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Polaron band theory as linearized soliton theory

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A nonlinear equation of motion recently developed for the study of finite-temperature soliton dynamics is linearized and compared with corresponding results from traditional polaron theory. Numerous points of agreement are found, and points of disagreement are interpreted in the context of the full nonlinear theory. New interpretations of well-known features of traditional polaron theory are made possible through this approach.

I. INTRODUCTION

The polaron problem has a vast history spanning some fifty years, with a literature enriched by contributions from many creative practitioners of condensed matter physics and allied fields. The problem is ubiquitous as a model for systems in which the cooperative interaction of a particle with deformation or polarization modes may result in dynamics profoundly different from those of the uncoupled entities. The polaron problem is thus of relevance to such diverse concerns as the dynamics of defects, electronic and ionic conduction, exciton and vibron dynamics, mechanical and electronic properties of polymers, etc. Each area of application makes a unique set of demands upon theory, which results in the theory of the polaron having many faces.

In the present paper we deal with a new theoretical development which brings into apposition two of the faces of the polaron problem as presented by the Fröhlich Hamiltonian. Below we refer to these two faces of the polaron problem as "polaron band theory"[1-11] and "soliton theory."[3,12-27]

A substantial fraction of the literature on polaron dynamics is based on the use of judiciously chosen "dressing" transformations and (time-dependent) perturbation theory. The purpose of transformation is to pose the theory in a set of basis states which are as close to the eigenstates of the fully coupled system as possible. It is expected that perturbation theory in such a basis should possess improved convergence properties and, to a given order of truncation, provide a more accurate representation of the true polaron dynamics. There is one limit (see below) in which this program provides an exact solution and thus identifies a quasiparticle as the polaron in that case. In other cases, the principal aims of this approach are to determine optimal transformations and perturbation techniques. In such developments, one often refers to the state as a "polaron," though "dressed electron" or "dressed exciton" may be more appropriate.

Typical of the results of such approaches are the following: Equations of motion for reduced distribution functions (probabilities or density matrices) are obtained within which renormalized energy band structures can be identified. In the simplest cases, which is all we shall be concerned with here, this renormalization is simply manifested in the basic tunneling parameter J being supplanted by a reduced tunneling parameter $\tilde{J}(T)$ which is a decreasing function of the temperature T. The ratio $\tilde{J}(T)/J$ is sometimes called the "polaron band narrowing factor." The remaining terms of the equations are nondiagonal in the basis of polaron band states. Though these terms doubtless contain some residual systematic effects, every theory reaches a point at which the remaining terms must be approximated and such effects are lost. The approximated scattering terms usually have the form of damping terms, hopping terms, or stochastic potentials.

A qualitative feature held in common by all such polaron band theories is that the equations of motion are linear in the distribution function. This distinguishes polaron band theory from a growing body of work which, through related but distinct reduction and approximation techniques, obtains systems of nonlinear equations for the reduced distribution functions of the same Hamiltonian. We refer to this body of work as "soliton theory," since the role of the polaron band excitation is played by the solitary wave solutions of nonlinear evolution equations.

In a recent paper,[19] the present authors obtained a nonlinear equation of motion for the reduced density matrix of an excitation coupled to the vibrations of a host medium as described by the Fröhlich Hamiltonian. Rather than transforming to an optimally chosen basis, a time-dependent reduction procedure was engineered having the property that the leading order evolution is equivalent to a statistical mechanical generalization of the wave-function equations used by Davydov[12–14] and others[21–27] to describe soliton transport. Nonlinearity enters through the time dependence of the reduction procedure, which is determined self-consistently. The systematic framework of the reduction procedure makes possible the construction of correction terms which implement essential improvements on the Davydov dynamic. As a nonlinear theory of the Fröhlich Hamiltonian, the present theory is a "soliton theory."

In this paper we analyze an approximation in which we neglect the nonlinear terms appearing in the nonlinear density matrix equation. Apart from a transient sense to be discussed below, this amounts to neglecting the cooperative interaction of the mobile excitation with the deformation which it induces in the host medium. It is somewhat surprising then that we find numerous points of agreement between the linearized soliton theory and polaron band theory, whose traditional interpretation rests on the existence of such cooperative dynamical behavior. Points of disagreement exist; however, these may be satisfactorily interpreted in the context of the full nonlinear theory.

The Fröhlich Hamiltonian[1] may be written

$$H=\sum_{m,n} J_{mn} a_m^\dagger a_n+\sum_q \hbar\omega_q b_q^\dagger b_q + \sum_{q,n} \chi_n^q \hbar\omega_q (b_q^\dagger + b_{-q}) a_n^\dagger a_n \ , \tag{1.1}$$

in which a_n annihilates an excitation in the site state n and b_q annihilates a vibrational quantum in the normal mode q with frequency ω_q. In some systems of interest the excitation is electronic and in others it is vibronic. We will refer to both kinds of excitations as "excitons." In either case, the resonant transfer integrals J_{mn} connect distinct site states and provide the sole mechanism through which excitons may migrate among the various sites. The coupling functions χ_n^q quantify the strength and detail of the exciton-phonon interaction. The interaction is taken to be linear in the vibrational coordinates and local in the exciton coordinates. This causes the local potential experienced by the exciton to depend on the configuration of surrounding molecules. For later use, we note that in an acoustic chain, for which neighboring molecules are coupled by nearest-neighbor harmonic forces, the phonon frequencies are given by

$$\omega_q=\omega_B \sin\frac{|\mathbf{q}\cdot\mathbf{a}|}{2} \ , \tag{1.2}$$

and the coupling functions reflecting the interaction of a molecular excitation with contiguous molecules is given by

$$\chi_n^q=\frac{\chi(-2i\sin\mathbf{q}\cdot\mathbf{a})}{(2NM\hbar\omega_q^3)^{1/2}} e^{-i\mathbf{q}\cdot\mathbf{R}_n} \ , \tag{1.3}$$

in which χ is the force constant controlling the interaction and N is the number of molecules of mass M comprising the chain of length Na.

Following the application of a time-dependent reduction procedure and subsequent approximations, Brown *et al.*[19] obtained the nonlinear evolution equations

$$\dot\rho_{mn}(t)=\frac{1}{i\hbar}[H_{\text{ex}},\rho(t)]_{mn}-i[f_m(t)-f_n(t)]\rho_{mn}(t)-i\int_0^t d\tau \sum_l [K_{ml}(t-\tau)-K_{nl}(t-\tau)]\dot\rho_{ll}(\tau)\rho_{mn}(t) -\tfrac{1}{2}[\dot{\mathit{ff}}_{mm}(t)+\dot{\mathit{ff}}_{nn}(t)-2\dot{\mathit{ff}}_{mn}(t)]\rho_{mn}(t) \tag{1.4}$$

for the matrix elements of the reduced density operator

$$\rho(t)\equiv \mathrm{Tr}_{\text{ph}}\sigma(t) \tag{1.5}$$

in which $\sigma(t)$ is the density operator of the full exciton-phonon system. The time-dependent functions appearing in (1.4) are defined by

$$f_m(t)\equiv\sum_q \chi_m^q \omega_q [e^{i\omega_q t}\beta_q^*(0)+e^{-i\omega_q t}\beta_{-q}(0)] \ , \tag{1.6a}$$

$$K_{mn}(t)=2\sum_q \chi_m^q \chi_n^{-q} \omega_q \cos\omega_q t \ , \tag{1.6b}$$

$$\mathit{ff}_{mn}(t)=2\sum_q \chi_m^q \chi_n^{-q}(1-\cos\omega_q t) \ . \tag{1.6c}$$

The complex quantities $\beta_q(0)$ are coherent-state amplitudes[28] corresponding to linear combinations of the classical coordinate pairs $[q_n(0),p_n(0)]$ that specify the initial positions and momenta of all the material constituents at the initial time. Since these quantities are inherently unknown, they can be specified only through a distribution function. The functions $f_m(t)$ are thus fluctuations with a specific distribution characterizing the initial condition of the medium, which we take to be the condition of thermal equilibrium. The distribution function for this case is given by

$$P\{\beta_q(0)\}=\prod_q \frac{e^{-|\beta_q(0)|^2/\langle n_q\rangle}}{\pi\langle n_q\rangle} \tag{1.7}$$

in which $\langle n_q\rangle=(e^{\hbar\omega_q/k_B T}-1)^{-1}$ is the Bose distribution for the qth phonon mode.[28] The temperature enters explicitly only when thermal averages are constructed. The kernels $K_{mn}(t)$ contribute to the description of the response of the phonon system to the exciton dynamics, and have a role in the fluctuation-dissipation relation of the system [see (1.12) below]. The damping functions $\mathit{ff}_{mn}(t)$ appear because the fluctuation properties of the quantum system cannot be completely accounted for by the scalar fluctuations $f_m(t)$; the $\dot{\mathit{ff}}_{mn}(t)$ can be derived directly from the noncommutation of operator fluctuations in the exact theory of West and Lindenberg[29] [see (A2)].

In linearizing (1.4), we simply neglect the nonlinear terms and consider the remaining equation. Specializing to the case of two sites, the linear equations we consider hereafter have the form

$$\dot{\rho}_{11}(t)=\frac{-J}{i\hbar}[\rho_{12}(t)-\rho_{21}(t)]\ , \tag{1.8a}$$

$$\dot{\rho}_{22}(t)=\frac{J}{i\hbar}[\rho_{12}(t)-\rho_{21}(t)]\ , \tag{1.8b}$$

$$\dot{\rho}_{12}(t)=\frac{-J}{i\hbar}[\rho_{11}(t)-\rho_{22}(t)]-\lambda(t)\rho_{12}(t)\ , \tag{1.8c}$$

$$\dot{\rho}_{21}(t)=\frac{J}{i\hbar}[\rho_{11}(t)-\rho_{22}(t)]-\lambda^*(t)\rho_{21}(t)\ , \tag{1.8d}$$

in which $\lambda(t)$ is the complex scalar function

$$\lambda(t)=\mu(t)+i\nu(t)\ , \tag{1.9a}$$

$$\mu(t)=\tfrac{1}{2}[\dot{\mathit{ff}}_{11}(t)+\dot{\mathit{ff}}_{22}(t)-2\dot{\mathit{ff}}_{12}(t)]\ , \tag{1.9b}$$

$$\nu(t)=[f_1(t)-f_2(t)]\ . \tag{1.9c}$$

The real part $\mu(t)$ acts as a damping function while the imaginary part $\nu(t)$ acts as a fluctuating energy. The kernels $K_{mn}(t)$ appear explicitly only in the nonlinear terms and therefore do not contribute explicitly in this approximation.

The simplest nontrivial solutions to (1.8) obtain in the limit $J=0$, in which we find $\rho_{11}(t)=\rho_{11}(0)$, $\rho_{22}(t)=\rho_{22}(0)$, and $\rho_{12}(t)=\rho_{21}^*(t)$, where

$$\rho_{12}(t)=\exp\left[-\int_0^t d\tau\,\lambda(\tau)\right]\rho_{12}(0)\ . \tag{1.10}$$

Since $\lambda(t)$ is dependent on the fluctuations $f_n(t)$ of a particular realization, we must average $\rho_{12}(t)$ over phonon initial data as appropriate for a thermal ensemble. The averaged solution is

$$\langle\rho_{12}(t)\rangle=\rho_{12}(0)\exp\{-[\mathit{ff}_{11}(t)-\mathit{ff}_{12}(t)]\}\times\exp\left[-\int_0^t d\tau\int_0^t d\tau'[\langle f_1(\tau)f_1(\tau')\rangle-\langle f_1(\tau)f_2(\tau')\rangle]\right] \tag{1.11}$$

in which we have used $\mathit{ff}_{11}=\mathit{ff}_{22}$ and $\langle f_1(t)f_1(t')\rangle=\langle f_2(t)f_2(t')\rangle$, which follow from assuming the host lattice to be translationally invariant. The explicit form of the correlation functions is given by

$$\langle f_m(t)f_n(t')\rangle=2\sum_q \chi_m^q\chi_n^{-q}\omega_q^2\cos[\omega_q(t-t')]\langle n_q\rangle\ . \tag{1.12}$$

It has been shown in Ref. 11 that (1.11) is the exact $J=0$ solution for the density matrix of an exciton interacting with a phonon bath initially in equilibrium. The exciton solution is nonstationary and evolves into a form at long times which is precisely the time-independent solution for the density matrix of a similarly prepared polaron. This and other quantities which may be calculated exactly in the $J=0$ limit allow the dynamics of the $J=0$ limit to be interpreted as the dynamics of polaron formation. Since polaron formation is the *only* dynamical process occurring in this system when $J=k_BT=0$, the damping functions $\mathit{ff}_{mn}(t)$ may be unambiguously identified with this process.

II. GENERALIZED MASTER EQUATION

When $J\neq 0$, the solution (1.10) for the off-diagonal element $\rho_{12}(t)$ must be replaced with the integral relation

$$\rho_{12}(t)=\exp\left[-\int_0^t d\tau\,\lambda(\tau)\right]\rho_{12}(0)-\frac{J}{i\hbar}\int_0^t dt'\exp\left[-\int_{t'}^t d\tau\,\lambda(\tau)\right]\times[\rho_{11}(t')-\rho_{22}(t')]\ . \tag{2.1}$$

Defining $P\equiv\rho_{11}-\rho_{22}$, we may use (1.8) and (2.1) to construct the integro-differential equation

$$\dot{P}(t)=\frac{2J^2}{\hbar^2}\int_0^t dt'\exp\left[-\int_{t'}^t d\tau\,\mu(\tau)\right]\times\cos\left[\int_{t'}^t d\tau\,\nu(\tau)\right]P(t')\ . \tag{2.2}$$

In obtaining (2.2) we have set $\rho_{12}(0)=0$ for simplicity. This restricts our present discussion to exciton matrices which are initially site-diagonal.

To facilitate comparison with results of polaron band theory, we arrange (2.2) in the form of a generalized master equation

$$\dot{\rho}_{mm}(t)=\int_0^t dt'\sum_n[W_{mn}(t,t')\rho_{nn}(t')-W_{nm}(t,t')\rho_{mm}(t')]\ . \tag{2.3}$$

The generalized master equation is not the most common form of transport equation used in this context; however, its memory kernels provide a convenient means of characterizing transport models. We find that the memory kernels for our linearized equations have the form

$$W_{12}(t,t')=W_{21}(t,t')=\frac{J^2}{\hbar^2}\exp\left[-\int_{t'}^t d\tau\,\mu(\tau)\right]\cos\left[\int_{t'}^t d\tau\,\nu(\tau)\right]\ . \tag{2.4}$$

We note that the generalized master equation we obtain involves memory kernels which are nonstationary. This is not surprising since the memory $W_{12}(t,t')$ is actually a fluctuating quantity that depends on the fluctuations $f_n(\tau)$ of a *particular realization* of the phonon system. Only in the thermal average $\langle W_{12}(t,t')\rangle$ may one anticipate stationarity. However, carrying out this thermal average we find

$$\langle W_{12}(t,t')\rangle=\frac{J^2}{\hbar^2}\exp\{-[\mathcal{F}_{11}(t)-\mathcal{F}_{12}(t)-\mathcal{F}_{11}(t')+\mathcal{F}_{12}(t')]\}$$
$$\times\exp\left[-\int_{t'}^{t}d\tau\int_{t'}^{t}d\tau'[\langle f_1(\tau)f_1(\tau')\rangle-\langle f_1(\tau)f_2(\tau')\rangle]\right]. \tag{2.5}$$

The integrated correlation functions in the second exponential factor depend on t and t' only through the combination $t-t'$ [see (1.12)]; i.e., the second exponential factor is *stationary*. On the other hand, the first exponential factor is *nonstationary*. The nonstationarity of the thermal average implies the existence of a privileged point in time and an ongoing change in the character of the evolution.

Since it is always the case that $t\geq t'$, let us consider new time variables t and t_0 such that $t'\rightarrow t_0$ and $t\rightarrow t_0+t$. We wish to consider the averaged memory $\langle W_{12}(t_0+t,t_0)\rangle$ for various reference times t_0. First setting $t_0=0$, the explicit form of $\langle W_{12}(t_0+t,t_0)\rangle$ yields

$$\langle W_{12}(t,0)\rangle=\frac{J^2}{\hbar^2}\exp\left[-\sum_q|\chi_1^q-\chi_2^q|^2[1-\cos(\omega_q t)]\coth(\hbar\omega_q/2k_BT)\right]. \tag{2.6}$$

This may be compared with the polaron memory $W_{12}^{\mathrm{pol}}(t)$ obtained by Kenkre and Rahman,[6]

$$W_{12}^{\mathrm{pol}}(t)=\mathrm{Re}\left[\frac{J^2}{\hbar^2}\exp\left[-\sum_q|\chi_1^q-\chi_2^q|^2\{[1-\cos(\omega_q t)]\coth(\hbar\omega_q/2k_BT)-i\sin(\omega_q t)\}\right]\right], \tag{2.7}$$

which is in agreement with results of Grover and Silbey.[5] Inspection shows that the only difference between $\langle W_{12}(t,0)\rangle$ and $W_{12}^{\mathrm{pol}}(t)$ appears in the imaginary part of the exponent in (2.7) which is absent from (2.6). Since $W_{12}^{\mathrm{pol}}(0)=\langle W_{12}(0,0)\rangle$ and $W_{12}^{\mathrm{pol}}(\infty)=\langle W_{12}(\infty,0)\rangle$, this difference does not affect the comparison of memory function behavior based on limiting values obtaining at short and long times. The origin of the difference between (2.6) and (2.7) is addressed in the Appendix. For the purposes of the present discussion the principal difference between the two memory functions arises from the nonstationarity of $\langle W_{12}(t_0+t,t_0)\rangle$.

The temporal behavior of the polaron memory function $W_{12}^{\mathrm{pol}}(t)$ is well known and easily read from (2.7). The polaron memory function falls from the value $J^2/\hbar^2$ at $t=0$ to a final value $\tilde{J}(T)^2/\hbar^2$ at long times, where $\tilde{J}(T)$ is the renormalized polaron bandwidth given by

$$\tilde{J}(T)=J\exp\left[-\tfrac{1}{2}\sum_q|\chi_1^q-\chi_2^q|^2\coth(\hbar\omega_q/2k_BT)\right]. \tag{2.8}$$

Taking into account the nonstationarity of $\langle W_{12}(t_0+t,t_0)\rangle$ we may consider the long t limit as a function of the reference time t_0. Thus we find

$$\lim_{t\rightarrow\infty}\langle W_{12}(t_0+t,t_0)\rangle=\frac{\tilde{J}(T)^2}{\hbar^2}\exp\{[\mathcal{F}_{11}(t_0)-\mathcal{F}_{12}(t_0)]\}. \tag{2.9}$$

That is, when $t_0=0$ we have the usual polaron result; however, other values of t_0 result in different limiting values. For example, for times t_0 near the maxima of $[\mathcal{F}_{11}(t)-\mathcal{F}_{12}(t)]$, the average memory $\langle W_{12}(t_0+t,t_0)\rangle$ may actually *exceed* $J^2/\hbar^2$, the constant memory of the "bare" exciton, at least at low temperatures. We find in the zero-temperature case that as t_0 grows large,

$$\lim_{t_0\rightarrow\infty}\langle W_{12}(\infty,t_0)\rangle_{T=0}=\frac{J^2}{\hbar^2}\geq\frac{\tilde{J}(0)^2}{\hbar^2}. \tag{2.10}$$

That is, for reference times t_0 sufficiently large, $\langle W_{12}(t_0+t,t_0)\rangle_{T=0}$ departs negligibly from the constant bare value $J^2/\hbar^2$. At finite temperatures, the large t_0 limit may be expressed

$$\lim_{t_0\rightarrow\infty}\langle W_{12}(\infty,t_0)\rangle=\frac{J^2}{\hbar^2}\left[\frac{\tilde{J}(T)^2}{\tilde{J}(0)^2}\right]\geq\frac{\tilde{J}(T)^2}{\hbar^2}, \tag{2.11}$$

carrying the apparent implication that only the thermal part of the polaron band narrowing factor has persistent significance in the linearized dynamics following from (1.8). The nonstationary memory $\langle W_{12}(t_0+t,t_0)\rangle$ thus distinguishes between the zero temperature and thermal parts of the usual polaron memory decay, modifying the zero-temperature part in a nonstationary fashion while preserving the stationary thermal part. Since the zero-temperature part contributes at *all* temperatures, the net result is nonstationary behavior.

The resolution of $\langle W_{12}(t_0+t,t_0)\rangle$ into stationary and nonstationary factors which are also the thermal and nonthermal factors has the consequence that at any temperature T, and for any times t_0 and t, the thermal factor of $\langle W_{12}(t_0+t,t_0)\rangle$ and the corresponding thermal factor of $W_{12}^{\mathrm{pol}}(t)$ are identical,

$$\frac{\langle W_{12}(t_0+t,t_0)\rangle}{\langle W_{12}(t_0+t,t_0)\rangle_{T=0}}=\frac{W_{12}^{\mathrm{pol}}(t)}{W_{12}^{\mathrm{pol}}(t)_{T=0}}, \tag{2.12}$$

despite the general difference between $\langle W_{12}(t_0+t,t_0)\rangle$ and $W_{12}^{\mathrm{pol}}(t)$ noted earlier (see Appendix). We may consider departures of this ratio from unity to be the thermal contribution to the memory function decay.

All thermal effects in our theory, and hence the ratio (2.12), are derived entirely from the fluctuations $f_n(t)$. The fluctuations depend only on phonon initial values, and these are uncorrelated with the initial exciton system. The propagation of the $f_n(t)$ through time is the same as the free phonon evolution. In particular, there is no cooperation of thermal fluctuations which can be interpreted as a participation in the formation or preservation of a coherent structure.

III. LINEARITY AS A LIMIT

In obtaining the nonlinear equations (1.4), phonon coordinates were eliminated using the definition $\beta_q(t)=\mathrm{Tr}\sigma(0)b_q(t)$, from which follows the exact formal relation

$$\beta_q(t)=e^{-i\omega_q t}(0)-i\int_0^t d\tau\, e^{-i\omega_q(i-\tau)}\sum_n \chi_n^q\omega_q\rho_{nn}(\tau) . \tag{3.1}$$

This is the relation one would use in a simulation to follow the dynamics of the medium in tandem with the dynamics of the exciton. In linearizing the equations of motion for the reduced-density matrix, however, we have neglected the contributions of the integral or "response" term that (3.1) contributes to the exciton evolution equations. This affects the dependence of the exciton evolution on the phonon coordinates, but does *not* affect the dependence of the parallel phonon evolution on the exciton probabilities. Equation (3.1) continues to describe the evolution of the medium, including the response of the medium to the *linearized evolution* of $\rho_{nn}(\tau)$.

Since the two contributions to the vibrational dynamics, the free phonon evolution and the response of the medium to the exciton dynamics, are not approximated in our *numerischen Gendankenexperiment*, the medium clearly responds to the motion of the exciton in the expected fashion; however, the mechanism by which this response feeds back into the exciton equations of motion, viz., the nonlinear terms, has been eliminated in the linear approximation. Although the medium responds to the exciton dynamics by organizing a deformation, the linearized exciton dynamics are insensitive to this deformation since such sensitivity is *essentially nonlinear.* Thus, while the resulting picture of an exciton dragging a deformation about is cosmetically correct, the "drag" which one is wont to read into the picture is *absent* from the linearized exciton dynamics.

We have thus far considered Eqs. (1.8) merely as a "linear approximation" to the complete nonlinear system of equations embodied in (1.4). We now consider how Eqs. (1.8) may result as a physically meaningful limit of the full nonlinear system. We note that for the two-site problem (1.4) may be rewritten

$$\dot P(t)=\frac{-2J}{i\hbar}[\rho_{12}(t)-\rho_{21}(t)] , \tag{3.2a}$$

$$\dot\rho_{12}(t)=\frac{-J}{i\hbar}P(t)-[\lambda(t)+i\eta(t)]\rho_{12}(t) , \tag{3.2b}$$

$$\dot\rho_{21}(t)=\frac{J}{i\hbar}P(t)-[\lambda^*(t)-i\eta(t)]\rho_{21}(t) , \tag{3.2c}$$

in which

$$\eta(t)\equiv\int_0^t d\tau[K_{11}(t-\tau)-K_{12}(t-\tau)]\dot P(\tau) . \tag{3.3}$$

The integro-differential equation (2.2) may be formally rewritten in terms of the quantity $\eta(t)$ as

$$\dot P(t)=-\frac{2J^2}{\hbar^2}\int_0^t dt'\exp\left[-\int_{t'}^t d\tau\mu(\tau)\right]\cos\left[\int_{t'}^t d\tau[\nu(\tau)+\eta(\tau)]\right]P(t') . \tag{3.4}$$

We now introduce the scaled variable $P'(t)\equiv P(t)/P(0)$ which is of order unity at least at short times, and the scaled function $\eta'(t)\equiv\eta(t)/P(0)$. The equation of motion then reads

$$\dot P'(t)=-\frac{2J^2}{\hbar^2}\int_0^t dt'\exp\left[-\int_{t'}^t d\tau\mu(\tau)\right]\cos\left[\int_{t'}^t d\tau[\nu(\tau)+P(0)\eta'(\tau)]\right]P'(t') . \tag{3.5}$$

Written in this form, the dependence of the equation of motion on the initial exciton distribution is explicit. The linearized dynamics are clearly recovered in the limit that $P(0)\rightarrow 0$; that is, in the limit of a uniform initial distribution. The evolution in the strict limit is, of course, trivial in that the unscaled probability differences $P(t)=P(0)P'(t)$ are equal to zero for all times. The strict $P(0)=0$ limit is not necessary, however, for the linearized dynamics to be a meaningful limit. It is necessary only that $P(0)$ be small enough to render the contribution of $P(0)\eta'(t)$ negligible throughout the time of observation. For this condition to hold it must prove possible to bound $\eta'(t)$ by some function of $P(0)$ for the period of interest. Instabilities may prevent such a bounding relation from existing in some parameter regimes; however, in any case, the linear approximation is self-consistent since $\eta'(t)$ is independent of $P(0)$ within the linearized dynamics (a bounding relation exists). Thus, our treatment of the linearized dynamics supplies a self-consistent approximation to the full nonlinear problem posed by (3.2) in the small $P(0)$ regime. This conclusion generalizes to the full system of Eqs. (1.4) if "small $P(0)$" is interpreted as "long wavelength," since for nearly uniform excitations $\dot\rho_{mm}(t)-\dot\rho_{nn}(t)$ may be expected to be a small quantity.

IV. STOCHASTIC MEMORY

The comparison between the linearized dynamics and the polaron band theory has been made through comparisons of the polaron memory function $W_{12}^{\rm pol}(t)$ with the averaged memory function $\langle W_{12}(t_0+t,t_0)\rangle$ of the linearized dynamics. It must be kept in mind, however, that the averaged memory $\langle W_{12}(t_0+t,t_0)\rangle$ does not provide a complete characterization of the linearized dynamics since the evolution of the site occupation probabilities is actually driven by the fluctuating memory $W_{12}(t_0+t,t_0)$ and not its thermal average.

The strength of the fluctuations of $W_{12}(t_0+t,t_0)$ can be measured by their mean-square value or variance. For convenience we normalize the mean square with respect to the square of the mean, finding

$$\frac{\langle W_{12}(t_0+t,t_0)^2\rangle}{\langle W_{12}(t_0+t,t_0)\rangle^2}=\cosh\left[2\int_{t_0}^{t_0+t}d\tau\int_{t_0}^{t_0+t}d\tau'[\langle f_1(\tau)f_1(\tau')\rangle-\langle f_1(\tau)f_2(\tau')\rangle]\right] . \tag{4.1}$$

Obviously, (4.1) is unity when $t=0$. Moreover, due to the stationarity of the correlation functions, (4.1) is independent of the reference time t_0. In the limit of long times t, we find

$$\lim_{t\to\infty}\frac{\langle W_{12}(t_0+t,t_0)^2\rangle}{\langle W_{12}(t_0+t,t_0)\rangle^2}=\frac{1}{2}\left[\frac{\tilde{J}(0)^2}{\tilde{J}(T)^2}+\frac{\tilde{J}(T)^2}{\tilde{J}(0)^2}\right] . \tag{4.2}$$

Similarly, the long-time limit of the normalized variance is

$$\lim_{t\to\infty}\frac{\langle W_{12}(t_0+t,t_0)^2\rangle-\langle W_{12}(t_0+t,t_0)\rangle^2}{\langle W_{12}(t_0+t,t_0)\rangle^2}=\frac{1}{2}\left[\frac{\tilde{J}(0)}{\tilde{J}(T)}-\frac{\tilde{J}(T)}{\tilde{J}(0)}\right]^2 . \tag{4.3}$$

At low temperatures, $\tilde{J}(T)\approx\tilde{J}(0)$ and the variance is negligible relative to the square of the mean, implying that $W_{12}(t,t')\approx\langle W_{12}(t,t')\rangle$. However, at elevated temperatures, $\tilde{J}(T)\ll\tilde{J}(0)$ and the variance is many times the square of the mean, implying that the fluctuating memory differs strongly from its mean most of the time.

Figures 1–3 show the results of numerical simulations which bear out these implications. Each figure displays one realization of the fluctuating thermal factor $W_{12}(t,0)/\langle W_{12}(t,0)\rangle_{T=0}$ (solid curves), and the average corresponding to (2.12) obtained on combining 1000 realizations (dashed curves). The system used in the calculations was an acoustic chain comprised of 50 molecules identical in their vibrational properties. The functions ω_q and X_n^q were defined as in (1.2) and (1.3), respectively, and sites 1 and 2 were taken to be adjacent. Intrinsic system parameters were constrained such that $32X^2=NM\hbar\omega_B^3$. The random quantities in the simulation were the complex initial mode amplitudes $\beta_q(0)$; moduli and phases were chosen independently according to the distribution (1.7), and the initial values for the mode q were chosen independently of those for the mode $-q$. The same random sequences were used in generating all three figures, so the changes in the character of the fluctuations from figure to figure and differences in the resultant mean values are attributable to differences in temperature *only*.

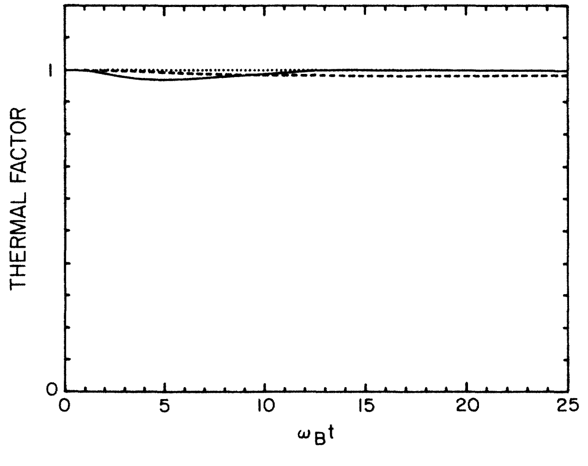

FIG. 1. Solid line (——): Stochastic memory factor $W_{12}(t,0)/\langle W_{12}(t,0)\rangle_{T=0}$; dashed line (— — —): Average $\langle W_{12}(t,0)\rangle/\langle W_{12}(t,0)\rangle_{T=0}$ for an ensemble of 1000 realizations; $k_BT=\hbar\omega_B/10$.

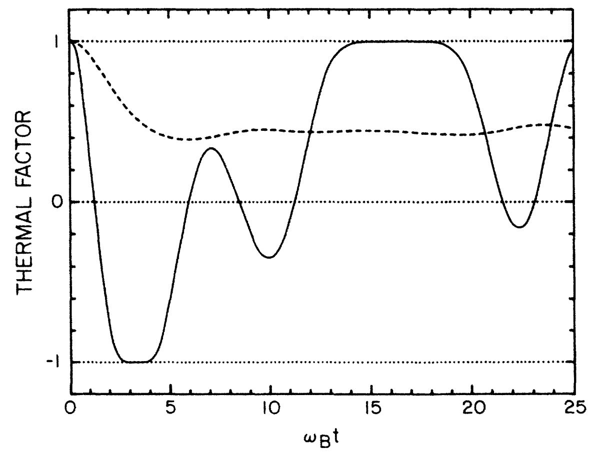

FIG. 2. Solid line (——): Stochastic memory factor $W_{12}(t,0)/\langle W_{12}(t,0)\rangle_{T=0}$; dashed line (— — —): Average $\langle W_{12}(t,0)\rangle/\langle W_{12}(t,0)\rangle_{T=0}$ for an ensemble of 1000 realizations; $k_BT=\hbar\omega_B$.

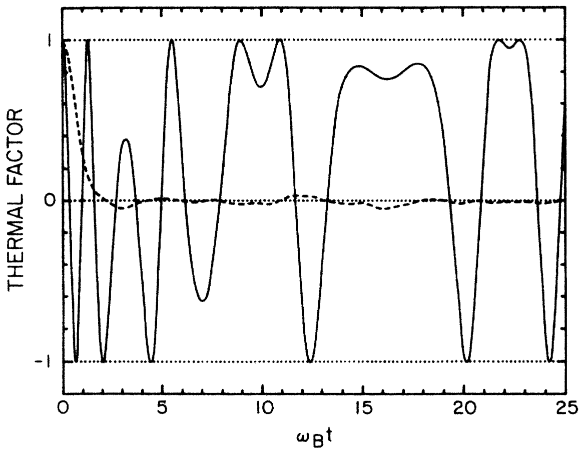

FIG. 3. Solid line (——): Stochastic memory factor $W_{12}(t,0)/\langle W_{12}(t,0)\rangle_{T=0}$; dashed line (— — —): Average $\langle W_{12}(t,0)\rangle/\langle W_{12}(t,0)\rangle_{T=0}$ for an ensemble of 1000 realizations; $k_B T = 10\hbar\omega_B$.

It must be emphasized that the time dependences contributing to the fluctuating thermal factors are the same as those occurring in the free phonon evolution, and the initial data for distinct phonon modes are uncorrelated. The individual realizations, and therefore the ensemble average, of the thermal part of $W_{12}(t,t')$ thus contain no contributions interpretable as being derivable from cooperative phenomena. That the thermal factors depend on the same coupling functions as do rigorous polaron effects[11] is a fortuitous consequence of the fact that thermal and cooperative effects are communicated to the excitation via the same system-bath interaction terms of the Fröhlich Hamiltonian.

V. CONCLUSION

In this paper we have considered in detail a linear approximation to the nonlinear density matrix equations recently obtained by Brown *et al.*[19] as a dynamical description for the Fröhlich Hamiltonian. It has been shown previously that a complementary approximation in which certain quantum-mechanical properties are neglected yields the nonlinear Davydov dynamic as a special case. The retention of linear terms in the present treatment allows some of the quantum effects *absent* from the Davydov dynamic to be studied.[18] The linearized theory describes the evolution of both diagonal and off-diagonal density matrix elements and is exact in the transportless ($J=0$) limit. Since the linearized theory is a valid approximation in any case that the site occupation probabilities are nearly time independent, it is possible that the linearized theory may provide a self-consistent approximation for extended excitations, or in any case for short times. However, the immediate value to be realized from the linearized theory is the contact with traditional polaron theory it affords and the reinterpretation of that theory which is thus made possible.

The principal polaron effects, the dressing of the bare excitation with a deformation of the medium, the concomitant increase in the effective mass, the decrease in diffusivity, and self-trapping phenomena are intimately tied to polaron band narrowing in traditional polaron theory, and hence to $\tilde{J}(T)$. Since all these aspects of the polaron dynamic (with the possible exception of diffusivity) may be considered in isolation from the thermal motion of the medium, the zero-temperature polaron bandwidth $\tilde{J}(0)$ is perhaps the most pervasive feature of polaron theory. The various polaron effects implicitly or explicitly involve the expectation that the cooperative interaction of the exciton and phonons results in ponderable effects within the space of the exciton. In linearizing our equations of motion, however, we have interfered with the feedback channel through which such cooperative interactions can affect the exciton evolution. All results of the linearized dynamics explicitly exclude the sensitivity of the exciton dynamics to the deformation which it induces in the medium *without* excluding the deformation itself. It is thus not surprising that $\tilde{J}(0)$ and its attendant interpretations have at best an ephemeral existence in the linearized theory here presented.

We have found significant points of agreement in our comparison of the memory functions of the linearized dynamics with the memory functions which characterize polaron band theory. On the other hand, significant differences suggest alternatives to the common interpretations of memory function structure. We interpret the zero-temperature (nonstationary) memory function decay not as arising from the comovement of an exciton and medium deformation, but rather as originating in the polaron formation process only. The polaron formation process involves a transient loss of energy from the exciton system. The existence of an energy-loss process is consistent with usual memory function interpretations once the transient nature of the process is taken into account. Since the energy loss is a transient associated with polaron formation and not an ongoing energy exchange process such as thermal scattering, there is a privileged point in time which introduces nonstationarity. The recovery of the memory toward its bare form at long reference times t_0 is consistent with the linearity of the dynamics since in the wake of initial transients there is no agency in the linearized equations of motion through which the induced deformation can affect the exciton evolution.

The thermal (stationary) part of the averaged memory agrees in every detail with the corresponding thermal part of the polaron memory function. Similarly, the thermal part $\tilde{J}(T)/\tilde{J}(0)$ of the polaron band narrowing factor is obtained in complete agreement with polaron band theory. In our linearized theory there is no sensible connection between the deformation of the medium and the thermal part of the band narrowing factor; in our theory such thermal band narrowing is a consequence of ordinary thermal scattering. We further find that at high temperatures, characterized by the inequality $\tilde{J}(T) \ll \tilde{J}(0)$, the memory function is strongly stochastic so that the averaged memory provides a very limited characterization of the dynamics.

In polaron band theory, one encounters a dilemma. There is no qualitative difference between polaron memory function decays at zero temperature $[J^2 \rightarrow \tilde{J}(0)^2]$ and at finite temperature $[J^2 \rightarrow \tilde{J}(T)^2]$; the decay of memory in each case is sufficient to introduce incoherence and cause the damping of quantum transport. (This is easily verified for small systems such as the two-site segment of the acoustic chain we have considered in this paper.) While we may ascribe the *excess* decay at finite temperatures to thermal processes, we cannot account for the zero-temperature decay without appealing to some unknown, but intrinsic, nonthermal scattering process. While such a possibility is becoming increasingly credible in nonlinear dynamical systems, its occurrence in an ordered linear system is problematic. The memory functions we have calculated from the linearized equations (1.8) obviate this difficulty through their nonstationarity. The only persistent memory function decay is that ascribable to thermal processes.

It is a matter for speculation whether retaining the nonlinear terms may restore a picture of energy transport consistent with the traditional polaron interpretations based on $\tilde{J}(0)$. At the present time there are no calculations based on (1.4) which support or contradict such a conjecture. On the other hand, we have noted that the nonlinear Davydov dynamic can be recovered from our general theory as an approximation. Both numerical[22–27] and analytical[20] results indicate that self-trapping phenomena and reductions of transport rates can be found in Davydov-type dynamical systems. It must be anticipated that some manifestation of these features of the Davydov-type approximation will persist in the more general theory, and thus contribute to at least a partial restoration of the intuitive content of polaron theory tied to $\tilde{J}(0)$.

Note added in proof. The forms of the integral terms given in (1.4) and (3.3) differ from those of the corresponding terms in Ref. 19 through the neglect of surface terms obtained on integrating the latter by parts. The justification for neglecting these surface terms will be discussed elsewhere.

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APPENDIX

The purpose of this appendix is to determine the origins of both the similarities and differences between $\langle W_{12}(t,0)\rangle$ and the polaron memory $W_{12}^{\text{pol}}(t)$ of Kenkre and Rahman. The more general behaviors of $W_{12}(t,t')$ and $\langle W_{12}(t,t')\rangle$ are quite different from that of $W_{12}^{\text{pol}}(t)$.

The memory functions of interest have been derived by very different methods. It is shown in the text how $\langle W_{12}(t,0)\rangle$ is obtained from a density matrix equation of motion. It is an essential feature of the equation of motion that the damping functions $\mathcal{F}_{mn}(t)$ are determined *nonperturbatively* by requiring that all terms of the equation not explicitly dependent on the transfer integral J agree with corresponding terms in the *exact* $J=0$ equation. The consequence for the memory function $\langle W_{12}(t,0)\rangle_{T=0}$ is that

$$\langle W_{12}(t,0)\rangle_{T=0}=\frac{J^2}{\hbar^2}\exp\{-[\mathcal{F}_{11}(t)-\mathcal{F}_{12}(t)]\}\ , \tag{A1}$$

$$\mathcal{F}_{mn}(t)=\text{Re}\left[\int_0^t d\tau_1\int_0^t d\tau_2\langle F_m(\tau_1)F_n(\tau_2)\rangle_{T=0}\right]\ , \tag{A2}$$

in which the $F_n(t)$ are fluctuating operators defined in Ref. 11. The damping function $\mathcal{F}_{11}(t)-\mathcal{F}_{12}(t)$ is the exponent of the memory $\langle W_{12}(t,0)\rangle_{T=0}$; however, it is derived from the exact $J=0$ solution $\rho_{12}(t)_{J=0}$ for which it is also the exponent. We thus rewrite (A1) using the results of Ref. 11

$$\langle W_{mn}(t,0)\rangle=\frac{J^2}{\hbar^2}\text{Tr}_{\text{ph}}\rho_{\text{ph}}^{\text{eq}}(T)e^{-S_n(0)}e^{S_n(t)}e^{-S_m(t)}e^{S_m(0)}\ . \tag{A3}$$

The memory function of Kenkre and Rahman is a result of second-order perturbation theory in the basis of dressed states. After transforming the Fröhlich Hamiltonian into the dressed basis, Kenkre and Rahman obtain

$$W_{mn}^{\text{pol}}(t)=\text{Re}\left[\frac{J^2}{\hbar^2}\text{Tr}_{\text{ph}}\rho_{\text{ph}}^{\text{eq}}(T)e^{S_m(t)}e^{-S_n(t)}e^{S_n(0)}e^{-S_m(0)}\right]\ . \tag{A4}$$

Equations (A3) and (A4) are ambiguous as they stand because the operators $S_n(t)$ have not been defined and the states over which the traces are taken have not been explicitly stated. In the calculation of Brown *et al.* all phonon operators are *bare* operators; i.e., those representing the normal modes of the isolated medium. In the calculation of Kenkre and Rahman, all phonon operators are *dressed* operators; i.e., those representing modified modes of vibration which include part of the effects of exciton-phonon coupling. While these dressed modes are normal modes in the $J=0$ limit, neither the bare nor the dressed modes are normal modes when $J\neq 0$. Both (A3) and (A4) are traces over the relevant phonon states [i.e., bare for (A3) and dressed for (A4)] and $\rho_{\text{ph}}^{\text{eq}}(T)$ is the relevant equilibrium density operator. The exponential operators are defined such that

$$e^{S_n(t)}=\exp\left[\sum_q \chi_n^q(e^{i\omega_q t}b_q^\dagger-e^{-i\omega_q t}b_{-q})\right]\ , \tag{A5}$$

and thus may be recognized as products of coherent state displacement operators.

Were it not for the distinct ordering of the displacement operators in (A3) and (A4), the structure of the traces would be *identical* and would yield the same result despite the differences in the interpretations of the operators involved. Yet the exponent yielded by (A3) is real, while the exponent yielded by (A4) is complex. One may verify using simple properties of displacement operators that it is the distinct ordering of the operators in the two traces which is responsible for this difference in phase.

The order of displacement operators in (A4) is determined by the derivation of (A4) from a perturbation theory which gives the memory function as a correlation function

$$\langle V_{mn}(t)V_{nm}(0)\rangle \rightarrow \mathrm{Tr}\rho e^{S_m(t)}e^{-S_n(t)}e^{S_n(0)}e^{-S_m(0)} . \quad (\mathrm{A6})$$

On the other hand, the order of displacement operators in (A3) is determined by the derivation of (A2) from a density matrix equation, in which the density matrix element $\rho_{mn}(t)$ is given by

$$\mathrm{Tr}\sigma(0)a_n^\dagger(t)a_m(t) \rightarrow \mathrm{Tr}\rho e^{-S_n(0)}e^{S_n(t)}e^{-S_m(t)}e^{-S_n(0)} . \quad (\mathrm{A7})$$

Since the difference in ordering is intrinsic to the different methods of calculation, the only way to bring the two methods into agreement would be to modify one or the other memory function in an *ad hoc* fashion. The modification of our theory which would be necessary to "resolve" this disagreement consists of removing the restriction of $\mathcal{ff}_{mn}(t)$ to the real part of the operator correlation function in (A2). A serious consequence of such a modification would be that the resulting *ad hoc* theory would fail to reproduce the known exact density matrix solution in the $J=0$ limit. Moreover, such a modification would not resolve the disagreement we find in the transient behavior of the system, so the agreement thereby gained would be short lived.

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