1}] \\ \times [1-\tfrac{1}{2}\gamma(T)\sigma_i(\sigma_{i-1}+\sigma_{i+1})] , \end{aligned} \tag{14a}$$

with

$$\begin{aligned} \alpha(T) = \frac{1}{2\pi}\left[\frac{C_1+4C_2}{m}\right]^{1/2} \\ \times \exp\{1-\mathrm{erf}[B(a^2-b^2)^{1/4}]+\beta J_0\}\cosh^2 K , \end{aligned} \tag{14b}$$

$$\delta(T) = \tanh^2 K, \quad \gamma(T) = \tanh 2K ,$$

and

$$\begin{aligned} K = 2\beta\eta|J_0| + \frac{2}{\sqrt{\pi}}\eta B(a^2-b^2)^{1/4} e^{-B^2(a^2-b^2)^{1/2}} \\ \to 2\beta\eta|J_0| \quad \text{for } T \to 0 . \end{aligned} \tag{14c}$$

erf denotes the error function.

This transition rate is precisely the *most general* rate of Glauber's kinetic Ising model without external field, and only nearest neighbor interaction [16]. That only the nearest-neighbor interaction appears is due to the assumption that $\eta \ll 1$. The parameters $\alpha$, $\delta$, and $\gamma$ are uniquely determined by the microscopic parameters of our model defined by Eq. (2).

## IV. MOLECULAR-DYNAMICS SIMULATION

We studied the dynamics of our model by numerically integrating Newtonian equations of motion. We have used a predictor-corrector algorithm of Oesterwinter, which has shown to have the largest accuracy with respect to speed. Other integration schemes had difficulties to handle the nondifferentiability of $V_1(x)$ at

$x=c$ (for more details see [13]). We used scaled variables, i.e., we set $C_1=m=1$. Hence a time unit is always given in units of $(m/C_1)^{1/2}$. The temperature $T$ can be obtained from the mean kinetic energy of the particles

$$k_B T=\frac{m}{N}\sum_{i=1}^{N}\dot{x}_i^2(t) \tag{15}$$

and is measured in units of $7.25\times10^{23}$ [$C_1$ (kg/sec$^2$)] K.

To equilibrate the system, we first generated $N$ Gaussian distributed random numbers with the mean value equal to $c$ for the coordinates and $N$ further numbers generated in the same way for the velocities of the particles. The standard deviations for these numbers were chosen such that the resulting temperature was high with respect to the minimum barrier height $b_{\min}$ for the single spin flip. After equilibration we switched on a small damping force leading to a decrease of the temperature. Dependent on the time the damping force was active, we could extract (after further equilibration) several initial configurations for the system corresponding to different temperatures.

To calculate the spin-autocorrelation function $C(t)=\langle\sigma_i(t)\sigma_i(0)\rangle$ we did not store the exact coordinates of the particles but only the spin configuration of the system. Having stored $m=kh$, $k=0,1,2,\ldots$ ($h$ is the time step of the algorithm) configurations, we can proceed as follows:

$$C(t)\equiv C(kh)=\frac{1}{N}\frac{1}{m}\sum_{l=0}^{m-1}\sum_{i=1}^{N}\sigma_i(lh)\sigma_i((l+k)h)\ . \tag{16}$$

The summation over $l$ is the time average. For the simulation we have chosen $N=5000$ particles for temperatures not far below the minimum barrier height $b_{\min}$ and $N=2500$ for rather low temperatures. As the time step we chose $h$ between 0.008 and 0.025 time units for low and rather high temperatures, respectively.

We calculated the correlation function for $C(t)\geq10^{-2}$. For values of $C(t)$ smaller than $10^{-2}$ the integration algorithm became incorrect. $C(t)$ can be fitted by a Kohlrausch-Williams-Watts (KWW) law, also called stretched exponential, but the decay of the correlation functions is too small to determine the Kohlrausch parameters properly. The simulation runs were performed over $10^3$–$10^5$ time units, depending on the temperature and the choice of the model parameters. For very low temperatures $k_B T\ll b_{\min}(\sigma)$ the exploration of the configuration space will progress only slowly, since the potential-energy landscape has exponentially many valleys and the transitions between them become very rare. To get a reasonable statistic at low temperatures also, we had to perform simulations much longer than the timescale on which $C(t)$ decays to $10^{-2}$. We also determined an error for $C(t)$ by choosing different initial configurations.

For most of the temperatures, there was a small increase of the temperature which could not be eliminated by a smaller integration time step $h$. When this temperature drift exceeded 1% we used a "heat bath" to keep the mean kinetic energy constant. The simulations were done on an IBM computer work station 320H, where the longest runs took about 100 h CPU time.

## V. KINETIC DESCRIPTION VERSUS MOLECULAR-DYNAMICS SIMULATION

In order to compare the molecular-dynamics (MD) results for the spin-autocorrelation function $C(t)$ with the corresponding result from the kinetic description, deduced in Sec. III, we have to calculate $C(t)$ from Eq. (7) using the transition rates Eq. (14). For $\delta\neq0$ this cannot be done rigorously. Among several approximation schemes (e.g., a continued fraction expansion [17]) we will choose the generalized moment expansion (GME) by Bauer, Schulten, and Nadler [18]. This approach enables us to calculate the spin-correlation functions even for arbitrary transition rates and particularly for $\delta\neq0$. This method is valid for *all* times and *all* temperatures, as long as the correlation length $\xi(T)$ is smaller than the system size. The GME can reproduce the long-time as well as the short-time behavior of dynamical observables in a stochastic system. The method requires the numerical inversion of the corresponding master operator $L$ and therefore can only be applied to *finite* systems. In the following we shortly review the GME in matrix notation, which is suitable for the discrete state space of a spin system. Numbering the $2^N$ Ising spin configurations $\sigma$ of the $N$-particle system by $i=1,2,\ldots,2^N$ and representing the set of probabilities $\{p(\sigma)\}$ by the $2^N$-component vector $\mathbf{p}$ with $p_i\hat{=}p(\sigma)$, the master equation (7) takes the simple form

$$\frac{\partial}{\partial t}\mathbf{p}(t)=L\,\mathbf{p}(t)\ . \tag{17}$$

A formal solution of Eq. (17) is

$$\mathbf{p}(t)=e^{Lt}\mathbf{p}(t=0)\ . \tag{18}$$

The matrix element $(e^{Lt})_{ij}$ gives the probability of finding the system in state $i$ at time $t$, provided it was in state $j$ at time $t=0$. The equilibrium distribution $\mathbf{p}_0$ represents the eigenvector of $L$ with eigenvalue zero.

We consider a correlation function $M(t)$ of an observable $f$ at time $t$ and an observable $g_0$ at time $t=0$

$$M(t)=\langle f(t)g_0\rangle=\mathbf{f}^T e^{Lt}\mathbf{g}\ , \tag{19}$$

where $\mathbf{f}^T$ denotes the transposed vector of $\mathbf{f}$ and $g_i=g_{0,i}p_i(t=0)$. If $\mathbf{f}$ is identical to $\mathbf{g}_0$ and $\mathbf{p}(t=0)=\mathbf{p}_0$, then $M(t)$ is an equilibrium autocorrelation function. In the following we determine the deviations $\Delta M$ of $M(t)$ from the equilibrium value

$$\begin{aligned}\Delta M(t)&=M(t)-M(t\to\infty)\\&=\langle f(t)g_0\rangle-\langle f\rangle\langle g_0\rangle\\&=\mathbf{f}^T e^{Lt}\mathbf{g}-\sum_i f_i p_{0,i}\sum_j g_{0,j}p_{0,j}\ .\end{aligned} \tag{20}$$

$\Delta M(T)=M(t)$ if the expectation value of $g_0$ in equilibrium vanishes. This means that $\mathbf{g}_0$ is orthogonal to $\mathbf{p}_0$. Furthermore, we define a projection operator $J_0$ which projects onto the equilibrium distribution $\mathbf{p}_0$. Conse-

quently $(1-J_0)$ projects onto the orthogonal complement of $\mathbf{p}_0$. Since the operators $L$ and $J_0$ commute, we can write

$$\Delta M(t)=\mathbf{f}^T(1-J_0)e^{Lt}(1-J_0)\mathbf{g} \ . \tag{21}$$

Next, we consider the Laplace transform $\Delta\hat{M}(\omega)$ of $\Delta M(t)$:

$$\begin{aligned}\Delta\hat{M}(\omega)&=\int_0^\infty dt\, e^{-\omega t}M(t), \quad \mathrm{Re}(\omega)>0\\ &=\int_0^\infty dt\, e^{-\omega t}\mathbf{f}^T(1-J_0)e^{Lt}(1-J_0)\mathbf{g}\\ &=\mathbf{f}^T(1-J_0)\frac{1}{\omega-L}(1-J_0)\mathbf{g} \ .\end{aligned} \tag{22}$$

$\Delta\hat{M}(\omega)$ can be expanded around $\omega=0$ and $\omega=\infty$:

$$\Delta\hat{M}(\omega)\sim\begin{cases}\displaystyle\sum_{\nu=0}^{\infty}\mu_{-\nu-1}(-\omega)^\nu, & \omega\to 0 \quad (23a)\\ \displaystyle\frac{1}{\omega}\sum_{\nu=0}^{\infty}\mu_\nu\left[\frac{-1}{\omega}\right]^\nu, & \omega\to\infty \ . \quad (23b)\end{cases}$$

The expansion coefficients are called the *generalized moments* $\mu_\nu$,

$$\mu_\nu=(-1)^\nu\mathbf{f}^T L^\nu\mathbf{g} \ . \tag{24}$$

The moments with $\nu\geq 0$ and $\nu<0$ are the high-frequency and low-frequency moments, respectively, which characterize the short- and the long-time behavior of $M(t)$. $\mu_0$ is just the initial value $\Delta M(0)$.

The crucial point of the GME is that the high- and low-frequency behavior of $\Delta\hat{M}(\omega)$ is interpolated by an $[N_h,N_l]$ Padé approximant $\Delta\hat{m}(\omega)$ which yields a high- and low-frequency expansion consistent with the expansion of $\Delta\hat{M}(\omega)$ around $\omega=0$ and $\omega=\infty$. Then the Laplace transform $\Delta\hat{M}(\omega)$ can be represented by

$$\Delta\hat{M}(\omega)\approx\Delta\hat{m}(\omega)=\sum_{n=1}^{N_0}\frac{a_n}{\lambda_n+\omega} \ . \tag{25}$$

If we have calculated $N_h$ high- and $N_l$ low-frequency moments with $N_h+N_l=2N_0$, we get in the time regime

$$\Delta M(t)\cong\Delta m(t)=\sum_{n=1}^{N_0}a_n e^{-\lambda_n t} \ , \tag{26}$$

where $a_n$ and $\lambda_n$ are uniquely determined by the generalized moments $\mu_\nu$.

The final step is to evaluate the transition-rate matrix $L$ for the kinetic Ising model. There is a state space of dimension $2^N\times 2^N$ for an $N$-spin system. The elements of $L$ are the transition rates between two different states. For two states not connected by a single spin flip, the corresponding matrix elements vanish. An appropriate ordering of the spin configurations is such that the $i$th spin configuration is given by the binary representation of $i$, implying a 1 for spin up and a 0 for spin down. For $\mu_\nu$ $(\nu\leq -1)$ one needs $L^{-1}$ [cf. Eq. (24)], which can be obtained exactly from $L$ for $N$ not too large.

In our application of the GME we have chosen $N_l=N_h=7$ and $N_0\equiv N=14$. The results obtained for $C(t)$ from the MD simulation and the kinetic-Ising model are represented in Figs. 3(a)–3(c) for different temperatures and model parameters. We stress that the choice of the model parameters [cf. Eq. (2)] uniquely determines both the numerical result and the result following from the kinetic approach. Thus there is *no* fit parameter. The temperatures for these three examples are about *one-fourth* of the minimum barrier height $b_{\min}$. Both results

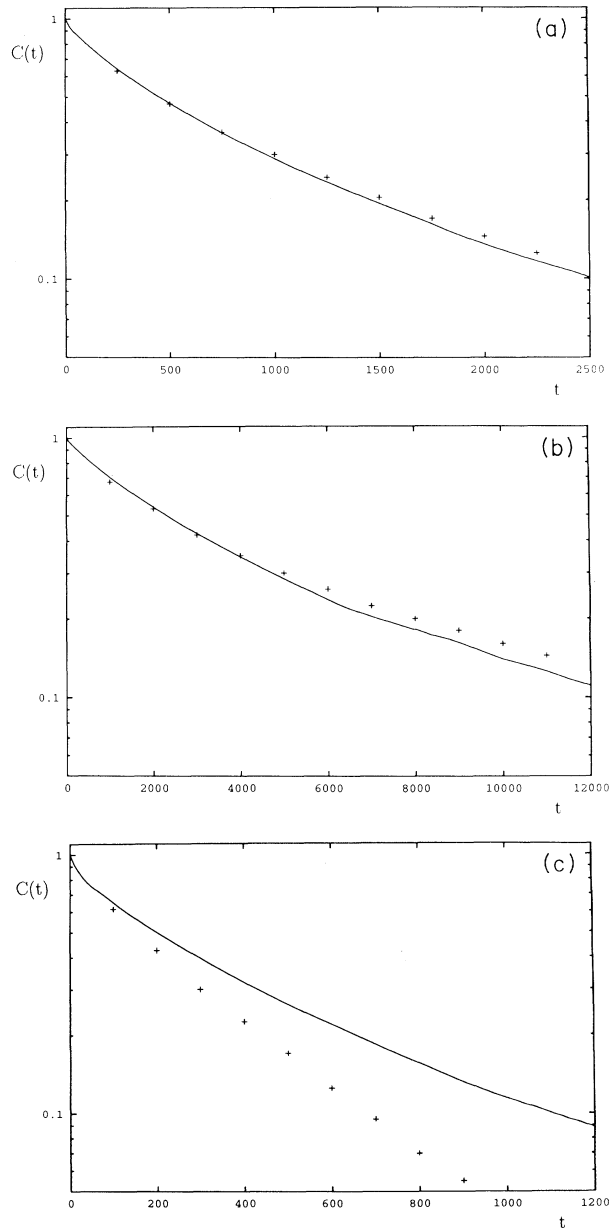


FIG. 3. Spin-autocorrelation function $C(t)$ for different temperatures and model parameters. (a) $T\simeq 0.0183$, $C_1=1$, $C_2=-0.044$ $(\to\eta\simeq 0.0483)$, $a_+=5$, $a_-=0.4$, $b=10$, $c=5$ $(\to b_{\min}\simeq 0.0711)$. (b) $T\simeq 0.0096$, $C_1=1$, $C_2=-0.044$ $(\to\eta\simeq 0.0483)$, $a_+=5$, $a_-=0.3$, $b=10$, $c=5$ $(\to b_{\min}\simeq 0.040)$. (c) $T\simeq 0.0043$, $C_1=1$, $C_2=-0.044$ $(\to\eta\simeq 0.0483)$, $a_+=5$, $a_-=0.2$, $b=11.7$, $c=4.818$ $(\to b_{\min}\simeq 0.178)$.

agree better than 10% over the time scale where $C(t)$ decays from 1.0 to about 0.1, in the cases of Figs. 3(a) and 3(b). If we consider that even a *small* deviation of the mean relaxation time for both results manifests itself in a *large* relative deviation of the corresponding correlation functions $C(t)$ at *large* times, the results in Figs. 3(a) and 3(b) are surprisingly good. Therefore the huge discrepancy of both results in Fig. 3(c) of more than a factor of 5 at $t=900$ does not necessarily imply a failure of the kinetic-Ising-model approach. This can be demonstrated by the *direct* determination of the three transition rates for the transitions:

$$\uparrow\uparrow\uparrow \rightarrow \uparrow\downarrow\uparrow ,$$

$$\uparrow\downarrow\uparrow \rightarrow \uparrow\uparrow\uparrow ,$$

$$\uparrow\uparrow\downarrow \rightarrow \uparrow\downarrow\downarrow ,$$

from the MD simulation. For instance, for the transition $\uparrow\uparrow\uparrow \rightarrow \uparrow\downarrow\uparrow$ the number $N_{\uparrow\uparrow\uparrow}(t)$ of up spins with two neighboring up spins are deduced as a function of time. For temperatures low enough composed to $b_{\min}$, an exponential $t$ dependence was found. The corresponding transition rate $W_i(\uparrow\uparrow\uparrow \rightarrow \uparrow\downarrow\uparrow)$ is just the decay rate. By use of Eq. (14a), these three transition rates allow one to determine $\alpha$, $\delta$, and $\gamma$ for a given temperature. On the other hand $\alpha$, $\delta$, and $\gamma$, following from the transition-state result Eq. (14b), can be calculated for that temperature and the microscopic model parameters. A comparison between both results is shown in Table I for three different temperatures. For $T=0.0043$ [the case of Fig. 3(c)] there is a discrepancy for $\alpha$, $\delta$, and $\gamma$ of $\sim 25\%$, 30%, and 5%, respectively. With decreasing temperature, the deviation between both results decreases, confirming our expectation that the kinetic-Ising-model description should become better at lower temperatures.

## VI. SUMMARY AND CONCLUSIONS

For a chain of classical particles exhibiting a complex energy landscape in configuration space with exponentially many metastable configurations, we have investigated its dynamical behavior. This has been done in two different ways. First, the *deterministic* microscopic (Newtonian) equation of motion has been investigated numerically. From this simulation we determined the time-dependent spin-autocorrelation function $C(t)$ of the pseudospins $\sigma_i(t)$, which specify whether the $i$th particle displacement $x_i(t)$ is larger [$\hat{=}\sigma_i(t)=+1$] or smaller [$\hat{=}\sigma_i(t)=-1$] than $c$. Second, considering that (under some conditions) all the metastable configurations are in a one-to-one correspondence with Ising spin configurations $\boldsymbol{\sigma}=\{\sigma_i\}$, the dynamical exploration of the configuration space can be regarded as a *deterministic* dynamics $\boldsymbol{\sigma}(t)$ in pseudospin space. Since Kob and Schilling [13] have found strong evidence that this dynamics is *ergodic,* it is tempting to describe the deterministic dynamics of the pseudospin by a stochastic process, i.e., by a *kinetic equation.* Assuming Markovian behavior, this has been performed in the framework of the transition-state theory. The result was a one-dimensional kinetic Ising model. For low temperatures and $\eta \ll 1$ the transition rates $W_i(\sigma)$ agree with the most general Glauber rates for an Ising model with nearest-neighbor coupling. A comparison [Figs. 3(a)–3(c)] between the numerical result for $C(t)$ with that obtained from the kinetic Ising model yields *without* any fit parameter fairly good agreement, at least at low enough temperatures. This result is also supported by a direct determination of the transition rates from the MD simulation which are in reasonable

TABLE I. Comparison of $\alpha$, $\delta$, and $\gamma$ obtained from the transition-state result [Eq. (14b)] [upper half] with the corresponding values deduced from the MD simulation [lower half] for three different temperatures and the same model parameters as for Fig. 3(c).

| Parameter \ $T$ | 0.0043 | 0.0032 | 0.0020 |
|---|---|---|---|
| $\gamma$ | 0.7540 | 0.8662 | 0.9710 |
| $\delta$ | 0.2063 | 0.3344 | 0.6142 |
| $\alpha$ | $2.18\times10^{-3}$ | $4.48\times10^{-4}$ | $1.25\times10^{-5}$ |
| $\gamma$ | 0.7970 | 0.8870 | 0.9873 |
| $\delta$ | 0.2731 | 0.4123 | 0.6837 |
| $\alpha$ | $2.85\times10^{-3}$ | $4.78\times10^{-4}$ | $1.42\times10^{-5}$ |

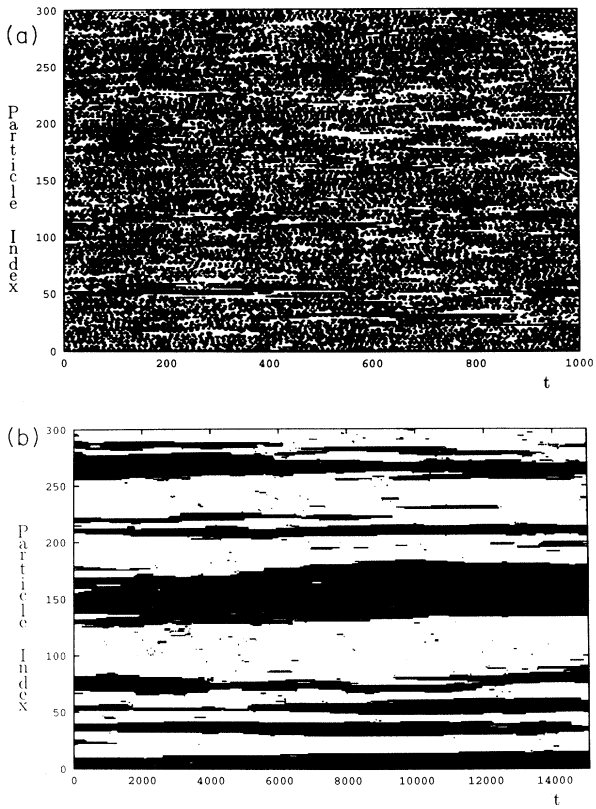


FIG. 4. Pseudospins $\sigma_i(t)$ as a function of time for a part of the chain. $\sigma_i(t)=+1$ and $\sigma_i(t)=-1$ are represented by white and black dots, respectively. $C_1=1$, $C_2=-0.094$, $a_+=5$, $a_2=0.2$, $b=11.7$, $c=4.487$ ($\rightarrow b_{\min}\simeq 0.0138$). (a) $T=0.0312$, (b) $T=0.0054$.

agreement with the rates obtained from transition-state theory.

For higher temperatures the kinetic description by the master equation (7) becomes worse. The reason for this is the appearance of *dynamically correlated clusters* of particles performing *collective oscillations* over a certain time scale. This behavior is reminiscent of intermittency in chaotic systems [19], since the collective oscillations are followed by chaotic motion, which again may result in oscillatory motion. This behavior is depicted in Fig. 4(a), which shows the pseudospin dynamics for particles $i=1,2,\ldots,300$. $\sigma_i=+1$ and $\sigma_i=-1$ are presented by white and black dots, respectively. The collective oscillations show up as *periodic stripes* along the time axis. The size of the clusters is the extension of the stripes in the vertical direction, which is about five particles. It is also interesting that it has recently been speculated [20] that such dynamically correlated clusters play a role for the glass transition. That their existence invalidates our kinetic approach is obvious since the periodic oscillations between $\sigma_i=+1$ and $-1$ represent a sort of memory, which is not accounted for by the master equation (7). For low enough temperatures these periodic oscillations disappear, as shown in Fig. 4(b). Large domains of up and down spins occur and the dynamics results in stochastic single spin flips leading to, e.g., Brownian motion of the domain walls. In this temperature regime the kinetic description of the Newtonian dynamics becomes meaningful.

To conclude, we have demonstrated that the Newtonian dynamics of a one-dimensional model with competing and anharmonic interactions can be mapped onto a one-dimensional kinetic Ising model, provided the temperature is low enough compared with the minimum barrier height. At higher temperatures memory effects due to collective oscillations of small clusters occur.

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