Brownian motion and finite-temperature effects in the discrete nonlinear Schrödinger equation: Analytic results for the nonadiabatic dimer

P. Grigolini,* H.-L. Wu, and V. M. Kenkre

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

(Received 8 May 1989)

The system under study is a moving quasiparticle interacting strongly with lattice vibrations. Our investigation uncovers the effects of finite temperature through an analytical study of the quasiparticle evolution in a dimer. We display appropriate Fokker-Planck equations at several stages and, through a generalized Kramers analysis, show that localized stationary states, which are the signature of nonlinear evolution, (polaronic/solitonic behavior) are destroyed above a characteristic temperature. This result agrees with recent computer simulations in extended systems and lends analytical support to the numerical finding of the destruction of nonlinear structures above a critical temperature.

I. INTRODUCTION

The purpose of this paper is to study the interplay of Brownian motion with the kind of nonlinearity that one encounters in the discrete nonlinear Schrödinger equation,[1-6] specifically, to understand the effects of finite, i.e., nonzero, temperature on the evolution of the nonlinear dimer studied recently by Kenkre and collaborators.[7-12] The attractive feature of the dimer is that, as has been shown recently, considerable progress can be made on the basis of exact analytic solutions,[7-9] the results can be applied to experimentally realizable dimers in the context of observations[9] such as neutron scattering and fluorescence depolarization, and useful insights can be gained into extended systems[7] provided chaos in the latter is not under investigation. Striking results have been recently obtained[11,12] in the nonlinear dimer when the adiabatic assumption is dropped, i.e., when vibrational relaxation which leads to the nonlinear transport is *not* assumed to be infinitely fast. The goal of the present analysis is to extend the nonadiabatic (finite relaxation) analysis of Refs. 11 and 12 to finite (nonzero) temperatures.

Among earlier studies which have addressed the effects of finite temperature on the transport of nonlinear entities, the one most relevant to us here is that by Lomdahl and Kerr[6] who showed, through numerical simulations, that solitons exist below a certain temperature but are destroyed above it through the effect of fluctuations in the stochastic bath. As in the analysis of Ref. 6, our interest in the present paper is in investigating how robust nonlinear entities such as solitons and polarons are against bath fluctuations induced by heightened temperatures, the point of departure being coupled equations for the moving quantum-mechanical quasiparticle and a set of semiclassical oscillators. The difference is that our treatment is analytical and our system is simpler as it incorporates only two sites.[13] The question posed in Ref. 6, as well as in several other recent investigations,[14-17] expressed in a form appropriate to the present dimer investigation, is as follows. It is known[11,12] that the nonlinear nonadiabatic dimer settles into localized states (the sta-

tionary states of the adiabatic dimer) at zero temperature ($T=0$). Is there a characteristic temperature T_c such that, while the dimer settles into those localized states for $T < T_c$, it attains equal population in the two sites for $T > T_c$, thus signifying in the latter case the destruction of the localization phenomenon?

The paper is laid out as follows. The rest of Sec. I introduces the nonlinear dimer studied in Refs. 7–12, and makes clear the point of departure of the present analysis. A Fokker-Planck equation for the system of the moving quasiparticle and the vibrations that interact with it is obtained in Sec. II and is then reduced to a Fokker-Planck equation for the system alone through the use of projection techniques.[18-21] Attention is focused in Sec. III on the evolution of a *slow* variable, for which another Fokker-Planck equation is obtained. In Sec. IV, an approximation is made to that equation in order to make it analytically tractable, numerical results are presented to ascertain the validity and estimate the applicability of the approximation, and the rate for the passage of the quasiparticle from one localized state to the other is calculated, analytically as well as numerically, through a generalized Kramers analysis.[22-24] A discussion is the content of Sec. V.

The physics behind the system we study has been described in several places in the literature.[7-12] We will not repeat those discussions but refer the reader to the appropriate articles. We begin our investigation on the basis of the analysis of Kenkre and Wu[11,12] who take as their point of departure coupled evolution equations for the moving quasiparticle and the vibrating oscillators which interact with it. Those equations are modified versions of the ones used by Scott and his collaborators[1,2] earlier. The modification consists of the introduction of damping and the removal of dispersion in the oscillator evolution. In the context of a simple one-dimensional chain, one then has the following coupled evolution of the amplitude c_m that the quasiparticle is at site m and the displacement x_m of the oscillator at the mth site:

$$\frac{i\,dc_m}{dt} = V(c_{m+1} + c_{m-1}) + Ex_m c_m \,, \tag{1.1}$$

$$\frac{d^2x_m}{dt^2} + \alpha \left[\frac{dx_m}{dt} \right] + \omega^2 x_m = -\text{const} \times |c_m|^2 . \quad (1.2)$$

We follow Kenkre and Wu[11,12] in assuming further, for the sake of simplicity, that the damping coefficient α in the vibrational equation (1.2) is large enough to justify the neglect of the second derivative of the x's and consequently to characterize the evolution of the oscillators x towards their equilibrium positions through a single "vibrational relaxation" time, viz. $\alpha/\omega^2 \equiv 1/\Gamma$. We also restrict our study to the dimer, i.e., m takes on the values 1,2 only. The new feature of the physics we inject into the present study is *an interaction of the oscillators with a stochastic bath at a temperature T.* We start with

$$\frac{idc_1}{dt} = Vc_2 + Ex_1c_1 , \quad (1.3)$$

$$\frac{idc_2}{dt} = Vc_1 + Ex_2c_2 , \quad (1.4)$$

$$\frac{dx_1}{dt} + \Gamma x_1 = -(\chi\Gamma/E)|c_1|^2 + F_1(t) , \quad (1.5)$$

$$\frac{dx_2}{dt} + \Gamma x_2 = -(\chi\Gamma/E)|c_2|^2 + F_2(t) , \quad (1.6)$$

which are, respectively, identical to Eqs. (2.2)–(2.5) of Ref. 11 or to Eqs. (3)–(4) of Ref. 12, except for the addition here of the stochastic driving terms F_1 and F_2. In (1.3)–(1.6), c_1 and c_2 are the respective amplitudes for the quasiparticle to be on the two sites 1 and 2, V describes the intersite transfer interaction for the quasiparticle, x_1 and x_2 are the two oscillator displacements, Γ is the (single) vibrational relaxation rate mentioned above, and E and χ are constants. The stochastic "forces," assumed to be Gaussian white noises, obey the fluctuation-dissipation relation

$$\langle F_m(0)F_m(t) \rangle = 2\Gamma\langle x_m^2 \rangle_{eq}\delta(t) , \quad (1.7)$$

where m equals 1 and 2, respectively, the symbols $\langle \cdots \rangle$ denote an ensemble average, the subscript eq on $\langle x_m^2 \rangle$ denotes the equilibrium value (given by k_BT/ω^2 through the equipartition theorem, k_B being the Boltzmann constant and the oscillator mass being taken to equal 1) in the absence of the oscillator-quasiparticle coupling, i.e., for $\chi = 0$.

As in Refs. 11 and 12, we convert Eqs. (1.3)–(1.6) into evolution equations for the density-matrix elements $\rho_{11}, \rho_{22}, \rho_{12}, \rho_{21}$ which describe the quasiparticle, and the suitably normalized difference of the displacements

$$y(t) = -(E/\chi)[x_1(t) - x_2(t)]$$

which describes the oscillators. We will write this coupled set in terms of the real quantities p, q, r, defined as

$$p = \rho_{11} - \rho_{22}, \quad q = i(\rho_{12} - \rho_{21}), \quad r = \rho_{12} + \rho_{21} , \quad (1.8)$$

which describe the quasiparticle, and y, defined as

$$y = -(E/\chi)(x_1 - x_2) , \quad (1.9)$$

which describes the oscillators. The point of departure

for the analysis in this paper is thus

$$\frac{dp}{dt} = 2Vq , \quad (1.10)$$

$$\frac{dq}{dt} = -2Vp - \chi ry , \quad (1.11)$$

$$\frac{dr}{dt} = \chi qy , \quad (1.12)$$

$$\frac{dy}{dt} = -\Gamma(y - p) + F(t) . \quad (1.13)$$

The stochastic force $F(t)$ appearing in the evolution of the displacement difference y is defined as

$$-(E/\chi)[F_1(t) - F_2(t)]$$

and is, therefore, a white Gaussian noise with vanishing mean value

$$\langle F(0)F(t) \rangle = 2\Gamma\langle y^2 \rangle_{eq}\delta(t) , \quad (1.14)$$

the equilibrium value that the square of the displacement difference would have in the absence of the interaction term Γ_p in (1.13) being given by

$$\langle y^2 \rangle_{eq} = 2(E/\chi)^2(k_BT/\omega^2) = (2/\chi)k_BT , \quad (1.15)$$

where the second equality is obtained by recognizing that $\chi = (E/\omega)^2$. The assumption inherent in the above results is that the stochastic forces F_1 and F_2 are uncorrelated with each other.

II. FOKKER-PLANCK EQUATIONS

Equations (1.10)–(1.13) constitute a set of Langevin equations for the stochastic variables p, q, r, y. Our method of attack consists of deriving the corresponding Fokker-Planck equations, first for the entire system, then for the reduced system consisting of the quasiparticle alone (i.e., for p, q, r), and then, finally, for a further reduced variable which is particularly slow in its evolution. We do the first in the standard manner by inspection and the second through the use of the projection techniques developed for this purpose by Grigolini and collaborators.[18–21] It is clear that it is convenient to begin by rewriting the Langevin set (1.10)–(1.13) in terms of a new quantity z defined as

$$z(t) = y(t) - p(t) . \quad (2.1)$$

We then have

$$\frac{dp}{dt} = 2Vq , \quad (2.2)$$

$$\frac{dq}{dt} = -2Vp - \chi rp - \chi rz , \quad (2.3)$$

$$\frac{dr}{dt} = \chi qp + \chi qz , \quad (2.4)$$

$$\frac{dz}{dt} = -\Gamma z + F(t) - 2Vq . \quad (2.5)$$

It is evident that (2.2)–(2.5) reduce to the *adiabatic* dimer[8–10] if one puts $z = 0$. This represents the assumption made in the adiabatic analysis that the displacement

difference follows the probability difference *infinitely* fast. One of the purposes of introducing z rather than continuing the analysis with y is to avoid technical complications in the application of projection techniques. Similar considerations have appeared in Refs. 19 and 20. It might be helpful to observe that it might appear at first sight, from a comparison of (1.13) and (2.5), that no gain has been achieved through the passage from y to z, since, whereas y equilibrates to p, z equilibrates to q. This is not correct: z does indeed vanish at long times unlike y (q tends to 0, whereas p does not).

Following the approach of Refs. 18 and 21, we write the Fokker-Planck equation for the entire (p,q,r,z) system obeyed by the distribution function $\rho(p,q,r,z;t)$. The equation is found to be

$$\frac{\partial \rho(p,q,r,z;t)}{\partial t} = (L_q + L_v)\rho(p,q,r,z;t) , \qquad (2.6)$$

with a clear separation of the full Liouville operator into a part L_q which describes the adiabatic quasiparticle evolution, and a part L_v which represents the additional terms contributed by the interaction with the vibrations of the oscillators. The adiabatic quasiparticle part is given by

$$L_q = 2V\left[p\left[\frac{\partial}{\partial q}\right] - q\left[\frac{\partial}{\partial p}\right]\right] + \chi p\left[r\left[\frac{\partial}{\partial q}\right] - q\left[\frac{\partial}{\partial r}\right]\right] . \qquad (2.7)$$

The vibrational part L_v is a sum of two terms, L_{v0} and L_{v1}, which, respectively, describe the oscillator evolution and the interaction of the oscillator with the quasiparticle,

$$L_{v0} = \Gamma\left[\left[\frac{\partial}{\partial z}\right]z + \langle y^2 \rangle_{eq}\left[\frac{\partial^2}{\partial z^2}\right]\right] , \qquad (2.8)$$

$$L_{v1} = \chi z\left[r\left[\frac{\partial}{\partial q}\right] - q\left[\frac{\partial}{\partial r}\right]\right] + 2Vq\left[\frac{\partial}{\partial z}\right] . \qquad (2.9)$$

Only the oscillator coordinate appears in L_{v0} but both quasiparticle and oscillator coordinates appear in L_{v1}.

We now employ projection techniques to obtain a Fokker-Planck equation for the *reduced* distribution function $\sigma(p,q,r;t)$ defined through

$$\sigma(p,q,r;t) = \int dz\, \rho(p,q,r,z;t) , \qquad (2.10)$$

The projection operator P we use carries out an integration over the oscillator variable z and multiplies the result by the equilibrium distribution function in z,

$$Pf(p,q,r,z;t) = [(2\pi\langle y^2 \rangle_{eq})^{-1/2}$$

$$\times \exp(-\tfrac{1}{2}z^2/\langle y^2 \rangle_{eq})]$$

$$\times \int dz' f(p,q,r,z';t) . \qquad (2.11)$$

The application of (2.11) to (2.6) allows us to write a formally exact memory equation for the reduced distribution function $\sigma(p,q,r;t)$. Evaluation of the terms is, however, possible only approximately. As is normal in essentially all nontrivial situations, we are able to take into account the effect of a part of the Liouville operator exactly but are forced to use a weak-coupling approximation for the rest. The part we treat exactly is the sum of L_q and L_{v0} and will be called the "unperturbed part" L_0. The part which requires a perturbation expansion is the quasiparticle-oscillator interaction L_{v1}. Because L_{v0} is proportional to Γ, retaining terms of small order in L_{v1} represents the physical case of fast-relaxation rates, the appropriate expansion being in powers of the dimensionless ratios V/Γ and χ/Γ. It is thus guaranteed that the zero-order limit of the perturbation expansion will reduce to the adiabatic dimer (infinitely fast relaxation), and that small perturbations will correspond, for $T=0$, to the fast-relaxation nonadiabatic case studies in Refs. 11 and 12.

The details of the projection technique and the subsequent weak-coupling approximation are not shown here because they are quite similar to those given in Ref. 19. Among the operator properties which facilitate the calculation of the memory kernel in the weak-coupling approximation in the present case, is the fact that the adjoint of L_{v0} acting on z produces $-\Gamma z$. The effect of the adjoint of $\exp(-tL_{v0})$ on z is, therefore, a simple multiplication by the factor $\exp(-t\Gamma)$. The Markovian approximation is applied on the memory kernel[18] in the usual manner. The final result of the calculation is the following Fokker-Planck equation for the reduced distribution function:

$$\frac{\partial \sigma(p,q,r;t)}{\partial t} = L_{red}\sigma(p,q,r;t) , \qquad (2.12)$$

$$L_{red} = L_q + (2V/\Gamma)(\chi q)\left[q\left[\frac{\partial}{\partial r}\right] - r\left[\frac{\partial}{\partial q}\right]\right] + (\chi^2\langle y^2 \rangle_{eq}/\Gamma)\left[\left[\frac{\partial^2}{\partial q^2}\right]r^2 - \left[\frac{\partial}{\partial q}\right]r\left[\frac{\partial}{\partial r}\right]q\right.$$

$$\left. - \left[\frac{\partial}{\partial r}\right]q\left[\frac{\partial}{\partial q}\right]r + q^2\left[\frac{\partial^2}{\partial r^2}\right]\right] . \qquad (2.13)$$

Equation (2.12) describes the finite-temperature evolution of the nonlinear dimer in the fast-relaxation limit. We have used the subscript "red" to denote the fact that we have here a reduced description which describes the

dimer alone. The first term in L_{red}, viz., L_q, represents the dynamics of the adiabatic dimer. The next two introduce the effects of noninfinite relaxation and are seen to vanish in the limit of infinite Γ. Of these two, the first de-

scribes the zero-temperature nonadiabatic evolution studied earlier by Kenkre and Wu.[11,12] The second is a new consequence of the present analysis. It describes the effects of temperature in two ways: through the explicit multiplicative factor $\langle y^2 \rangle_{eq}$, which is proportional to the temperature [see (1.15)], and through the introduction of the second-order derivatives with respect to r and q, which signify diffusion in p,q,r space.[25]

III. EVOLUTION OF A SLOW VARIABLE

Equations (2.12) and (2.13) constitute one of the main results of this paper. They describe the time evolution of the quasiparticle distribution function σ in the nonlinear dimer, for any temperature T, in the limit of fast relaxation, i.e., when the rate Γ is substantially larger than all other characteristic rates in the system. They can be made to yield the generalization of the analytical results of Refs. 11 and 12 to arbitrary temperatures. In order to address the question posed at the beginning of the paper concerning the existence of a characteristic temperature for the destruction of localized stationary states, we shall now derive a Fokker-Planck equation for a new single variable which is particularly slow in its evolution. The new equation will then allow us to determine an escape rate through first-passage-time analysis.

It is well known that the identity

$$p^2 + q^2 + r^2 = 1 \tag{3.1}$$

always holds since it is a consequence of the definition of p, q, and r. Indeed, as is well known from the analysis of Feynman et al., [26] (3.1) represents the conservation of the magnitude of the representative "spin" which describes the density matrix of a two-state system.[27] There are thus only *two* independent variables required to characterize the evolution of the dimer. We seek to choose one of these to be a combination of p,q,r, which is known to be a constant of the motion in the adiabatic case. Such a choice ensures that the variation of the quantity selected is slow in the nonadiabatic case in the limit of fast relaxation which is under investigation.

An obvious choice is the energy of the fictitious oscillator whose classical dynamics under the quartic potential[8,11] represents the adiabatic dimer evolution. The slow variable we select is related to this energy but can be found directly without reference to the quartic potential. The quantity $[r - (\chi/4V)p^2]$ is a constant of the motion for the adiabatic dimer. This result can be deduced immediately on making the adiabatic substitution $y = p$ in (1.12) and invoking (1.10), and has been used earlier for the extraction of the evolution of r from that of p in the description of fluorescence depolarization.[9(b)] We add terms to $[r - (\chi/4V)p^2]$ for convenience, call the complete expression $\mathcal{E}$, and select it as our slow variable,

$$\mathcal{E} = r - (\chi/4V)p^2 + (V/\chi) + (\chi/4V) . \tag{3.2}$$

The quantity $\mathcal{E}$ is a constant of the motion for the adiabatic case, a slow variable for the nonadiabatic large Γ case under investigation, and has the property that it decreases as the dimer relaxes and vanishes when, in the case of zero temperature, the dimer settles into one of its

stationary states. It might be of use to recall here that, for stationary states[8]

$$r = -(2V/\chi), \quad (1-p^2) = r^2 . \tag{3.3}$$

The first of these results has been derived in Ref. 8(b) and the second is obvious from (3.1) since $q = 0$ for stationary states.

Equation (3.2) along with (3.1) can be used to obtain from (2.12) and (2.13), a reduced Fokker-Planck equation involving $\mathcal{E}$ and r alone or $\mathcal{E}$ and p alone. The virtue of such an equation is that, since the variation of $\mathcal{E}$ is much slower than that of p or R, a *one-dimensional* Fokker-Planck equation, involving only $\mathcal{E}$, can then be derived by carrying out an average over the rapid variable p or r.

The passage from the p,q,r space to the $\mathcal{E},p$ space is exact and is made through the substitution

$$\frac{\partial}{\partial p} \rightarrow \left[\frac{\partial \mathcal{E}}{\partial p}\right]\left[\frac{\partial}{\partial \mathcal{E}}\right] + \left[\frac{\partial}{\partial p}\right]$$

$$= -(\chi/2V)p\left[\frac{\partial}{\partial \mathcal{E}}\right] + \left[\frac{\partial}{\partial p}\right] , \tag{3.4}$$

$$\frac{\partial}{\partial q} \rightarrow \left[\frac{\partial \mathcal{E}}{\partial q}\right]\left[\frac{\partial}{\partial \mathcal{E}}\right] + \left[\frac{\partial p}{\partial q}\right]\left[\frac{\partial}{\partial p}\right]$$

$$= -\left[\frac{\partial}{\partial p}\right](q_1/p) , \tag{3.5}$$

$$\frac{\partial}{\partial r} \rightarrow \left[\frac{\partial \mathcal{E}}{\partial r}\right]\left[\frac{\partial}{\partial \mathcal{E}}\right] + \left[\frac{\partial p}{\partial r}\right]\left[\frac{\partial}{\partial p}\right]$$

$$= \left[\frac{\partial}{\partial \mathcal{E}}\right] - \left[\frac{\partial}{\partial p}\right](r_1/p) . \tag{3.6}$$

The calculation of the derivatives of $\mathcal{E}$ proceeds from (3.2) and that of the derivatives of p from (3.1), i.e., from the expression $p = (1 - q^2 - r^2)^{1/2}$. The quantities q_1 and r_1 in (3.5) and (3.6) are, respectively, q and r expressed as functions of $\mathcal{E}$ and p through (3.1) and (3.2). Explicitly,

$$r_1 = \mathcal{E} + (\chi/4V)p^2 - (V/\chi) - (\chi/4V) , \tag{3.7}$$

$$q_1 = \{1 - p^2 - [\mathcal{E} + (\chi/4V)p^2 - (V/\chi) - (\chi/4V)]^2\}^{1/2} . \tag{3.8}$$

The result of these manipulations is an evolution equation for the distribution function $\rho(\mathcal{E},p;t)$ which we will not display here. That equation is exact in the sense that its level of description of the dimer evolution is identical to that provided by (2.12) and (2.13). We contract the description provided by that equation by eliminating the rapid variable p through the application of an averaging procedure applied to each of the terms in (3.8). The average consists of an integration over p within the appropriate limits, with $\mathcal{E}$ held constant, followed by a division of the result by the p interval. We represent this average by the symbol $\langle \cdots \rangle_{\mathcal{E}}$ and obtain

$$\frac{\partial \sigma(\mathcal{E};t)}{\partial t} = L_{\mathcal{E}} \sigma(\mathcal{E};t) , \tag{3.9}$$

$$L_{\mathcal{E}} = \left[\frac{\partial}{\partial \mathcal{E}} \right] \Psi_1(\mathcal{E}) + \left[\frac{\partial^2}{\partial \mathcal{E}^2} \right] \Psi_2(\mathcal{E}) , \qquad (3.10)$$

$$\Psi_1(\mathcal{E}) = (2V\chi/\Gamma)\langle q_1^2 \rangle_{\mathcal{E}} + (\chi^2/\Gamma)\langle y^2 \rangle_{\mathrm{eq}}\langle r_1 \rangle_{\mathcal{E}} , \qquad (3.11)$$

$$\Psi_2(\mathcal{E}) = (\chi^2/\Gamma)\langle y^2 \rangle_{\mathrm{eq}}\langle q_1^2 \rangle_{\mathcal{E}} . \qquad (3.12)$$

Equations (3.9)–(3.12) form the one-dimensional Fokker-Planck equation which describes the evolution of the single slow variable $\mathcal{E}$. In order to evaluate the averages $\langle q_1^2 \rangle_{\mathcal{E}}$ and $\langle r_1 \rangle_{\mathcal{E}}$ it is necessary to understand the time variation of p in (3.7) and (3.8) with $\mathcal{E}$ held constant. It is clear that p oscillates quasiperiodically between turning points $p_{\pm}$ given by $q = 0 = dp/dt$. Equating (3.8) to 0, we obtain these turning points

$$p_{\pm}^2 = 1 - (2V/\chi)^2 - (4V/\chi)\mathcal{E} \pm (4V/\chi)[(4V/\chi)\mathcal{E}]^{1/2} . \qquad (3.13)$$

We consider the system only under considerations of high nonlinearity, so that the localized stationary states are formed (i.e., $\chi > 2V$). An inspection of (3.13) shows that there are, generally, four values of the turning points. The region $\mathcal{E} < 0$ is of no interest since it corresponds to complex values of the turning points. For $\mathcal{E} = 0$, which represents the stationary states, p_+ equals p_- and the four values collapse into the two stationary values $\pm[1 - (2V/\chi)^2]^{1/2}$. For small positive values of $\mathcal{E}$, p oscillates around one of these two values, depending on which of the two localized states the system finds itself trapped around. The two regions of oscillation are separated by $2p_-$. They touch when p_- vanishes, i.e., when $\mathcal{E}$ attains the value $\mathcal{E}_T$,

$$\mathcal{E}_T = (V/\chi) + (\chi/4V) - 1 . \qquad (3.14)$$

For larger values of $\mathcal{E}$, P_- is complex and only two turning points exist, separated by a single region of extent $2p_+$. The system is now no longer localized.

IV. LIFETIME OF THE TRAPPED STATE

The discussion of the oscillations of p given above makes clear the fact that $\mathcal{E}$ is an excellent choice for a first-passage-time calculation of the escape of the system from one localized state to the other. The value $\mathcal{E} = 0$ serves as the "reflection" point and the value $\mathcal{E} = \mathcal{E}_T$ as the "absorption" point. We place the system initially into one of the localized stationary states ($\mathcal{E} = 0$) and calculate the rate for $\mathcal{E}$ to attain the value $\mathcal{E}_t$ under the action of the stochastic bath. The rate describes the escape over the $\mathcal{E}$ barrier.

The apparatus of the first-time-passage formalism[28] allows one to express the time τ for the escape over the barrier as

$$\tau = \int_0^{\mathcal{E}_T} d\mathcal{E} [\Psi_2(\mathcal{E}) P_{ss}(\mathcal{E})]^{-1} \int_0^{\mathcal{E}} d\mathcal{E}' P_{ss}(\mathcal{E}') , \qquad (4.1)$$

where $\Psi_1(\mathcal{E})$ and $\Psi_2(\mathcal{E})$ are given by (3.11) and (3.12), respectively, and $P_{ss}(\mathcal{E})$ is the steady-state solution of the Fokker-Planck equation (3.9) given by

$$P_{ss}(\mathcal{E}) = [\Psi_2(\mathcal{E})]^{-1} \exp\left[-\int_0^{\mathcal{E}} d\mathcal{E}' \frac{\Psi_1(\mathcal{E})}{\Psi_2(\mathcal{E})} \right] . \qquad (4.2)$$

The exact calculation requires numerical analysis because of the complicated nature of the Fokker-Planck equation (3.9)–(3.12). We have carried out such a calculation and will comment on the results below. However, we have also found that it is possible to make a simplification of Ψ_1 and Ψ_2 which permits analytic evaluation of the first passage time. The averages of r_1 and q_1^2 appearing in (3.11) and (3.12) are straightforward, if tedious, to obtain. Thus, for instance,

$$\langle r_1 \rangle_{\mathcal{E}} = \mathcal{E} - (V/\chi) - (\chi/4V) + \frac{1}{3}(\chi/4V)(p_+^2 + p_+ p_- + p_-^2) , \qquad (4.3)$$

the $p_{\pm}$ being given by (3.13). For sufficiently large values of the nonlinearity ratio $\chi/4V$, the expression for $\langle q_1^2 \rangle_{\mathcal{E}}$ takes on a simple form which can be approximated remarkably well by a linear dependence over most of the interval $0 \le \mathcal{E} \le \mathcal{E}_T$. Figure 1(a), in which the exact dependence is displayed by a solid line and the linear approximation (with slope $8V/3\chi$) by a dashed line, shows this explicitly. The linear dependence corresponds to a harmonic potential in the Fokker-Planck equation and facilitates analytic calculations. We also show, in Fig. 1(b), the corresponding approximation of $\langle r_1 \rangle_{\mathcal{E}}$ by a constant. Although the two approximations appear to be rather drastic near $\mathcal{E} = \mathcal{E}_T$, they are actually not unreasonable. The calculation of first passage times is based much more sensitively on the evolution of the system near $\mathcal{E} = 0$ (i.e., near the reflection point) than that near $\mathcal{E} = \mathcal{E}_T$ (i.e., near the absorption point). The strongly varying part of $\langle q_1^2 \rangle_{\mathcal{E}}$ or $\langle r_1 \rangle_{\mathcal{E}}$ near the absorption point is, therefore, not of great concern. The value of $\langle r_1 \rangle_{\mathcal{E}}$ at $\mathcal{E} = 0$, shown by the dotted line in Fig. 1(b), is $-2V/\chi$. However, we approximate it by $\frac{4}{3}$ times this value. This adjustment brings about considerable analytical simplification and puts the present complicated problem into the form treated analytically by Kramers[22–24] in a straightforward manner. With these approximations, viz.,

$$\langle q_1^2 \rangle = (8V/3\chi)\mathcal{E}, \quad \langle r_1 \rangle = -8V/3\chi = -d\langle q_1^2 \rangle/d\mathcal{E} \qquad (4.4)$$

the Ψ functions appearing in the Fokker-Planck equation (3.9), (3.10) simplifies to

$$\Psi_1(\mathcal{E}) = (16V^2/3\Gamma)\mathcal{E} - (8V\chi/3\Gamma)\langle y^2 \rangle_{\mathrm{eq}} , \qquad (4.5)$$

$$\Psi_2(\mathcal{E}) = (8V\chi/3\Gamma)\langle y^2 \rangle_{\mathrm{eq}}\mathcal{E} . \qquad (4.6)$$

The steady-state distribution function from (4.2) can then be calculated analytically as

$$P_{ss} = (1/\mathcal{E}_{\mathrm{th}})\exp(-\mathcal{E}/\mathcal{E}_{\mathrm{th}}) , \qquad (4.7)$$

$$\mathcal{E}_{\mathrm{th}} = (\chi/2V)\langle y^2 \rangle_{\mathrm{eq}} = k_B T/V , \qquad (4.8)$$

and the lifetime from (4.1) has the form

$$\tau = \int_0^{\mathcal{E}_T} d\mathcal{E}'[(8V\chi/3\Gamma)\langle y^2 \rangle_{\mathrm{eq}}\mathcal{E}']^{-1}\exp(\mathcal{E}'/\mathcal{E}_{\mathrm{th}})$$
$$\times \int d\mathcal{E}''\exp(-\mathcal{E}''/\mathcal{E}_{\mathrm{th}}) . \qquad (4.9)$$

Equation (4.9) has the same structure as does the well-known Kramers formula[22-24] and the same pathology as well. To get rid of the pathology, we follow Kramers and replace the lower limit of integration by the finite value $\mathscr{E}_{th}$. The significance of $\mathscr{E}_{th}$ is that it is a measure of the mean (thermal) value of the "energy" $\mathscr{E}$ and, as the second part of (4.8) shows, equals $k_B T$ in units of V. The approximate but analytic expression for the lifetime is then

$$\tau = (3\Gamma/16V^2)(\mathscr{E}_{th}/\mathscr{E}_T)\exp[(\mathscr{E}_T/\mathscr{E}_{th})-1] . \quad (4.10)$$

The factor $(\mathscr{E}_T/\mathscr{E}_{th})$ gives τ its main temperature dependence. It equals

$$(1/k_B T)[(\chi/4)+(V^2/\chi)-V]$$

and may be approximated well by $\chi/4k_B T$ for large nonlinearity. Both the exact lifetime which we calculate numerically from (4.1), and the approximate version (4.10), exhibit the typical Arrhenius behavior. The characteristic temperature is calculated easily in the analytic case

$$T_c = \text{const} \times (1/k_B)[(\chi/4)+(V^2/\chi)-V]$$

$$\approx \text{const} \times \chi/4k_B . \quad (4.11)$$

The constant in (4.11) is of the order of 1 but is otherwise arbitrary. We find the choice $(\frac{1}{5})$ to be visually convenient. We show the temperature variation of the escape rate $1/\tau$ in Fig. 2. The exact numerical calculation
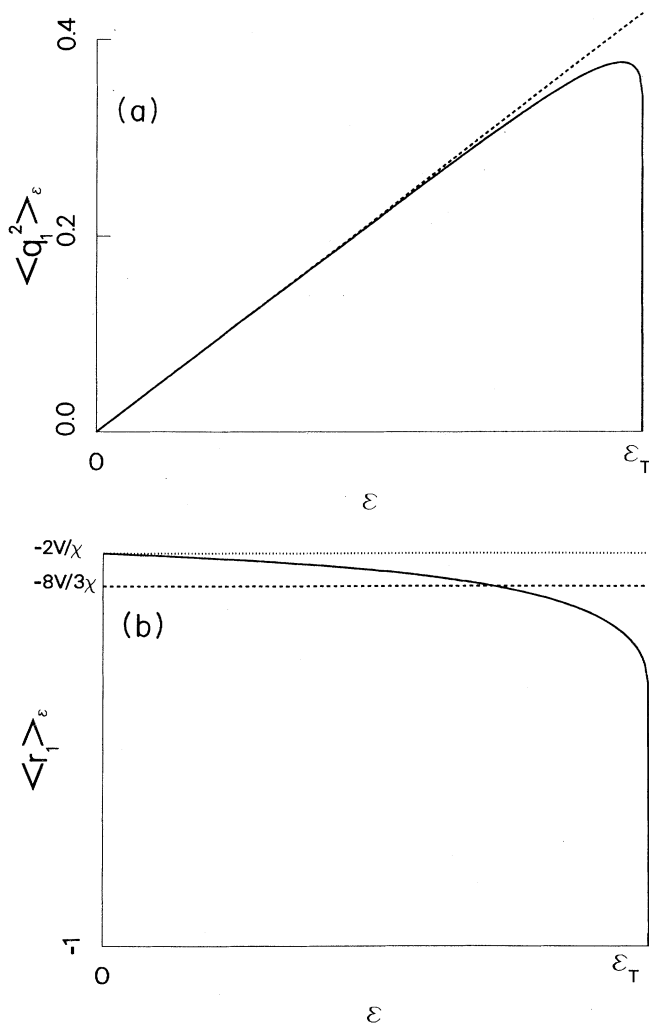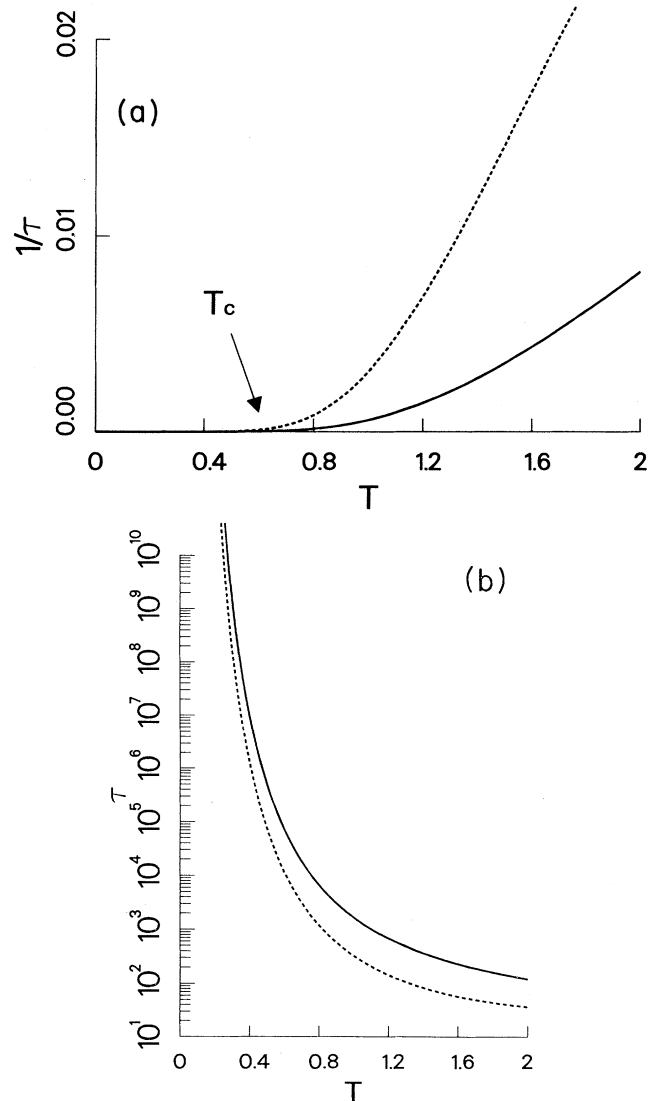

FIG. 1. Quantities $\langle q_1^2 \rangle$ (a) and $\langle r_1 \rangle$ (b) plotted as a function of $\mathscr{E}$ in the range $0 \leq \mathscr{E} \leq \mathscr{E}_T$ in order to estimate the error committed in the use of the approximate analytical replacement of (3.7) and (3.8) by (4.4). The dashed or dotted line corresponds to the approximation and the solid line to the exact result. In (a) the slope of the dashed line is $(8V/3\chi)$. In (b) the constant value of $\langle r_i \rangle$ is $-(8V/3\chi)$ as given by the dashed line, and $-(2V/\chi)$ as given by the dotted line. Parameters chosen are $\Gamma = 50$, $\chi = 10$, and $V = 1$.

FIG. 2. Dependence of the process of escape from the trapped state on the temperature T. In (a) we plot the escape rate on a linear scale, and in (b) the escape time on a logarithmic scale. The units of the rate, time, and temperature are V, $1/V$, and V/k_B, respectively. Solid lines denote the exact result of Eq. (4.1) and dashed lines denote the analytic approximate Kramers-like result of Eq. (4.2). Parameters chosen are $\Gamma = 50$, $\chi = 10$, and $V = 1$.

is depicted by the solid line and the approximate analytical version by the dashed line. Figure 2(a) uses a linear scale while Fig. 2(b) uses a logarithmic scale. The figures show clearly that the localized state is long-lived (the quasiparticle, if one localized, is trapped for all time practically) for $T < T_c$ but escapes (the localized state is destroyed) for $T > T_c$. It is also seen that the analytical approximation we have made produces a reasonable representation of the actual situation.

V. CONCLUDING REMARKS

The point of departure for the analysis presented in this paper is Eqs. (1.3)–(1.7) or, equivalently, (1.10)–(1.14). They constitute a set of Langevin equations and describe the coupled evolution of the quasiparticle and the oscillators, the latter being in interaction with the heat bath. As in our earlier investigations, we have taken the vibrational system to have a single relaxation time $1/\Gamma$ and the stochastic force to be Gaussian Markov in nature. The new results we have obtained are as follows.

(i) A set of Fokker-Planck equations: (2.7)–(2.9) which are exact and describe the entire quasiparticle-oscillator system; (2.12) and (2.13) which are obtained under the weak-coupling and Markovian approximation made on the projected equation and describe the quasiparticle alone in the limit of fast relaxation; and (3.9)–(3.12) which are derived through an averaging procedure and describe the evolution of the slow variable $\mathcal{E}$.

(ii) An expression for τ, the lifetime of the localized state (which exists only for sufficiently large nonlinearity, i.e., for $\chi > 2V$), viz. (4.1), which is valid in the rapid-relaxation limit (large Γ) discussed in this paper. While the expression itself is not new, the form of Ψ_2 and P_{ss} appearing in it are. The expression is obtained as an exact consequence of the Fokker-Planck equation (2.12) but can be evaluated only numerically.

(iii) An expression for τ under the same conditions as in (ii) above but under the approximations (4.4) which allow a Kramers analysis to be carried out and an analytical result, viz. (4.10), to be obtained.

(iv) The demonstration of Arrhenius temperature dependence in the destruction of the localized state [see Figs. 2 and Eq. (4.10)] and an expression under the approximation of (iii) for the characteristic temperature T_c, viz. (4.11).

(v) An answer to the question posed at the beginning of the paper: There is no abrupt transition to any temperature above 0, i.e., the localized state is always destroyed for $T > 0$ if one waits sufficiently long. However, the time involved in the escape is enormous unless $T > T_c$, the rise of the escape rate being very sharp around T_c (Arrhenius behavior) even though not abrupt. This means that for all practical purposes, the localized state is destroyed above T_c but is robust below that characteristic temperature.

In light of the several investigations[14−17] that have recently been reported on the robustness or destruction of solitons at room temperature, (v) above requires further comment. The question of the stability of the soliton at finite temperatures is of great importance. The idea of invoking solitons as the transporting entity in biological systems, suggested by Davydov[29] and others, depends, for its validity, on whether the solitons are destroyed at biologically relevant temperatures (e.g., room temperature). Lomdahl and Kerr,[6] working from equations similar to those used in the present investigation, concluded that solitons are *not* stable at room temperatures. Cruzeiro et al.[14] argued through a different method of analysis that solitons *are* stable at room temperatures as had Davydov.[29] Lawrence et al.[16] have questioned that finding. A recent quantum Monte Carlo investigation by Wang et al.[17] has also cast doubt on the soliton stability. Two characteristics of our present investigation do not permit it to help settle the issue: its being restricted to a two-site system, and its use of semiclassical oscillators. However, our findings show clearly that nonlinear entities, which are without doubt polaronic, and probably related closely to solitons in extended systems, are indeed destroyed sharply (but not abruptly) above a characteristic temperature. For high nonlinearities, the characteristic temperature is as given by (4.11) and is essentially the "Stokes-shift temperature."

The obvious calculational assumptions specific to our analysis are (i) the weak-coupling and Markovian approximations on the projected equation to derive (2.13), (ii) the averaging over the evolution of p which allows the derivation of the Fokker-Planck equation for the single variable $\mathcal{E}$, and (iii) the assumption that $\langle q_1^2 \rangle$ and $\langle r_1 \rangle$ may be approximated by, respectively, a linear and constant dependence on $\mathcal{E}$ as in (4.4). Approximation (i) is valid in the fast-relaxation (large Γ) limit which is under investigation in this paper and which is quite physical for most systems of interest. Approximation (ii) is again valid in the fast-relaxation limit: In the limit of infinite Γ, the quantity $\mathcal{E}$ is a constant of the motion. Its variation is much slower than that of p and therefore the averaging procedure we have used is justified. Approximation (iii) is the weakest of the three, its extent of validity is seen pictorially in Figs. 1 and 2, and it has been made *only* for analytic tractability. Indeed, we have also presented exact results without making that approximation: solid lines in Figs. 2(a) and 2(b).

Our use of projections in the standard way has also involved another approximation which may not be immediately evident. The standard Zwanzig manner[30] of the application of projections, which we follow here,[18] in its passage from the exact Fokker-Planck equation (2.7) in p,q,r,z space to the derived (2.12) in p,q,r space, has the following intermediate step:

$$\frac{dP\rho}{dt} = PLP\rho + \mathcal{M} + \mathcal{J}, \tag{5.1}$$

where $\mathcal{M}$ is a memory term and $\mathcal{J}$ an initial term. We will not provide the detail of the two last terms here because it can be found in numerous places.[30] As in most applications of the projection method, we have taken the initial term to be identically zero or, at least, to vanish within the time scale of the memory kernel. The assumption that it vanishes identically means, in the present context, that the initial state of the system is an outer prod-

uct of a state in the p,q,r space and of a state in z space. Even if such a condition were not to apply, it appears likely that the fast-relaxation limit under investigation will result in the disappearance of the initial term in (5.1) on the time scale of the memory kernel which is expected to be $1/\Gamma$. Further considerations of the initial term have been given by Janner et al.,[31] Grigolini,[32] and by Kenkre.[33]

We have come across two instances of contraction of the description in this paper: the passage from (2.7) to (2.12) and that from the $(\mathcal{E},p)$ Fokker-Planck equation which we have mentioned (but not displayed) in Sec. III to the single-variable equation (3.9). We have employed projection techniques in both instances although it might appear that a different (averaging) procedure has been applied in the second case. It is straightforward to show that the averaging procedure is equivalent to the use of (5.1) with a projection operator which is similar to (2.11) but which averages over p and retention of the lowest nonvanishing terms. In this case, however (which is nothing other than the application of the Stratonovich[34] procedure), the lowest nonvanishing terms involve the first term $PLP\rho$ in (5.1) only.

A few remarks about the evolution of the system may be useful. Consider the case that $2V < \chi < 4V$, and assume that the initial condition of the quasiparticle is that it is localized on one of the sites and that the temperature is 0. The quasiparticle will oscillate from one site to the other and will lose "energy" as a result of the noninfinite relaxation rate Γ. Let us consider this energy to be represented by the quantity $\mathcal{E}$ which we have defined in (3.14). When $\mathcal{E}$ decreases below the "barrier-top" value $\mathcal{E}_T$, the quasiparticle falls into one of the two "wells" and is quasilocalized around one of the two sites. The initial conditions and the relaxation rate determine delicately which of the two sites is "chosen" for localization.[11] Fur-

ther reduction in $\mathcal{E}_T$ occurs and eventually the system settles in the localized state.

The above considerations are appropriate at zero temperature and have been shown to occur by Kenkre and Wu.[11,12] Let us now assume that $T > 0$. Starting from the localized state with $\mathcal{E} = 0$, the quasiparticle will diffuse quickly as a result of finite temperature and will attain the value $\mathcal{E}_{th} > 0$, characteristic of thermalization with the bath. Fluctuations from this thermalization will now cause $\mathcal{E}$ to increase randomly at a rate which will be extremely slow at small temperatures. When the quasiparticle succeeds, under the action of these fluctuations, to surmount the barrier, i.e., when $\mathcal{E}$ reaches the value $\mathcal{E}_T$, the quasiparticle will escape to the other localized state and equilibration with equal population at the two sites will occur: The nonlinear entity will be destroyed.

The analysis of the escape rate we have presented in Sec. IV is valid in the extreme limit of small temperatures. It is also possible to obtain useful results[35] in the opposite limit of high temperatures. One of the outcomes of our investigation along those lines is a new nonlinear stochastic Liouville equation for the description of the quasiparticle transport. We have thus constructed a reasonably complete formalism for the investigation of finite-temperature effects in the nonlinear nonadiabatic dimer. Ongoing work on related issues involves numerical simulations of the Langevin equations, studies of spatially extended systems, and solutions of the Fokker-Planck equation (2.13) that we have obtained above.

ACKNOWLEDGMENTS

*On leave of absence from the University of Pisa, Italy.

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