Discrete theory of kink diffusion in the ϕ^4 lattice with comparison to the continuum approximation

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We use the memory function formalism to study kink dynamics in a thermal ϕ^4 lattice. By introducing kink-fluctuation interactions as a perturbation, and by including discrete effects of kink structure nonperturbatively, we are able to reproduce the qualitative behavior of the kink diffusion constant D_K and the kink-velocity autocorrelation spectrum as calculated from molecular-dynamics simulation. The continuum approximation obtained by ignoring discrete structure associated with the lattice kink yields results which are qualitatively incorrect at low temperatures and weak interatomic coupling. In particular, D_K goes to zero at low temperatures only when the discrete structure of the kink is included.

I. INTRODUCTION

In recent years a number of efforts have been made to understand the nature of thermal kink dynamics in one-dimensional lattices that support solitary waves.[1-6] It is widely believed that the diffusion of kinks is responsible for the extremely intense and narrow central peak observed in neutron inelastic scattering from ferroelectrics near ferrodistortive phase transitions.[1] What has puzzled most theoreticians is that the peak is so narrow—too narrow for a neutron spectrometer to resolve. A phenomenological theory of kink dynamics based upon molecular-dynamics simulation has suggested that intrinsic effects of lattice discreteness are sufficient to trap a kink and make the kink diffusion constant extremely small (and thus the central peak extremely narrow) in experimental cases of interest.[5] Our approach yields similar findings, but does so from a first-principles approach without resorting to adjustable parameters.

Theoretical efforts to calculate the kink diffusion constant have generally utilized a continuum approximation which yield analytical solutions.[1-4] Most conclude that kink motion is indeed diffusive. This has been confirmed by molecular-dynamics simulation;[5] however, the best theoretical values for the kink diffusion constant D_K are off by more than an order of magnitude.

We have made theoretical calculations of the kink diffusion constant which agree with molecular dynamics results to within a factor of two in most cases of interest, and which reproduce the qualitative behavior of D_K with temperature T and interatomic coupling strength. We have done this by using classical perturbation theory to calculate the memory function (cf. Sahni and Mazenko[3]) and by including discrete effects upon kink structure nonperturbatively.

We find that D_K vanishes at low temperatures T only when the discrete structure of the kink is included in the calculation; the continuum theory that results by ignoring the discrete kink structure yields a nonzero value of D_K at $T=0$. Furthermore, our calculations of the discrete kink velocity autocorrelation spectrum reveal a strong oscillatory peak at low temperatures characteristic of trapped kink oscillations, a prediction absent in the continuum theory but present in computer simulation.[6] Thus it becomes clear that discrete effects are essential even to a qualitative understanding of thermal kink dynamics at low temperatures.

The organization of the paper is as follows. In the first part of Sec. II we discuss the general model, where the displacements in the ϕ^4 lattice are separated into a single kink plus small fluctuations. The resulting Hamiltonian consists of a sum of three parts: a lattice-kink Hamiltonian, a fluctuation Hamiltonian, and an interaction Hamiltonian that describes the interactions of the kink with phonons. The most important discrete effects are contained in the kink Hamiltonian, whose potential part varies periodically with a period of the lattice spacing and an amplitude E_a.[6] It is this kink potential that causes the trapping of kinks and drives the diffusion constant to zero at low temperature. A kink equation of motion is derived to provide the basis for calculating its dynamics. The forces upon the kinks separate into two contributions: discrete effects and kink-fluctuation interactions.

The memory function, the velocity autocorrelation function and their relation to diffusion are then discussed in the latter part of Sec. II. We discuss our basic approach (which follows the approach of Sahni and Mazenko[3]) and the approximations we use. The kink memory function $K(t)$ is calculated to the lowest nonvanishing order in perturbation theory[3] and is used to calculate D_K and the velocity autocorrelation spectrum.

In Sec. III we discuss our results for the diffusion constant and the velocity autocorrelation function. Comparisons are made with the molecular-dynamics results of Combs and Yip,[5] as well as with the results of the continuum approximation in which the discrete structure of the kink is ignored. Closing remarks are made in Sec. IV.

II. DESCRIPTION OF THE DISCRETE MODEL OF KINK DIFFUSION

A. The discrete kink equations of motion

Our model Hamiltonian is based upon the ϕ^4-lattice Hamiltonian

$$H=\sum_l \frac{m}{2}\dot{u}_l^2+\frac{C}{2}\sum_l (u_{l+1}-u_l)^2+\sum_l V_K(u_l)\ , \quad (1)$$

where m is the particle mass, u_l is the position of the lth particle relative to the lattice point $x_l=lb$, b is the lattice constant, C is the Hooke's-law force constant, and V_K is the bistable ϕ^4 potential

$$V_K(\phi)=-\frac{A}{2}\phi^2+\frac{B}{4}\phi^4 \quad (2)$$

that gives rise to nonlinear forces in the lattice. The parameters A, B, and C are all greater than zero. The sum is extended over N particles. Note that the first two terms in Eq. (1) comprise a simple harmonic chain.

The continuum approximation to (1), obtained by letting $u_l(t)\cong u(x,t)$, $u_{l+1}-u_l\cong b\,du/dx$, and $\sum_l \to \int dx/b$, leads to equations of motion that support stable solitary density waves called kinks. We refer the reader to excellent discussions of kinks which already exist in the literature (cf. Refs. 1, 2, and 6). We use the symbol $u_K(X)$ to denote the kink waveform which is a function of the kink position $X(t)$. The continuum ϕ^4 theory yields a hyperbolic tangent waveform with a wave number (i.e., inverse width) $K\sim 1/\sqrt{C/A}$.

The dispersion forces which cause the deviation of the lattice-kink waveform from the continuum-kink waveform are, to lowest order, proportional to $1/(C/A)$. The ratio C/A becomes an inverse measure of discrete lattice effects. Thus one expects that for large C/A the continuum theory will be valid; however, this is not entirely true. Consider, for example, the potential energy of the lattice kink

$$U(X)=\frac{C}{2}\sum_l [u_K^{l+1}(X)-u_K^l(X)]^2+\sum_l V_K[u_K^l(X)]\ , \quad (3)$$

where $u_K^l(X)$ is the lattice-kink waveform. If u_K^l is approximated by the continuum form (i.e., $\tanh[K(x_l-X)]$), then $U(X)$ is periodic in the lattice spacing b. In fact, static solutions of the ϕ^4 lattice have been found as a function of X (subject to an appropriate equation of constraint).[6] We use the approximate form of $U(X)$ which is found to be

$$U(X)=U_0+\frac{E_a}{2}\cos(2\pi X/b)\ , \quad (4)$$

where E_a has the following dependence upon C/A:

$$E_a=A^2/4B\exp(-4.84C/A)\ . \quad (5)$$

Thus, at low temperatures ($T<E_a/k$, where k is Boltzmann's constant), a kink in thermal equilibrium with the lattice will become pinned between lattice sites, regardless of the value of C/A; at high temperatures ($T\gg E_a/k$) trapping effects can be ignored.

Of course, the low-temperature solutions corresponding to (1) are more general than single kinks alone. Multiple kinks are possible (especially as the system becomes large), and fluctuations exist as perturbations around kinks. We limit our attention to a system consisting of a single kink plus fluctuations

$$u_l(t)=u_K^l(X)+\xi_l(t)\ , \quad (6)$$

where now $u_K^l(X)$ is the waveform corresponding to the static solutions of (1) (subject to the appropriate constraint; cf. Ref. 6). We believe, however, that the single-kink results will not be significantly different from multiple-kink results, provided that kink-kink interactions can be ignored.

By substituting (6) into (1), we obtain a Hamiltonian that separates into kink, fluctuation, and interaction parts (for details, see the Appendix):

$$H=H_K+H_\xi+H_{\rm int}\ . \quad (7)$$

This is actually a model Hamiltonian, since we have used an equation of constraint which causes the fluctuations to remain small [see Eq. (A6)]; this results in the elimination of the interaction terms in the kink and fluctuation velocities.

We note that

$$H_K=P^2/2M+U(X)\ , \quad (8)$$

where M is the kink effective mass [see Eq. (A4)], $P=M\,dX/dt$ is the kink momentum, and $U(X)$ is given by (4). In the absence of interactions with the fluctuations, this represents the "free" lattice kink; of course, it is not strictly free due to the periodicity in $U(X)$, i.e., the kink is accelerated due to the effects of discrete kink structure.

H_ξ consists only of terms in ξ_l up to quadratic order. Thus, in the absence of kinks, it is a Hamiltonian for free phonons (extended normal modes) which oscillate about the bottom of one of the wells of V_K. The presence of kinks, however, has a number of effects upon the fluctuations. The continuum theory reveals that the extended normal modes are distorted near the kink; in addition, a low-frequency local mode appears. Following the normal procedure of perturbation theory, we choose to treat the extended modes as undistorted plane waves with the dispersion of frequencies characteristic of the lattice. We feel that we cannot ignore the local mode, since at thermal equilibrium it will have the largest amplitude (it has the lowest frequency); however, we are ignorant of its lattice frequency and waveform. Thus we attempt to include the local-mode effect by assuming that it has the continuum waveform and frequency, yet is still "orthogonal" to the extended modes in the system, i.e., it couples to other modes only through nonlinear forces.

The equation of motion for the kink corresponding to (6) is obtained from the Hamiltonian equations of motion which yield

$$M\ddot{X}=-\frac{\partial U}{\partial X}-\frac{1}{2}\frac{\partial M}{\partial X}\dot{X}^2-\frac{\partial H_{\rm int}}{\partial X}+\left[2m\sum_l \frac{\partial^2 u_K^l}{\partial X^2}\dot{\xi}_l\right]\dot{X}\ . \quad (9)$$

Note that as E_a goes to zero the first term vanishes, and the second term becomes small. We find later that the main contributions to thermal kink dynamics come from the first and third terms (which contain the discrete kink structure and nonlinear two-phonon perturbations, respectively).

B. The memory function, velocity autocorrelation spectrum, and kink diffusion

We begin our discussion of kink diffusion with the kink velocity autocorrelation function $\psi(t)$ whose time integral is the kink-diffusion constant

$$D_K = \int_0^\infty dt\, \psi(t) \,. \tag{10}$$

Note that the equal time value $\psi(0)$ is just the variance of the velocity, and is equal to kT/M for a particle obeying Maxwell-Boltzmann statistics.

The velocity autocorrelation function may be calculated from the memory function equation whose Laplace transformed representation is

$$\hat{\psi}(s) = \psi(0)[s + \hat{K}(s)]^{-1} \,, \tag{11}$$

where $\hat{\psi}(s)$ and $\hat{K}(s)$ are the Laplace transforms of $\psi(t)$ and the memory function $K(t)$, respectively [see Eq. (A9) for the real time representation of (11); for an excellent discussion of the memory function and self-diffusion, see Ref. 7]. $K(t)$ is a function of the normalized acceleration autocorrelation and normalized acceleration-velocity correlation functions $\phi(t)$ and $\zeta(t)$, respectively.[7] The latter three functions are related through their respective Laplace transforms by

$$\hat{K}(s) = \hat{\phi}(s)/[1 + \hat{\zeta}(s)] \,. \tag{12}$$

The diffusion constant can then be obtained from either $\hat{K}(0)$ or $\hat{\psi}(0)$

$$D_K = kT/[M\hat{K}(0)] = \hat{\psi}(0) \,. \tag{13}$$

In general, the memory function is very difficult to obtain directly from the equations of motion. Usually, it is used to build theoretical models of stochastic behavior by choosing a functional form of $K(t)$ with a variable parameter(s).

Our approach uses perturbation theory to lowest nonvanishing order in $H_{\rm int}$, which is essentially the approach used by Sahni and Mazenko in Ref. 3. Since the velocity-force correlation does not contribute to this order [see (A10) in the appendix], this amounts in approximating the memory function by the lowest nonvanishing contribution to the force-autocorrelation function. Therefore, we write

$$K(t) \cong \mathcal{C}(\phi(t)) \,, \tag{14}$$

where $\mathcal{C}$ indicates lowest order of $\phi(t)$ [see Eq. (A12) of the appendix]. We call this the "nearly-free-kink" approximation.

The memory function is found to consist of a sum of 14 terms $K_j(t)$ (see Appendix). Only four contribute significantly: The memory K_1 due to the periodic kink-acceleration autocorrelation (i.e., from $\langle dU/dX(t) \times [dU/dX(0)] \rangle$), K_7 due to the lowest-order nonlinear fluctuation forces $\langle \xi_l^2(t) \xi_l^2(t) \rangle$, the local-mode memory $K_{\rm loc}$, and K_{12} due to purely dissipative fluctuation forces acting upon the kink. The latter two only contribute at high temperatures compared to E_a/k. Note that K_1 is due to discrete kink structure and is identically zero in the continuum approximation.

III. RESULTS AND DISCUSSION

A. The kink diffusion constant

In the following discussion we often make use of the nondimensionalized temperature, diffusion constant, frequency and velocity autocorrelation spectrum. These can be obtained from the appropriate combination of length, time, and energy scales which are, respectively, b, $\sqrt{m/A}$, and A^2/B. In particular, the thermal behavior of the kink can be characterized by two nondimensional numbers, the nondimensional temperature and the ratio C/A.

We first discuss the temperature dependence of the kink diffusion constant where we hold the ratio C/A constant. We limit our present attention to the value $C/A = 0.5$ (see Fig. 1) for which molecular-dynamics results are available.[5] The diffusion constant is found to go to zero rapidly as T goes to zero. This is consistent with the molecular-dynamics results. The theoretical values are, however, too high by roughly a factor of two except at very low temperatures where the deviation is larger. The fact that the theoretical prediction is too high is an expected result of the nearly-free-kink approximation discussed above.

The effects of the discrete kink structure upon diffusion are striking when a comparison is made to the continuum theory (see Fig. 1). The latter is calculated by setting E_a to zero. Qualitative disagreement exists between the continuum theory and molecular dynamics for low tempera-

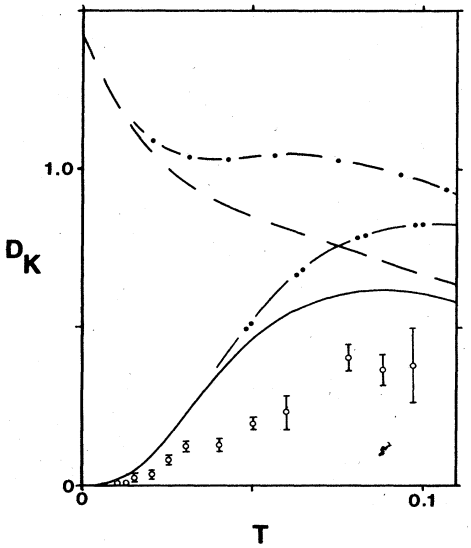

FIG. 1. The kink diffusion constant D_K (in reduced units of $b^2\sqrt{A/m}$) for $C/A = 0.5$ as a function of temperature (in reduced units of A^2/Bk). The solid curve is the discrete theory, the dashed curve is the continuum theory, and the circles are molecular-dynamics data from Ref. 5. The difference between the solid and dashed line is a measure of the effects of the discrete kink structure upon kink diffusion. The dashed-double-dotted and dashed-dotted curves are the diffusion constant with the local-mode contribution subtracted out from the discrete and continuum theories, respectively.

tures. The discrete and continuum results approach one another only at high temperatures. Aside from our calculations and those of Sahni and Mazenko,[3] we are aware of only one other calculation of the ϕ^4 kink-diffusion constant—that of Wada and Schrieffer.[2] When their results are plotted in Fig. 1 they are indistinguishable from the horizontal axis.

The fact that D_K does not go to zero as T goes to zero in the continuum approximation is attributable to the fact that the memory function K_7 goes to zero linearly as T. It should be noted that this result is different from that obtained by previous authors in Ref. 3 simply because we have avoided what should be considered poor approximations on their part; otherwise, their results would be identical to the continuum approximation which excludes the local-mode contribution (i.e., the dashed-dotted curve of Fig. 1).

The local-mode contribution lowers the diffusion constant at higher temperatures (see Fig. 1). This is expected since it can couple to other degrees of freedom and dissipate kink energy into extended lattice modes. The magnitude of the local-mode contribution that we have calculated should, however, be treated with some skepticism. The local-mode frequency corresponding to the discrete kink solution (which is probably lower than the continuum value) and temperature effects on phonon dispersion (which affects phonon-phonon interactions) are not included. Whether inclusion of these effects will cause an overall increase or decrease in the local-mode contribution is not clear to us at this point.

Now consider the dependence of D_K upon C/A, holding T constant. In Fig. 2 the discrete and continuum results are plotted for $T=0.02$. Clearly, discrete effects significantly lower D_K for $C/A<1$. At higher values of C/A, D_K increases linearly with C/A, with the discrete and continuum values becoming indistinguishable from one another. At high T the effects of discreteness are much less apparent (see Fig. 3) and the comparison to the molecular-dynamics results are more favorable than for low T (see Fig. 2). The Wada and Schrieffer theory[2] yields values of D_K which are independent of C/A and lie along curves which are indistinguishable from the horizontal axes in Figs. 2 and 3.

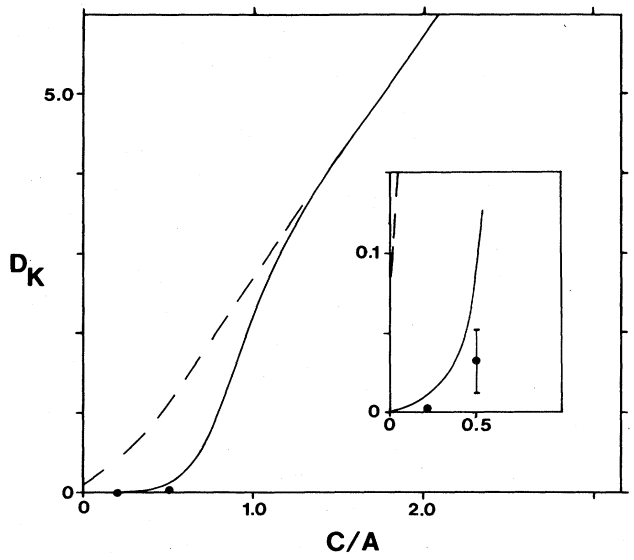

FIG. 2. D_K as a function of C/A for $T=0.02$. The inset expands the vertical axis at low C/A in order to compare the discrete theory (——) with molecular-dynamics results from Ref. 5 (●). The continuum theory is included as a dashed line for comparison, and essentially reflects the effects of the K_7 memory term. Note that D_K does not tend to vanish in the continuum theory as C/A vanishes. Also note the high-C/A behavior which is linear in C/A.

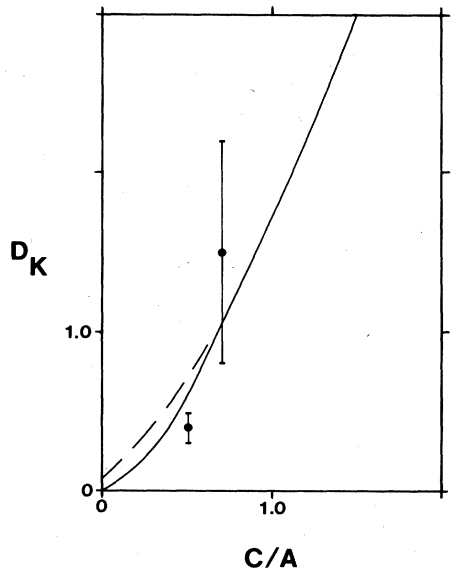

FIG. 3. Same as Fig. 2, but for $T=0.097$ (high temperature). The ratio of the continuum to discrete theory result does not deviate significantly from unity until C/A drops below 0.3. The linear increase with C/A is achieved only at much higher values of C/A (>10) at this temperature.

B. The velocity autocorrelation spectrum

We now turn our attention to the Fourier spectrum $\tilde{\psi}(\omega)$ of the velocity autocorrelation function. The long-time behavior of kinks is found at low frequencies. The diffusion constant is just $\tilde{\psi}(0)/2$ [the factor of two appears in the Fourier transform but not in the Laplace transform; cf. (13)]. The short-time kink behavior is manifested at higher frequencies; although the latter may not contribute to diffusion, it has interesting aspects of discrete origin which have already been observed in molecular-dynamics simulation,[5] thus allowing us to make another test of the validity of our theory.

In Fig. 4 we plot the low-temperature behavior of the kink-velocity autocorrelation spectrum. We compare it with simulation results.[5] A single side peak is predicted by the theory, and originates from the K_1 term, i.e., from the discrete kink structure. The peak is a manifestation of trapped kink oscillations, characteristic of low temperatures. The theoretical value of the frequency can be calculated from the curvature d^2U/dX^2 at the bottom of the kink potential minimum, and results in $\omega_0=(2\pi^2E_a/Mb^2)^{1/2}$. This value is roughly that observed in the

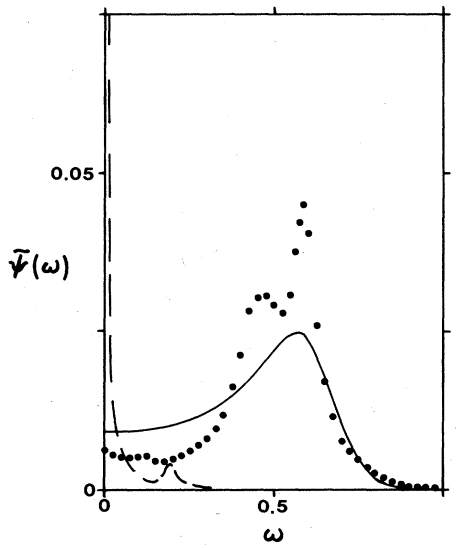

FIG. 4. Low-temperature behavior of the kink-velocity autocorrelation Fourier spectrum for $C/A=0.5$ and $T=0.005$ (ω is in reduced units of $\sqrt{A/m}$). The solid curve and dashed curves are the discrete and continuum theories, respectively; the solid circles are the molecular-dynamics results of Ref. 5. The large oscillatory peak is due to the discrete kink structure; the small continuum peak is caused by the local mode. Since the kink is almost completely trapped, the diffusive peak is vastly decreased below the continuum value which ignores trapping effects.

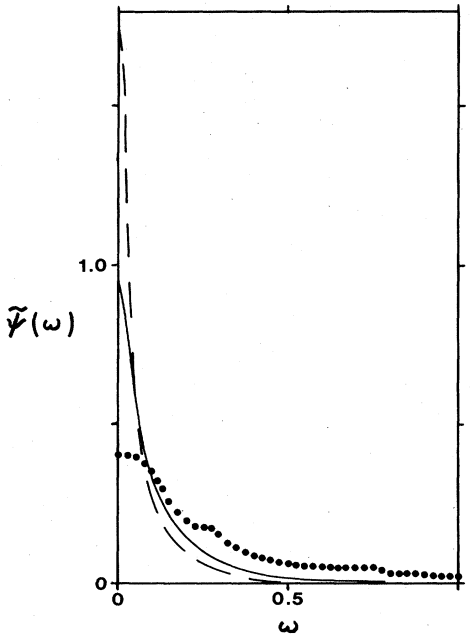

FIG. 6. The same as Fig. 4 for the same C/A ($=0.5$) with a higher temperature ($T=0.05$). Note that the continuum and discrete pictures are qualitatively similar, although the discrete calculation yields a value that is better than the continuum value by a factor of two.

molecular-dynamics simulation, although the splitting is absent. The magnitude of the oscillatory peak is roughly a factor of two too low. This is connected to the fact that the central diffusive peak is too high by about the same factor. As has been said, this is due to the limitations of the nearly-free-kink approximation.

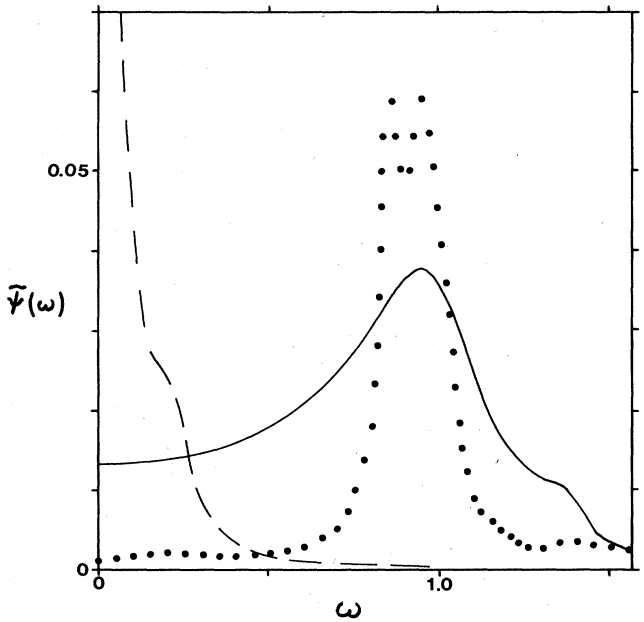

FIG. 5. The same as Fig. 4 for $T=0.02$ and $C/A=0.2$. Note the small peak at $\sqrt{2}$ that corresponds to the K_{12} contribution.

When we lower the value of C/A to 0.2, we find (see Fig. 5) that the position of the oscillatory peak is correct, although once again, the central peak is too large. As we expect, the short-time behavior is reproduced fairly well, even at low C/A values, whereas the predicted long-time behavior is poor. Nevertheless, the discrete theory is a striking improvement over the continuum theory which neglects discrete kink structure (see Fig. 5); no oscillatory peak is predicted by the continuum theory (aside from a small peak at low frequency produced by the local mode). Only when the temperature is increased to values large compared with E_a/k do the continuum and discrete pictures for $\tilde{\psi}(\omega)$ become similar (see Fig. 6).

It may be noted that additional peaks are present in the velocity autocorrelation spectrum, although they are usually of the order of 1% of the diffusive or oscillatory peaks. The additional peaks occur at frequencies near $\sqrt{2}$ and $2\sqrt{2}$. The first peak is due to K_{12}, i.e., to the dissipative fluctuation forces. The second peak is due to K_7. The position of the K_7 peak previously predicted was $\sqrt{2}$ (Ref. 3) instead of $2\sqrt{2}$, but this is due to the failure of the approximation of Ref. 3. In any case, it is a relatively minor point, as the peaks are extremely small.

IV. CONCLUSION

The discrete theory presented here has been surprisingly successful in reproducing the qualitative behavior of lattice kink diffusion from a first-principles approach. It is surprising because even though the fundamental approxi-

mation used (i.e., the nearly-free-kink approximation) is very crude, kink trapping is reproduced (a short-time phenomenon which is a bound state of the kink), as well as the qualitative behavior of the diffusion constant (a number determined by long-time behavior). Another treatment of kink diffusion, for example,[2] implicitly assumes a short-time approximation to directly evaluate what amounts to the velocity autocorrelation function in terms of the acceleration autocorrelation function; their results for the kink diffusion constant are erroneous. This shows the advantage of using the memory function formalism.[7]

Of course, we have neglected higher orders in perturbation theory. As a result, we have ignored systematic forces that cause dissipation, i.e., the velocity-acceleration correlations. We have also neglected any thermal effects upon the dispersion of frequencies. Furthermore, the nonlinear effects of phonon-phonon forces upon the kink are not incorporated exactly [cf. (A13)—(A15)].

It could be that some improvement in our results is attainable by treating the fluctuations in a manner similar to Ref. 3, deriving the dynamic structure factor for the discrete system (corresponding to the continuum treatment in Ref. 3), thereby including kink-phonon and nonlinear phonon-phonon effects more precisely. We believe, however, that kink diffusion is really a nonperturbative phenomenon; i.e., that many orders of perturbation theory, or even a nonperturbative approach, is required to yield a quantitative agreement between simulation and theory.

The limitations of our treatment are obvious, but the molecular-dynamics results suggest that the theory improves at larger values of C/A. It would be interesting, therefore, to have molecular-dynamics results at higher C/A values where the perturbation theory is expected to be more accurate.

APPENDIX

We shall first separate the Hamiltonian (1) in the text into kink-plus-fluctuation parts. This is done in a straightforward manner by introducing the separation of variables into a single kink plus fluctuations [Eq. (6)], and carrying out the algebra to obtain

$$H=H_K+H_\xi+H_{\rm int}\ , \tag{A1}$$

where

$$H_\xi=\sum_l\left[\frac{m}{2}\dot{\xi}_l^2+\frac{C}{2}(\xi_{l+1}-\xi_l)^2+A\xi_l^2\right], \tag{A2}$$

$$H_{\rm int}=\sum_l\left\{C(u_K^{l+1}-u_K^l)(\xi_{l+1}-\xi_l)-Au_K^l\xi_l+\frac{B}{2}\left[2(u_K^l)^3\xi_l+3\left[(u_K^l)^2-\frac{A}{B}\right]\xi_l^2+2u_K^l\xi_l^3+\xi_l^4/2\right]\right\}, \tag{A3}$$

and H_K is given by (8), with $U(X)$ as in (3), and the kink mass is

$$M=m\sum_l\left[\left[\frac{\partial u_K^l}{\partial X}\right]^2-2\frac{\partial^2 u_K^l}{\partial X^2}\xi_l\right]. \tag{A4}$$

The only terms missing from (A1) are the cross terms in $\dot{\xi}_l$ and $\dot{X}$. These have been eliminated due to the following considerations. We desire that the fluctuations remain small. In the continuum theory this is achieved by constraining the amplitude of the "translation mode," whose waveform is $\partial u_K/\partial X$ to be zero. The orthogonality condition that achieves this in the continuum theory is

$$\int dx\frac{\partial u_K}{\partial X}\xi(x,t)=0\ . \tag{A5}$$

This forces the mean square fluctuations to be minimized with respect to the choice of the kink position X. The corresponding discrete constraint is

$$\sum_l\frac{\partial u_K^l}{\partial X}\xi_l=0\ . \tag{A6}$$

Upon time differentiation, this condition yields

$$\sum_l\frac{\partial u_K^l}{\partial X}\dot{\xi}_l=-\sum_l\frac{\partial^2 u_K^l}{\partial X^2}\xi_l\dot{X}\ , \tag{A7}$$

which is sufficient to produce the model Hamiltonian (A1). The kink equation of motion derived from the canonical Hamiltonian equations of motion yields Eq. (9) in the text.

We assume that the mass M is approximately

$$M\cong M_0+\frac{\delta M}{2}\cos(2\pi X/b)-2m\sum_l\frac{\partial^2 u_K^l}{\partial X^2}\xi_l \tag{A8}$$

where $\delta M=0.02(C/A)^{-3/2}$ as in Ref. 6. E_a and δM both vanish in the continuum limit.

The memory function equation for the velocity autocorrelation function is

$$\dot{\psi}(t)=-\int_0^t dt'K(t')\psi(t-t')\ . \tag{A9}$$

The corresponding Laplace transform is just (11) in the text. In order to calculate $\phi(t)$ and $\zeta(t)$, the acceleration autocorrelation function and acceleration-velocity correlation function (both normalized by $\langle\dot{X}^2\rangle$), we use the following approach:

$$\zeta(t)=-\frac{1}{\langle\dot{X}^2\rangle}\langle\ddot{X}(0)e^{iLt}\dot{X}(0)\rangle$$
$$=-\frac{1}{\langle\dot{X}^2\rangle}\left\langle\ddot{X}(0)\left[e^{iL_0t}+i\int_0^t dt'e^{iL_0t'}L_{\rm int}+O(L_{\rm int}^2)\right]\dot{X}(0)\right\rangle , \quad \text{(A10)}$$

where $L=L_0+L_{\rm int}$ is the Liouville operator consisting of a free-kink–free-phonon part L_0 and an interaction part $L_{\rm int}$. The first term is identically zero. On the other hand,

$$\phi(t)=\frac{1}{\langle\dot{X}^2\rangle}\langle\ddot{X}(0)e^{iL_0t}\ddot{X}(0)\rangle+\cdots \quad \text{(A11)}$$

in the same manner, but the first term does not vanish. Thus using (A10) and (A11) and the inverse transform of (12) in the text, we obtain the nearly-free-kink approximation

$$K(t)\simeq\frac{1}{\langle\dot{X}^2\rangle}\langle\ddot{X}(0)e^{iL_0t}\ddot{X}(0)\rangle , \quad \text{(A12)}$$

which is the explicit representation of (14) in the text.

We now describe more explicitly details of our assumptions:

$$\langle\xi_l(0)\xi_{l'}(t)\rangle=kT/(Nm)\sum_q\exp[iq(x_l-x_{l'})]\cos(\omega_q t)/\omega_q^2 , \quad \text{(A13)}$$

$$\omega_q^2=\omega_0^2+\frac{2C}{m}[1-\cos(qb)]$$

where $\omega_0=\sqrt{2A/m}$. According to standard perturbation theory we have

$$\langle\xi_l^2(0)\xi_{l'}^2(t)\rangle\cong\langle\xi_l^2\rangle\langle\xi_{l'}^2\rangle+2\langle\xi_l(0)\xi_{l'}(t)\rangle^2 , \quad \text{(A14)}$$

$$\langle\xi_l^3(0)\xi_{l'}^3(t)\rangle\cong9\langle\xi_l^2\rangle\langle\xi_{l'}^2\rangle\langle\xi_l(0)\xi_{l'}(t)\rangle+6\langle\xi_l(0)\xi_{l'}(t)\rangle^3 . \quad \text{(A15)}$$

The thermodynamic average of a quantity $\mathcal{F}(X,\dot{X})$ is just

$$\langle\mathcal{F}(X,\dot{X})\rangle=\int\frac{dX}{Z_X}\int\frac{dP}{Z_P}\exp\left[-\frac{\beta P^2}{2M_0}-\frac{\beta E_a}{2}\cos(2\pi X/b)\right]\times\mathcal{F}\left[X,\frac{P}{M_0}\right] , \quad \text{(A16)}$$

where Z_X and Z_P are, respectively, the position and momentum parts of the partition function for the kink, given by

$$Z_X=\int dX\exp\left[-\frac{\beta E_a}{2}\cos(2\pi X/b)\right]=v_0I_0\left[\frac{\beta E_a}{2}\right] , \quad \text{(A17)}$$

$$Z_P=(2\pi M_0/\beta)^{1/2} . \quad \text{(A18)}$$

v_0 is the volume, $\beta=1/kT$, and I_j is the modified Bessel function of order j.

By inserting the expression for $\ddot{X}(0)$ from (9), which contains seven terms (one term linear in ξ_l and two terms nonlinear in ξ_l from $\partial H_{\rm int}/\partial X$, and two terms from $\partial M/\partial X$ [see Eq. (A8)]), into (A12), and computing all the products to lowest nonvanishing order, we obtain thirteen nonvanishing contributions $K_j(t)$, $j=1,\ldots,13$. Another term $K_{\rm loc}(t)$ arises due to the nonlinear local-mode coupling to the extended phonons. The result is a series of fourteen terms

$$K(t)=\sum_{j=1}^{13}K_j(t)+K_{\rm loc}(t) . \quad \text{(A19)}$$

We list explicitly only the most important terms: K_1 (the autocorrelation of the periodic kink potential with itself), K_7 (autocorrelation of the two-phonon nonlinear forces), K_{12} [autocorrelations of the damping term—the last term in (9) of the text], and $K_{\rm loc}$ (the local-mode contribution). All others are found to be small for all cases studied, and are therefore not mentioned here. Except for K_1 we assume that $u_K^l=\tanh[K(x_l-X)]$ and $E_a=0$. Also, it will be understood in all notation below that M is actually the mean value M_0 as in Eq. (A8). Thus,

$$K_1(t)=\frac{\beta}{M}\left[\frac{\pi E_a}{b}\right]^2\left\langle\sin\left[\frac{2\pi X_0}{b}\right]\sin\left[\frac{2\pi}{b}(X_0+Vt)\right]\right\rangle , \quad \text{(A20)}$$

$$K_7(t)=18\frac{\beta}{M}B^2\sum_{ll'}\left\langle\frac{\partial u_K^l(0)}{\partial X}u_K^l(0)\frac{\partial u_K^{l'}(t)}{\partial X}u_K^{l'}(t)\langle\xi_l(0)\xi_{l'}(t)\rangle^2\right\rangle , \quad \text{(A21)}$$

$$K_{12}(t)=4\frac{\beta}{M}m^2\sum_{ll'}\left\langle\frac{\partial^2u_K^l(0)}{\partial X^2}\frac{\partial^2u_K^{l'}(t)}{\partial X^2}V^2\langle\dot{\xi}_l(0)\dot{\xi}_{l'}(t)\rangle\right\rangle , \quad \text{(A22)}$$

$$K_{\rm loc}(t)=36\frac{\beta}{M}B^2\sum_{ll'}\left\langle\frac{\partial u_K^l(0)}{\partial X}u_K^l(0)\frac{\partial u_K^{l'}(t)}{\partial X}u_K^{l'}(t)\langle\xi_l(0)\xi_{l'}(t)\rangle\langle\xi_{\rm loc}^l(0)\xi_{\rm loc}^{l'}(t)\rangle\right\rangle , \quad \text{(A23)}$$

where

$$\langle\xi_{\rm loc}^l(0)\xi_{\rm loc}^{l'}(t)\rangle=\frac{Kb}{\beta A}u_K^l(0)[1-u_K^l(0)^2]^{1/2}u_K^{l'}(t)[1-u_K^{l'}(t)^2]^{1/2}\cos(\omega_{\rm loc}t) \quad \text{(A24)}$$

[note the similarity of $K_7(t)$ and $K_{\rm loc}(t)$]. In the calculation of $U(X)$ in $K_1(t)$ above [and of $u_K^l(t)$ and its derivatives in what follows], we have made the problem tractable by using the approximation $X=X_0+Vt$ instead of using the exact elliptical solutions of the Hamiltonian (8), with $M=M_0$. The results are as follows:

$$K_1(t)=\frac{2\pi^2}{b^2}\frac{E_a}{M}\frac{I_1(\beta E_a/2)}{I_0(\beta E_a/2)}\exp\left[-\frac{2\pi^2t^2}{b^2\beta M}\right], \tag{A25}$$

$$K_7(t)=\frac{9}{2}\frac{c_0^4}{\beta M}\int_{-\pi/b}^{\pi/b}dq\,dq'\frac{(q+q')^4\cos(\omega_q t)\cos(\omega_{q'}t)}{\omega_q^2\omega_{q'}^2\{\sinh[\pi(q+q')/2K]\}^2}\exp\left[\frac{-(q+q')^2t^2}{2\beta M}\right], \tag{A26}$$

$$K_{12}(t)=\frac{2\pi}{bK^2}\frac{A}{B}\frac{m}{M^2\beta}\int_{-\pi/b}^{\pi/b}dq\frac{q^4\cos(\omega_q t)}{[\sinh(\pi q/2K)]^2}\left[1-\frac{q^2t^2}{\beta M}\right]\exp\left[\frac{-q^2t^2}{2\beta M}\right], \tag{A27}$$

$$K_{\rm loc}(t)=\frac{1}{128}\frac{\pi}{\beta M}\frac{\omega_0^3}{c_0}\int_{-\pi/b}^{\pi/b}dq\frac{(1+q^2/K^2)^2(3-q^2/K^2)^2}{\omega_q^2[\cosh(\pi q/2K)]^2}\cos(\omega_q t)\cos(\omega_{\rm loc}t)\exp\left[\frac{-q^2t^2}{2\beta M}\right], \tag{A28}$$

where $c_0=b\sqrt{C/m}$ is the sound velocity, $Kb=1/\sqrt{2C/A}$, and $\omega_{\rm loc}^2=\frac{3}{4}\omega_0^2$. In our figures for the velocity autocorrelation spectrum we have used the Fourier cosine transform of $\psi(t)$:

$$\tilde{\psi}(\omega)=2\int_0^\infty dt\cos(\omega t)\psi(t)\ . \tag{A29}$$

This may be written in terms of the real and imaginary parts of the Fourier transform $\tilde{K}(\omega)$ of the memory function as

$$\tilde{\psi}(\omega)=\frac{2\,{\rm Re}\tilde{K}(\omega)}{[\omega-{\rm Im}\tilde{K}(\omega)]^2+[{\rm Re}\tilde{K}(\omega)]^2}\ , \tag{A30}$$

where

$$\tilde{K}(\omega)=\int_0^\infty dt\,e^{i\omega t}K(t)=\lim_{s\to -i\omega+0^+}\hat{K}(s) \tag{A31}$$

and $\hat{K}(s)$ is the Laplace transform. The main contributions to $\tilde{K}(\omega)$ then become

$$\tilde{K}_1(\omega)=\pi\left[\frac{\pi}{2}\right]^{1/2}\frac{E_a}{b}\left[\frac{\beta}{M}\right]^{1/2}\frac{I_1(\beta E_a/2)}{I_0(\beta E_a/2)}w(z)\ ,\quad z=\omega\left[\frac{\beta M b^2}{8\pi^2}\right]^{1/2} \tag{A32}$$

$$\tilde{K}_7(\omega)=\frac{9}{8}\left[\frac{\pi}{2}\right]^{1/2}\frac{c_0^4}{\sqrt{\beta M}}\int_{-\pi/b}^{\pi/b}dq\,dq'\frac{|q+q'|^3}{\omega_q^2\omega_{q'}^2\left[\sinh\left[\frac{\pi(q+q')}{2K}\right]\right]^2}\sum_{i=1}^{4}w(z_i)\ ,$$

$$z_i=\gamma(\omega\pm\omega_q\pm\omega_{q'}),\quad \gamma=\left[\frac{\beta M}{2(q+q')^2}\right]^{1/2} \tag{A33}$$

$$\tilde{K}_{12}(\omega)=\frac{\pi}{bK^2}\frac{A}{B}\frac{m}{M}\int_{-\pi/b}^{\pi/b}dq\frac{q^2}{\left[\sinh\left[\frac{\pi q}{2K}\right]\right]^2}[(\omega+\omega_q)\sqrt{\pi}z_5w(z_5)+(\omega-\omega_q)\sqrt{\pi}z_6w(z_6)-2i\omega]\ ,$$

$$z_{5,6}=(\omega\pm\omega_q)\alpha,\quad \alpha=\left[\frac{\beta M}{2q^2}\right]^{1/2} \tag{A34}$$

$$\tilde{K}_{\rm loc}(\omega)=\frac{1}{8^3}\frac{\pi^{3/2}\omega_0^3}{c_0\sqrt{2\beta M}}\int_{-\pi/b}^{\pi/b}dq\frac{(1+q^2/K^2)^2(3-q^2/K^2)^2}{\omega_q^2|q|\left[\cosh\left[\frac{\pi q}{2K}\right]\right]^2}\sum_{i=7}^{10}w(z_i),\quad z_i=\alpha(\omega\pm\omega_q\pm\omega_{\rm loc}) \tag{A35}$$

where $w(z)$ is

$$w(z)=\exp(-z^2)[1-{\rm erf}(-iz)]\ , \tag{A36}$$

and ${\rm erf}(z)$ is the error function of complex argument. The diffusion constant then becomes

$$D_K=\frac{kT/M}{\sum_j\tilde{K}_j(0)} \tag{A37}$$

and

$$\tilde{K}_1(0)=\pi\left[\frac{\pi}{2}\right]^{1/2}\frac{E_a}{b}\left[\frac{\beta}{M}\right]^{1/2}\frac{I_1(\beta E_a/2)}{I_0(\beta E_a/2)}\ , \tag{A38}$$

$$\tilde{K}_7(0)=\frac{9}{4}\left[\frac{\pi}{2}\right]^{1/2}\frac{c_0^4}{\sqrt{\beta M}}\int_{-\pi/b}^{\pi/b}dqdq'\frac{|q+q'|^3}{\omega_q^2\omega_{q'}^2\left[\sinh\left[\frac{\pi(q+q')}{2K}\right]\right]^2}\left[\exp\left[-\frac{\beta M(\omega_q+\omega_{q'})^2}{2(q+q')^2}\right]+\exp\left[-\frac{\beta M(\omega_q-\omega_{q'})^2}{2(q+q')^2}\right]\right], \tag{A39}$$

$$\tilde{K}_{12}(0)=4\left[\frac{\pi}{2}\right]^{3/2}\frac{A}{B}\frac{m\sqrt{\beta M}}{bK^2M}\int_{-\pi/b}^{\pi/b}dq\frac{|q|\omega_q^2}{\left[\sinh\left[\frac{\pi q}{2K}\right]\right]^2}\exp\left[-\frac{\beta M}{2q^2}\omega_q^2\right], \tag{A40}$$

$$\tilde{K}_{\rm loc}(0)=\frac{\pi\sqrt{2\pi}}{8^3c_0}\frac{\omega_0^3}{\sqrt{\beta M}}\int_{-\pi/b}^{\pi/b}dq\frac{(1+q^2/K^2)^2(3-q^2/K^2)^2}{\omega_q^2|q|\left[\cosh\left[\frac{\pi q}{2K}\right]\right]^2}\left[\exp\left[-\frac{\beta M(\omega_q+\omega_{\rm loc})^2}{2q^2}\right]+\exp\left[-\frac{\beta M(\omega_q-\omega_{\rm loc})^2}{2q^2}\right]\right]. \tag{A41}$$

Integrals were evaluated numerically.

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