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Citation: *J. Chem. Phys.* **87**, 6700 (1987); doi: 10.1063/1.453731

View online: <http://dx.doi.org/10.1063/1.453731>

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Polaron formation in the acoustic chain

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(Received 25 June 1987; accepted 19 August 1987)

Exact calculations are presented which detail the process of polaron formation in the one-dimensional acoustic chain. Exact solution is possible because the limit considered is the transportless limit in which the Hamiltonian matrix elements responsible for the motion of an excitation among site states have been set to zero. The polaron formation process is found to be decomposable into two subprocesses having distinct time scales. A disparity of time scales is possible in the case of long wavelength excitations. The consistency of our conclusions is demonstrated through the consensus of results obtained for the discrete acoustic chain, the Debye model, and the elastic continuum.

I. INTRODUCTION

In a recent paper, Brown *et al.*¹ presented an analysis of the problem of polaron formation based on the Fröhlich Hamiltonian in the transportless limit in which the problem may be solved exactly. A number of quantities were calculated and their behavior analyzed. In particular, it was found that two related processes are involved in the formation of a polaron which differ qualitatively and quantitatively. In one process, energy interpretable as the polaron binding energy is shed by the exciton system into the normal modes of the lattice. Another process results in the dispersal of this energy throughout the lattice and results in the development of a persistent deformation about the region occupied by the exciton. The crucial observation for the polaron formation problem is that a polaron cannot be considered to exist until the polaron binding energy has been dispersed and the lattice deformation completed.

The amount of energy shed into the lattice during polaron formation and the time dependence of this energy transfer are independent of the detail with which the initially bare exciton is distributed over the various sites. On the other hand, the lattice deformation and the time required to complete its development depend explicitly on the exciton probability distribution in site space. The qualitative difference in the dependences of these processes on the exciton probability distribution results in quantitative differences in the time scales which may be associated with each. The distinction is most evident for long wavelength excitations or in the related continuum limit. The conclusion one may draw on general grounds is that the time scale for polaron formation scales with the width of the excitation probability distribution in site space, and thus may be arbitrarily long, while the time scale for energy loss has a unique value of the order of a vibrational period.

In this paper we present an explicit evaluation of the quantities introduced in Ref. 1 using a nearest-neighbor acoustic chain as a model for the lattice vibrations. We give particular attention to the form of the coupling functions in

both the site and normal mode representations. The time functions describing energy transfer and lattice deformation are calculated exactly for this model and the time scale for each process is characterized. We then turn to the case of long wavelength excitations and the special considerations involved in the extraction of the continuum limit.

II. HAMILTONIAN AND COUPLING FUNCTIONS

We consider the Fröhlich Hamiltonian in the transportless limit in which there are no matrix elements connecting distinct exciton site states. The Hamiltonian then has the form

$$H = H_{\text{ph}} + H_{\text{ex-ph}}, \quad (2.1)$$

where

$$H_{\text{ph}} = \sum_q \hbar \omega_q b_q^\dagger b_q, \quad (2.2)$$

$$H_{\text{ex-ph}} = \sum_{m,n} g_{mn} (\hat{u}_m - \hat{u}_n) a_n^\dagger a_n. \quad (2.3)$$

Here b_q^\dagger creates a vibrational quantum in the normal mode q and a_n^\dagger creates an exciton in the local basis state n . We consider only longitudinal acoustic phonons due to harmonic nearest-neighbor forces. The dispersion relation for these phonons is given by

$$\omega_q = \omega_B \sin(|qa|/2). \quad (2.4)$$

The frequency ω_B is the bandwidth of acoustic phonons and the highest acoustic frequency, corresponding to the anti-phase oscillation of nearest-neighbor unit cells, and a is the lattice constant. The coupling energy depends on the molecular displacement operators \hat{u}_m through the forces g_{mn} . For the acoustic chain we will employ the simplest such coupling, for which the interaction potential extends only to the molecules adjacent to an excited site

$$g_{mn} = g_{m-n} = g(\delta_{mn+1} - \delta_{mn-1}). \quad (2.5)$$

In writing Eq. (2.5) the lattice has been taken to be translationally invariant.

In a translationally invariant lattice comprised of N molecules of mass M , the normal mode transformation to

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the creation and annihilation operators b_q^\dagger, b_q of each normal mode q allows the molecular displacement operators \hat{u}_m to be represented as^{2,3}

$$\hat{u}_m = \sqrt{\frac{\hbar}{2NM}} \sum_q \frac{e^{-iqR_m}}{\omega_q^{1/2}} (b_q^\dagger + b_{-q}). \quad (2.6)$$

The interaction Hamiltonian $H_{\text{ex-ph}}$ may be rewritten in the form

$$H_{\text{ex-ph}} = \sum_{q,n} \chi_n^q \hbar \omega_q (b_q^\dagger + b_{-q}) a_n^\dagger a_n, \quad (2.7)$$

in which we have defined the dimensionless coupling function χ_n^q :

$$\chi_n^q = \frac{1}{\sqrt{2NM\hbar\omega_q^3}} e^{-iqR_n} \sum_m e^{-iqR_m} g_m. \quad (2.8)$$

Using Eq. (2.5) for the specific example of the nearest-neighbor coupling in an acoustic chain,

$$\chi_n^q = \chi^q e^{-iqR_n} = \frac{g[-2i \sin(qa)]}{\sqrt{2NM\hbar\omega_q^3}} e^{-iqR_n}. \quad (2.9)$$

III. EXACT EVALUATION OF DIAGNOSTIC FUNCTIONS: DISCRETE CASE

Two kinds of initial states are of general interest in the polaron problem. One state, $|\Phi(0)\rangle$, was constructed to represent a single “bare” excitation:

$$|\Phi(0)\rangle = \sum_n \Phi_n(0) a_n^\dagger |0\rangle; \quad (3.1)$$

i.e., an *exciton*. A second state, $|\Psi(0)\rangle$, was constructed to represent a single “dressed” excitation:

$$|\Psi(0)\rangle = \sum_n \Psi_n(0) a_n^\dagger e^{-\sum_q \chi_n^q (b_q^\dagger + b_q)} |0\rangle; \quad (3.2)$$

i.e., a *polaron*. In the following we take $|\Phi_m(0)|^2 = |\Psi_m(0)|^2 = P_m$.

Using exact solutions available in the transportless limit, expectation values can be calculated for states propagating from these initial conditions. Particularly useful are the expectation values of the total phonon energy $\langle H_{\text{ph}}(t) \rangle$ and of the displacements of the individual molecules $\langle \hat{u}_m(t) \rangle$. For polaron states one finds¹

$$\langle \Psi(t) | H_{\text{ph}} | \Psi(t) \rangle \equiv 1\text{PBE} = \sum_q |\chi^q|^2 \hbar \omega_q, \quad (3.3)$$

$$\begin{aligned} \langle \Psi(t) | \hat{u}_n | \Psi(t) \rangle &\equiv D(n) \\ &= -\sqrt{\frac{2\hbar}{NM}} \sum_{q,m} \frac{e^{-iqR_n} \chi_m^{-q}}{\omega_q^{1/2}} P_m. \end{aligned} \quad (3.4)$$

The unit of energy in Eq. (3.3) is often referred to as the polaron binding energy (PBE). For states evolving from the bare initial condition $|\Phi(0)\rangle$, the results

$$\langle \Phi(t) | H_{\text{ph}} | \Phi(t) \rangle \equiv K(0) - K(t), \quad (3.5)$$

$$\begin{aligned} \langle \Phi(t) | \hat{u}_n | \Phi(t) \rangle &\equiv d(n,t) \\ &= -\sqrt{\frac{2\hbar}{NM}} \sum_{q,m} \frac{e^{-iqR_n} \chi_m^{-q}}{\omega_q^{1/2}} \\ &\quad \times [1 - \cos(\omega_q t)] P_m \end{aligned} \quad (3.6)$$

obtain, in which we have defined the energy profile function

$$K(t) = 2 \sum_q |\chi^q|^2 \hbar \omega_q \cos(\omega_q t). \quad (3.7)$$

The time dependence of $K(t)$ describes the process through which energy is transferred into the lattice during polaron formation. Using the quantities appropriate for the acoustic chain,

$$\begin{aligned} K(t) &= \frac{4g^2}{NM\omega_B^2} \sum_q \frac{\sin^2(qa)}{\sin^2(|qa|/2)} \\ &\quad \times \cos[\omega_B t \sin(|qa|/2)]. \end{aligned} \quad (3.8)$$

In the limit of infinite chain length, the allowed q values densely fill the Brillouin zone, and the discrete summation in Eq. (3.8) is replaced by an integration:

$$\frac{1}{N} \sum_q \rightarrow \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dq. \quad (3.9)$$

Thus in an infinite chain [Eq. (3.8)] yields⁴

$$\begin{aligned} K(t) &= \frac{16g^2}{M\omega_B^2} \frac{a}{\pi} \int_0^{\pi/a} dq \cos^2(qa/2) \\ &\quad \times \cos[\omega_B t \sin(qa/2)] \\ &= \frac{16g^2}{M\omega_B^2} \frac{J_1(\omega_B t)}{\omega_B t}. \end{aligned} \quad (3.10)$$

We may characterize the time scale for energy transfer τ_E by the time at which the first zero of $K(t)$ occurs. The transfer of polaron binding energy into the vibrations of the chain thus occurs on the time scale $\tau_E = O\{\omega_B^{-1}\}$, independent of the initial exciton distribution.

For the same coupling function, the polaron deformation Eq. (3.4) has the form

$$D(n) = \frac{-2g}{NM\omega_B^2} \sum_{q,m} \frac{i \sin(qa)}{\sin^2(|qa|/2)} e^{-iq(R_n - R_m)} P_m, \quad (3.11)$$

which in the limit of infinite chain length becomes

$$\begin{aligned} D(n) &= \frac{-4g}{M\omega_B^2} \sum_m \frac{2a}{\pi} \int_0^{\pi/2a} dq \\ &\quad \times \frac{\sin[2q(R_n - R_m)] \cos(qa)}{\sin(qa)} P_m. \end{aligned} \quad (3.12)$$

Choosing a coordinate system such that $R_m = ma$, this may be rewritten⁴

$$D(n) = \frac{-4g}{M\omega_B^2} \sum_m \text{sgn}(n-m) P_m, \quad (3.13)$$

in which

$$\begin{aligned} \text{sgn}(m) &= \frac{m}{|m|}, \quad m \neq 0 \\ &= 0, \quad m = 0. \end{aligned} \quad (3.14)$$

On the other hand, the time-dependent molecular displacements (3.6) which follow from the bare exciton initial condition (3.1) are expressed as

$$\begin{aligned} d(n,t) &= \frac{-2g}{NM\omega_B^2} \sum_{q,m} \frac{i \sin(qa)}{\sin^2(|qa|/2)} e^{-iq(R_n - R_m)} \\ &\quad \times [1 - \cos(\omega_q t)] P_m. \end{aligned} \quad (3.15)$$

Again taking the infinite chain limit we find

$$d(n,t) = \frac{-4g}{M\omega_B^2} \sum_m \frac{2a}{\pi} \int_0^{\pi/2a} dq \frac{\sin[2q(R_n - R_m)] \cos(qa) \{1 - \cos[\omega_B t \sin(qa)]\}}{\sin qa} P_m, \quad (3.16)$$

and again choosing coordinates such that $R_m = ma$,⁴

$$\begin{aligned} d(n,t) &= \frac{-4g}{M\omega_B^2} \sum_m \int_0^{\omega_B t} dz \frac{2(n-m)}{z} J_{2(n-m)}(z) P_m \\ &= D(n) + \frac{4g}{M\omega_B^2} \\ &\quad \times \sum_m \int_{\omega_B t}^{\infty} dz \frac{2(n-m)}{z} J_{2(n-m)}(z) P_m. \end{aligned} \quad (3.17)$$

From Eq. (3.17) it is clear that

$$\lim_{t \rightarrow \infty} d(n,t) = D(n). \quad (3.18)$$

This demonstrates explicitly for the acoustic chain that the limiting deformation of the chain at long times is the same as the polaron deformation despite the different initial condition.

As an example in which the detail of this process may be elaborated, consider the rectangular distribution

$$\begin{aligned} P_m^{\text{rect}} &= \frac{1}{2\Lambda + 1}, \quad m \in [-\Lambda, \Lambda] \\ &= 0, \quad \text{otherwise.} \end{aligned} \quad (3.19)$$

The polaron deformation corresponding to this distribution is the linear ramp illustrated in Fig. 1. The bare exciton initial condition leads to the same deformation at long times, but with a complex time dependence. In order to determine the time scale τ_D on which this process occurs, let us consider the displacement of a molecule near the center of the rectangular distribution. (The central molecule does not experience a displacement due to the symmetry built into the distribution and coupling functions.)

$$\begin{aligned} d(1,t) &= \frac{-4g}{M\omega_B^2} \sum_m \int_0^{\omega_B t} dz \frac{2(1-m)}{z} J_{2(1-m)}(z) P_m^{\text{rect}} \\ &= \frac{-4g}{M\omega_B^2} \int_0^{\omega_B t} dz \frac{1}{z} \left[\frac{2\Lambda}{(2\Lambda + 1)} J_{2\Lambda}(z) \right. \\ &\quad \left. + \frac{2(\Lambda + 1)}{(2\Lambda + 1)} J_{2(\Lambda + 1)}(z) \right]. \end{aligned} \quad (3.20)$$

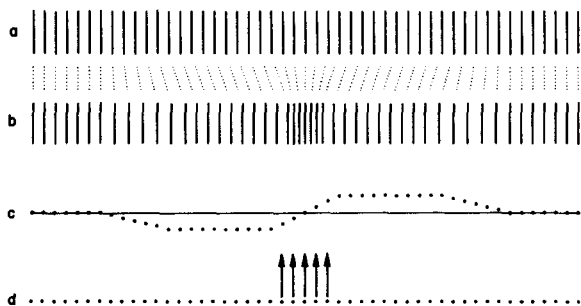


FIG. 1. Schematic representation of polaron formation: (a) P_m^{rect} with $\Lambda = 2$, (b) $d(n,t)$ for $v\omega_B t/2 = 0\{5\Lambda\}$, (c) absolute positions of molecules in the chain for $v\omega_B t/2 = 0\{5\Lambda\}$, (d) undeformed chain at $t = 0$.

Since the first maximum and zero of $J_\nu(z)$ occur at $z = O\{\nu\}$, $d(1,t)$ is monotone until a time $t = O\{(2\Lambda + 1)\omega_B^{-1}\}$, after which the oscillatory decay to its limiting value begins. This demonstrates explicitly that $\tau_D = O\{(2\Lambda + 1)\omega_B^{-1}\}$ and $\tau_E/\tau_D = O\{(2\Lambda + 1)^{-1}\}$. Thus, although the polaron binding energy is transferred into the lattice on a time scale of the order of a typical vibrational period, the deformation of the lattice may take a substantially longer time to develop since this time depends directly on the spatial extent of the excitation.

In addition to those calculated explicitly above one may consider quantities such as reduced density matrix elements $\rho_{mn}^{\text{bare}}(t)$ and Green's functions $G_{mn}^{\text{bare}}(t) = -i\langle 0|a_m^\dagger(t)a_n(0)|0\rangle$ which also reflect the vibrational relaxation of an initially bare excitation.¹ The time dependences of these quantities contain structure out to times $\tau_{mn} \gtrsim 2(m-n)\omega_{13}^{-1}$, which share with τ_E the property of being independent of the detail of the spatial distribution of the excitation, but share with τ_D the property of being proportional to physical lengths in the solid.

IV. DEBYE MODEL: LONG WAVELENGTHS

The Debye approximation²

$$\omega_q \approx v|q|, \quad -\frac{\pi}{a} < q < \frac{\pi}{a}, \quad (4.1a)$$

$$v \equiv \frac{d\omega_q}{dq} \Big|_{q=0} \quad (4.1b)$$

enjoys considerable success as a long wavelength approximation for acoustic phonons, since for the dispersion relation (2.4), for which $v = \omega_B a/2$, the bound

$$\frac{|\omega_q - v|q|}{v|q|} < \frac{1}{10} \frac{2|qa|}{\pi} \quad (4.2)$$

holds over the entire inner half of the Brillouin zone. The approximation is physically appropriate when the relevant wavelengths λ satisfy the condition

$$a \ll \lambda \ll L, \quad (4.3)$$

where L is the length of the acoustic chain. In this range of wavelengths the errors incurred in approximating short wavelength behavior are minimized while generic features of the microscopic granularity of the medium, such as a maximum acoustic frequency and a finite Brillouin zone, are retained. Handled with care, this approximation should yield results intermediate between exact properties of the discrete solid and those of the elastic continuum, the latter being sensitive only to the bulk properties of the solid.

The long wavelength criterion (4.3) implies that for the relevant wavelengths the dimensionless quantity qa can be considered small. This allows us to extend the Debye approximation to the coupling functions χ^q [see Eq. (2.9)] such that

$$\chi^q \approx \frac{-4ig}{\sqrt{NM\hbar\omega_B^3}a} \frac{q}{|q|^{3/2}}. \quad (4.4)$$

Using Eq. (4.1) and Eq. (4.4) in Eqs. (3.7) and (3.9) yields the Debye approximation to the exact $K(t)$ given in Eq. (3.10):

$$K_{\text{Debye}}(t) = \frac{16g^2}{M\omega_B^2} \frac{\sin[\pi\omega_B t/2]}{[\pi\omega_B t/2]}. \quad (4.5)$$

Although we have used the long wavelength criterion (4.3) to construct $K_{\text{Debye}}(t)$, there is no term in the exact $K(t)$ which selects long wavelengths as being the most relevant. The usefulness of Eq. (4.5) as an approximation thus depends on the use to which it is put. We may expect accuracy when $K_{\text{Debye}}(t)$ is used in conjunction with quantities varying on time scales longer than $O\{\lambda/\omega_B a\}$ since these characterize the time scales of waves having wavelengths greater than λ . This expectation is borne out in comparing Eq. (4.5) with the exact result (3.10), since the estimate of $K(0)$ (a short-time result) provided by Eq. (4.5) is twice the exact value given by Eq. (3.10); however, both Eq. (4.5) and (3.10) have the same strength $\int_0^\infty K(t)dt$ (a long-time result).

Greater discretion is called for in extending the Debye approximation to the computation of the polaron deformation $D(n)$. The phase factors $\exp[-iqR_n]$ must not be approximated, since the long wavelength condition is insufficient to render the phases qR_n small for an arbitrary molecule n . Otherwise applying the long wavelength criterion throughout yields

$$D_{\text{Debye}}(R_n) = \frac{-4g}{M\omega_B^2} \sum_m \frac{2}{\pi} \text{Si}\left[\frac{\pi}{a}(R_n - R_m)\right] P_m, \quad (4.6)$$

in which $\text{Si}(x)$ is the sine integral.⁴ Clearly, $(2/\pi)\text{Si}(\pi m)$ is an approximation to the $\text{sgn}(m)$ which appears in Eq. (3.13). Explicit dependence on extrinsic length scales appears in each term through the dependence of $D_{\text{Debye}}(R_n)$ on the probability distribution of the excitation. A predominance of long wavelengths in the spectrum of P_m is sufficient to justify the approximation.

As in the calculation of the polaron deformation $D_{\text{Debye}}(n)$, when computing the time-dependent deformation $d_{\text{Debye}}(n, t)$, the phase factors $\exp[-iqR_n]$ must not be approximated. However, in addition, the time-dependent phase factors $\cos(\omega_q t)$ must not be approximated, since the long wavelength condition which gives $\omega_q \approx \omega_B |qa|/2$ is insufficient to render the phase $\omega_B |qa|t/2$ small for arbitrary times t . Combining the spatial and temporal phase factors and otherwise applying the long wavelength criterion throughout yields

$$d_{\text{Debye}}(R_n, t) = D_{\text{Debye}}(R_n) - \frac{1}{2}D_{\text{Debye}}(R_n - vt) - \frac{1}{2}D_{\text{Debye}}(R_n + vt). \quad (4.7)$$

The intermediate position occupied by the Debye approximation is quite apparent in Eq. (4.7): Although $d_{\text{Debye}}(R_n, t)$ describes the movement of a particular molecule whose equilibrium position is specified by the discretized coordinate R_n , the motion can be expressed as a superposition of D'Lambert solutions of a continuum wave equation. Since the development of the lattice deformation cannot be complete until the traveling profiles

$D_{\text{Debye}}(R_n \pm vt)$ become well separated, we have the result that $\tau_D \approx \lambda/v$. The time scale estimates provided by the Debye approximation are consistent with the exact results for the discrete chain: $\tau_E = O\{a/v\}$, $\tau_D = O\{\lambda/v\}$, and $\tau_E/\tau_D = O\{a/\lambda\}$. Thus, for long wavelength excitations $\tau_E/\tau_D \ll 1$.

V. CONTINUUM LIMIT

The foregoing demonstrations show that for excitations spanning many lattice constants, i.e., *long wavelength excitations*, the two processes comprising polaron formation occur on disparate time scales. Since the behavior of such extended excitations should be only weakly dependent on structure on the scale of a single lattice constant, it is worthwhile to consider the continuum limit of the acoustic chain, which is a one-dimensional elastic continuum or line.^{3,5} The characterization of the polaron formation process in the elastic continuum should be consistent with the foregoing Debye approximation and remain valid for long wavelength excitations in materials having different microstructures.

In forming the continuum limit, physical quantities fall into three classes: those which vanish, those which diverge, and those which approach finite limits. In order for the limit to be physically meaningful, the dynamics in the continuum must depend only on the latter class. Any aspects of the continuum process dependent on vanishing or diverging quantities thus fall outside the scope of a continuum description.

The transition to the continuum is facilitated by repairing to the problem posed by a finite chain of length $L = Na$ and using the wave vector representation for both the phonons and excitons:

$$H_{\text{ex-ph}} = \sum_{p,q=-\pi/a}^{\pi/a} \chi^q \hbar\omega_q (b_q^\dagger + b_{-q}) a_p^\dagger a_{p-q}. \quad (5.1)$$

The allowed wave vectors q are integer multiples of $2\pi/L$, regardless of the magnitude of the lattice constant. Thus, as the continuum limit is approached, the lattice constant vanishes and the Brillouin zone expands while the spacing between the allowed wave vectors remains fixed. In the discrete lattice, the direct space and wave vector representations are related through the finite Fourier series

$$a_n = \frac{1}{\sqrt{N}} \sum_{q=-\pi/a}^{\pi/a} e^{-iqR_n} a_q. \quad (5.2)$$

In the continuum limit, this relation is replaced by the infinite Fourier series

$$a(x) = \frac{1}{\sqrt{L}} \sum_{q=-\infty}^{\infty} e^{-iqx} a_q. \quad (5.3)$$

In addition to the new dependence of the field operators on the continuous variable x , there has been a change in dimensionality such that the operator product $a^\dagger(x)a(x)$ is now a density. The representation of a site-diagonal operator \hat{O} is thus modified such that

$$\hat{O} = \sum_n O_n a_n^\dagger a_n \rightarrow \int_{-L/2}^{L/2} dx O(x) a^\dagger(x) a(x); \quad (5.4)$$

e.g., the number operator \hat{N} is obtained by setting $O_n = O(x) = 1$.

The phonon operators may be similarly transformed. The displacement coordinate of the continuum corresponding to the discrete lattice coordinate \hat{u}_m [see Eq. (2.6)] is

$$\hat{u}(x) = \sqrt{\frac{\hbar}{2L\rho}} \sum_{q=-\infty}^{\infty} \frac{e^{-iqx}}{\sqrt{v|q|}} (b_q^\dagger + b_{-q}), \quad (5.5)$$

in which $\rho = M/a$ is the macroscopic mass density. Though v is the same longitudinal velocity of sound that enters the Debye approximation, its appearance here is an exact consequence of the continuum limit. Since the maximum angular phonon frequency is given by

$$\omega_B = 2\sqrt{\frac{k}{M}} = \frac{2}{a} \sqrt{\frac{\tau}{\rho}}, \quad (5.6)$$

wherein k is the stiffness of the Hooke's law springs connecting adjacent molecules and τ is the tension, this limit is formulated

$$\lim_{a \rightarrow 0} \omega_q = \lim_{a \rightarrow 0} 2\sqrt{\frac{\tau}{\rho}} \frac{\sin(|qa|/2)}{a} = v|q|. \quad (5.7)$$

The harmonic lattice \rightarrow elastic continuum transition does not in itself provide a unique prescription for translating the exciton-phonon interaction Hamiltonian $H_{\text{ex-ph}}$ into continuum form, since the exciton-lattice coupling arises from a physical mechanism distinct from that responsible for elasticity. The coupling of an exciton to its host medium involves a potential with a characteristic range. Although our model of a discrete harmonic chain has taken this range to be a single lattice constant, we are now faced with the choice of allowing this range to vanish with the lattice constant, or maintaining the range at a physically prescribed value while the underlying lattice becomes ever more finely divided. The latter choice leads to a nonlocal exciton-continuum interaction expressed as a volume integral over the region influenced by the interaction potential. The former leads to an interaction energy dependent only on local properties of the continuum.

While the nonlocal interaction provides the more accurate description of a physical continuum, the difference between the two choices becomes significant only when there are relevant wavelengths of the order of, or shorter than, the range of the interaction. In forming the continuum limit, however, we are restricting the scope of our analysis to those excitations whose wavelengths are sufficiently long to be insensitive to such structure. We thus choose the simpler local form of the interaction

$$\begin{aligned} & \sum_m g_{m-n} (\hat{u}_m - \hat{u}_n) \\ &= 2\epsilon \sum_m \frac{(\delta_{mn+1} - \delta_{mn-1})}{2a} (\hat{u}_m - \hat{u}_n) \rightarrow 2\epsilon \nabla \hat{u}(x), \end{aligned} \quad (5.8)$$

in which we have identified the discrete variable n with the continuous variable x as in Eqs. (5.2) and (5.3). The characteristic energy $\epsilon \equiv ga$ is the energy change resulting from a molecular displacement of one lattice constant in the field of the linearized interaction potential. Combining Eq. (5.8) with Eq. (5.4) yields

$$\begin{aligned} H_{\text{ex-ph}} &= \sum_{m,n} g_{m-n} (\hat{u}_m - \hat{u}_n) a_n^\dagger a_n \\ &\rightarrow \int_{-L/2}^{L/2} dx \, 2\epsilon \nabla \hat{u}(x) a^\dagger(x) a(x). \end{aligned} \quad (5.9)$$

In order to complete the correspondence with the exact and Debye calculations for the discrete chain, we subsequently allow the chain length to diverge ($L \rightarrow \infty$). Combining these observations shows that in the continuum limit [note $\int_0^\infty dt \delta(t) = 1/2$]

$$K(t) \rightarrow \frac{4\epsilon^2}{\rho v^3} \delta(t), \quad (5.10a)$$

$$D(n) \rightarrow D(x) = \frac{-\epsilon}{\rho v^2} \int_{-\infty}^{\infty} dy \, \text{sgn}(x-y) P(y), \quad (5.10b)$$

$$d(n,t) \rightarrow d(x,t) = D(x) - \frac{1}{2} D(x-vt) - \frac{1}{2} D(x+vt). \quad (5.10c)$$

The latter relation is merely the continuum translation of the discrete relation

$$d(n,t) = D(n) - \frac{1}{2} D\left(n - \frac{v}{a} t\right) - \frac{1}{2} D\left(n + \frac{v}{a} t\right), \quad (5.11)$$

which follows from Eq. (3.15) using the dispersion relation $\omega_q = v|q|$ obtaining in the continuum limit.

From Eq. (5.10c) it is easy to see that the displacement of a material point x in the excited region of the continuum does not reach its asymptotic value until the propagating deformations $D(x \pm vt)$ become well separated. Thus if λ is a measure of the width of the probability density $P(x)$, then the time scale for deformation is $\tau_D = O(\lambda/v)$. On the other hand, Eq. (5.10a) clearly shows that $\tau_E = 0$ for the continuum so $\tau_E/\tau_D = 0$. This is consistent with the discrete-space conclusion $\tau_E/\tau_D = O\{2\Lambda + 1\}^{-1}$, since $(2\Lambda + 1)^{-1} \approx a/\lambda$ and the smallness of this ratio is the most essential condition for the continuum limit to be meaningful.

In neither the discrete space nor the continuum have we stated any restrictions on the values which may be taken by the parameters of the Hamiltonian or the scaled parameters of the continuum treatment. One of the conditions for the validity of a linear coupling model is that the oscillations of the molecules must remain small. There are two sources of this condition. One is the harmonic approximation for the lattice vibrations, the other is the linear approximation for the interaction energy. Assuming the small oscillation criterion to be valid in the discrete solid, the question arises whether it continues to be valid in the continuum limit. This criterion may appear to be violated in the continuum since we obtain finite displacements for material points while the nearest-neighbor distance in the underlying lattice vanishes. (The snapshot of the polaron formation process shown schematically in Fig. 1 illustrates how small relative displacements may accumulate to produce significant absolute displacements at large distances.)

This is not an indication of a breakdown in the theory. What is meaningful in the small oscillation criterion is the relative displacement of neighboring molecules and not their absolute spatial position. The displacements $d(n,t)$ and $D(n)$ are referenced to the absolute equilibrium positions

$\{R_m\}$ of the molecules in the *unexcited* chain and thus are absolute quantities. It is easy to show from Eq. (3.13) that a typical *relative* displacement of adjacent molecules in a deformed region of the chain is

$$\frac{|D(n) - D(n+1)|}{a} = O\left\{\frac{|D(\infty)|}{\lambda}\right\}, \quad (5.12)$$

in which $D(\infty)$ is the asymptotic displacement attained by a molecule far from the excitation region at long times and is the same in the continuum as in the physical lattice. Insofar as the net displacement $D(\infty)$ is small relative to the width of the probability distribution/density, the small oscillation criterion remains satisfied. Thus, a sufficient condition for compliance with the small oscillation criterion is that the excitation span many physical lattice sites. Since this is the only scenario in which the continuum limit is meaningful, we find the continuum limit to be consistent with the small oscillation criterion.

One quantity which is ordinarily considered to be meaningful, but which diverges in the strict continuum limit, is the polaron binding energy. From Eqs. (3.3), (3.7), and (3.10) we have

$$1\text{PBE} = \frac{1}{2} K(0) = \frac{8g^2}{M\omega_b^2}; \quad (5.13)$$

however, in terms of the parameters of the continuum, this becomes

$$1\text{PBE} = \frac{1}{a} \frac{2\epsilon^2}{\rho v^2}, \quad (5.14)$$

which clearly diverges in the limit of a vanishing lattice constant. The polaron binding energy arises from a shift in the zero of energy of the solid. The contribution of the q th mode to the polaron binding energy has the finite value

$$\hbar\omega_q |\chi^q|^2 = \frac{2\epsilon^2}{\rho L v^2} \quad (5.15)$$

in the continuum limit. The polaron binding energy thus diverges because there are an infinite number of vibrational modes. This is related to the zero point energy of the elastic line; however, the latter diverges even on a per mode basis since $\omega_q = v|q|$ and there is no cutoff wave vector in a continuum. The divergence of these quantities indicates that they are intrinsically microscopic in nature and thus fall outside the scope of a strict continuum limit. The divergence of the polaron binding energy and the average zero point energy per mode merely affect the zero of energy and thus present no difficulties for transport. In particular, static shifts in the zero of the energy scale have no effect on density matrix calculations since the zero of energy affects only the global phase of the wave function which is absent from density matrix treatments.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation Grants Nos. DMR 8315950 and CHE-8403841.

¹D. W. Brown, K. Lindenberg, and B. J. West, *J. Chem. Phys.* **84**, 1574 (1986).

²O. Madelung, *Introduction to Solid State Theory*, edited by M. Cardona, P. Fulde, and H.-J. Quisser, Springer Series in Solid State Sciences, Springer, New York, 1978), Vol. 2.

³H. Haken, *Quantum Field Theory of Solids: An Introduction* (North-Holland, Amsterdam, 1976).

⁴M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).

⁵C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).