Transport Dynamics of a Large Acoustic Polaron in One Dimension

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The transport dynamics of a large polaron has been studied in a one-dimensional system whose underlying vibrational spectrum is acoustic in character. Such a polaron moves as a heavy quasiparticle with transport relaxation time, τ, determined mainly by collisions with thermally ambient phonons. Concrete results show that τ decreases monotonically with increasing temperature, in sharp contrast to the previously treated problem of a large polaron in a one-dimensional Einstein lattice.

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In the past years, charge transport in quasi one-dimensional (1D) systems, such as polyacetylene, has received a great deal of attention. Whereas solitons and polarons seem to be the key to the understanding[1] of transport in such systems, the rigorous formulation of a transport theory for quasi 1D conductors has been lacking so far. In a recent paper[2] (hereafter denoted as "I"), one of the present authors (T.H.) developed an *a priori* quantum mechanical treatment for the dynamical behavior of a 1D large polaron within the framework of the well-known molecular crystal model (MCM)[3] in which the vibrational spectrum of the host lattice is of optical (Einstein) type ($\omega_q = \omega_0$). In the present work, the basic method of I is applied to a 1D deformation-potential model in which the vibrational spectrum has acoustic (Debye) character ($\omega_q = c_s|q|$). Avoiding the mathematical difficulties of the more elaborate models,[1] we elucidate some of the basic physical principles which govern polaron transport relaxation due to thermally ambient acoustic phonons. As pointed out below, the continuous character of this vibrational spectrum gives rise to profound differences in polaronic transport properties from those that obtain in the case of the molecular crystal model of I. These results, together with those of I, should hopefully provide insight into the more complicated models[1] of polaron (and soliton) transport in which both phonon species are present.

The Hamiltonian of a single electron coupled to the acoustic vibrations of a monoatomic linear chain via a deformation potential, in the continuum approximation, is

$$H = \int dn\{P^2(n)/2M + Mc_s^2\Delta^2(n)/2\} - (\hbar^2/2ma^2)\partial^2/\partial x^2 - C\Delta(x), \tag{1}$$

where $\Delta(n) \equiv a^{-1}\partial U/\partial n$ is the one-dimensional dilatation of an arbitrary vibrational distortion, $U(n)$, $P(n)$ is the canonically conjugate momentum, and x is the electron coordinate in units of the lattice constant, a; in addition, M, m, c_s, and C are the atomic mass, electron band mass, sound velocity, and deformation-potential coupling constant, respectively.

As in I, we treat the problem via the adiabatic approach in which the vibrational kinetic energy in (1) is initially dropped. The eigenfunctions and energy eigenvalues of this truncated Hamiltonian are then solved (in prinicple) as functions of the vibrational coordinates, $U(n)$. Of particular interest are the ground-state wave function, $\psi[x;U(n)]$, and energy eigenvalue $E[U(n)]$. According to the adiabatic approach, the effective vibrational Hamiltonian is then

$$H_L = \int dn\, P^2(n)/2M + E[U(n)]. \tag{2}$$

For the above-defined electronic problem, in which the vibrational kinetic energy term of (1) is dropped, the resulting Hamiltonian is completely equivalent to the corresponding truncated version of the MCM Hamiltonian, given in Eq. (3) of I. This correspondence is seen by replacing the symbols $\Delta(n)$, c_s, and C by the MCM variables u_n, ω_0, and A, respectively. Because of this correspondence, which, of course, holds only for the static problem, we take over the results of I without further ado. In particular, the equilibrium displacements, $U^{(0)}(n)$, and the corresponding minimum energy, $E[U^{(0)}(n)] \equiv -E_p$, are given by (cf. also Whitfield and Shaw[4])

$$U^{(0)}(n - \xi/a) = (Ca/Mc_s^2)\tanh[\gamma(n - \xi/a)], \tag{3}$$

$$E_p = \hbar^2/6mL^2, \tag{4}$$

where

$$L \equiv a/\gamma = (2\hbar^2/ma^2)(Mc_s^2/C^2)a \tag{5}$$

is the linear dimension of the polaron. The quan-

tity ξ occurring in Eq. (3) denotes the arbitrary "centroid" coordinate; this arbitrariness reflects the translational invariance of the system.

Furthermore, the vibrational potential energy for small deviations, $u(\eta)$, from the equilibrium is [cf. I, Eq. (10); also Shaw and Young[5]]

$$E_{\rm ph}[u] \equiv E[U^{(0)}+u] - E[U^{(0)}] = \frac{Mc_s^2}{2a^2}\int d\eta\, d\eta' \frac{\partial u(\eta)}{\partial \eta}\frac{\partial u(\eta')}{\partial \eta'}[\delta(\eta-\eta') - \hat{G}(\eta,\eta')] + O(u^3). \quad (6)$$

The term containing the matrix $\hat{G}(\eta,\eta')$ represents the change in the lattice dynamics of the host crystal arising from the presence of the polaron. $\hat{G}(\eta,\eta')$ is a function of "relative" site variables, $\eta,\eta' = n-\xi/a, n'-\xi/a$, as given in Eqs. (11a) and (11) of I.

In sharp contrast to the optical case treated in I, the vibrational normal modes, $u_\alpha(\eta)$, and frequencies, ω_α, associated with $E_{\rm ph}$ form a continuum containing all positive values of ω_α^2, corresponding to the underlying acoustic spectrum of the host lattice. Indeed, for $\omega_\alpha \neq 0$, the asymptotic form of the mode functions consists of appropriate combinations of plane waves, $\exp(iaq\eta)$ ($|q| \equiv \omega_\alpha/c_s$), depending on the boundary conditions. However, as in I, there also exists a *zero-frequency*, spatially localized mode $u_0(\eta) \sim \partial U^{(0)}/\partial\eta$ which represents an infinitesimal rigid translation of the polaron, when multiplied by an infinitesimal amplitude. Since the associated restoring-force constant is zero, the effect of the vibrational kinetic energy term of (2) will cause the actual physical amplitude to be dynamically unbounded, thereby invalidating the small-amplitude expansion which underlies (6).

Following I, we surmount this difficulty by introducing the transformation[6]

$$U(n) = U^{(0)}(n-\xi/a) + Q(n-\xi/a) \equiv U^{(0)}(n-\xi/a) + \sum_{\alpha\neq 0} Q_\alpha u_\alpha(n-\xi/a), \quad (7)$$

wherein the "centroid" parameter, ξ, is treated as a dynamical variable, together with the nontranslational ($\alpha \neq 0$) coordinates, Q_α. Introducing (7) into (2), we have, after a number of manipulations [cf. also Ref. 6, Eq. (25)]

$$H_L = H_{\rm ph} + H_p, \quad (8)$$

$$H_{\rm ph} = \int d\eta\, \Pi^2(\eta)/2M + E_{\rm ph}[Q(\eta)], \quad (9)$$

$$H_p \cong [(\hbar/i)\partial/\partial\xi - P_{\rm ph}]^2/2M_p, \quad (10)$$

where

$$\Pi(\eta) = \sum_{\alpha\neq 0} u_\alpha(\eta)(\hbar/i)\partial/\partial Q_\alpha, \quad (11)$$

$$P_{\rm ph} = \int d\eta\, Q(\eta) a^{-1}\partial\Pi/\partial\eta, \quad (12)$$

$$M_p = M\int d\eta [a^{-1}\partial U^{(0)}/\partial\eta]^2 = 4E_p/c_s^2. \quad (13)$$

Note that the quantities $\Pi(\eta)$ and $Q(\eta)$ do not obey conventional commutation relations, but rather

$$[\Pi(\eta), Q(\eta')] = (\hbar/i)\{\delta(\eta-\eta') - u_0(\eta)u_0(\eta')\}.$$

As in I, Eq. (21), we have neglected certain terms in the polaron kinetic energy, H_p, which would only give rise to small corrections to the polaron effective mass M_p for the case treated here, namely, polaron velocities small compared to c_s. The quantity $P \equiv (\hbar/i)\partial/\partial\xi$ is a constant of motion, representing the total momentum of the system. Note, in particular, that the *kinetic momentum* of the polaron, $M_p\dot{\xi} \neq P$, but rather

$$M_p\dot{\xi} = P - P_{\rm ph}. \quad (14)$$

Finally, as discussed in I, the quantity $P_{\rm ph}$ may be considered as the momentum associated with the vibrational field; we shall refer to it as "phonon momentum."

We now evaluate the "cross section," i.e., the reflection coefficient for a "collision" of the polaron with a single phonon. Knowledge of said reflection coefficient will permit a straightforward calculation of the rate of polaron transport relaxation due to interaction with thermally ambient phonons. For this calculation, it is convenient to introduce the retarded phonon Green's function

$$D(\eta,\eta',\omega) \equiv (-i)\int_0^\infty \langle P|[Q(\eta,t), Q(\eta',0)]|P\rangle \exp(i\omega t)dt, \quad (15)$$

where $|P\rangle$ is that eigenstate of H with total momentum P which has the lowest energy. The calculation of $D(\eta,\eta',\omega)$ is greatly simplified by introducing the approximation

$$H_p \equiv (P-P_{\rm ph})^2/2M_p \cong P^2/2M_p - V_pP_{\rm ph}, \quad (16)$$

where $V_p \equiv P/M_p$, i.e., by neglecting the term $P_{\rm ph}^2/2M_p$. The physical justification of this approximation is that when $kT \ll E_p$, as is assumed in this paper, the ratio of the mean thermal momentum of a

phonon, kT/c_s, to that of a polaron, $(2M_pkT)^{1/2}$, is $(kT/M_pc_s^2)^{1/2}$ and hence small. Our philosophy is to regard (16) as generating a zeroth-order Green's function, higher-order corrections to which may be obtained by treating the neglected term as a perturbation. Such calculations are deferred for future study.

With the replacement of (10) by (16), the Hamiltonian of the system becomes quadratic in the vibrational field operators, $Q(\eta)$ and $\Pi(\eta)$, and the equation-of-motion method yields for $D(\eta,\eta',\omega)$

$$\left[\left(a\frac{\omega}{c_s}-i\frac{V_p}{c_s}\frac{\partial}{\partial\eta}\right)^2+\frac{\partial^2}{\partial\eta^2}\right]D(\eta,\eta',\omega)$$
$$-\int d\eta''\left[\frac{\partial}{\partial\eta}\hat{G}(\eta,\eta'')-\frac{2a\omega V_p}{c_s^2}iu_0(\eta)u_0(\eta'')-\left(\frac{V_p}{c_s}\right)^2\left(\frac{\partial}{\partial\eta}-\frac{\partial}{\partial\eta''}\right)u_0(\eta)u_0(\eta'')\right]\frac{\partial}{\partial\eta''}D(\eta'',\eta',\omega)$$
$$=(\hbar a^2/Mc_s^2)[\delta(\eta-\eta')-u_0(\eta)u_0(\eta')]. \quad (17)$$

With the source point, η', at $-\infty$, (17) takes the form of a homogeneous linear equation, describing the propagation of a one-dimensional lattice wave "through" the polaron. Assuming a purely outgoing wave, $\exp(iaq_+\eta)$, at $\eta\to+\infty$, we obtain the incident and reflected wave amplitudes, of form $\exp(iaq_+\eta)$ and $\exp(-iaq_-\eta)$, where $q_\pm\equiv\omega/(c_s\mp V_p)$. In particular, for the limiting case of $V_p=0$, we find for the reflection amplitude, $r(\kappa, V_p)$,

$$r(\kappa,0)\cong-\tfrac{3}{2}i\kappa,\quad \kappa\ll1, \quad (18)$$

$$r(\kappa,0)\cong2\pi^2i\kappa^3\exp(-\pi\kappa),\quad \kappa\gg1, \quad (19)$$

where $\kappa\equiv L\omega/c_s$. For $V_p\neq0$, the corrections to (18) and (19) are of the order $|\kappa V_p/c_s|$ and $|\kappa^3V_p/c_s|\exp(-\pi\kappa)$, respectively, for $|V_p|\ll c_s$, and thus small. The result for $\kappa\gg1$ has been obtained by straightforward use of the Born approximation. The derivation of (18) will be presented in our more complete report.

In order to treat transport properties, we incorporate (18) and (19) into a semiclassical Boltzmann kinetic approach which, although in some sense heuristic, nevertheless, in our opinion, contains the correct physics. The basis of the treatment is an expression for the probability per unit time, $P(V\to V')dV'$, for a polaron of velocity V to make a collisional transition to a differential velocity range between V' and $V'+dV'$ which for thermal velocities $|V|, |V'|\sim(kT/M_p)^{1/2}\ll c_s$ reads (to sufficient accuracy)

$$P(V\to V')\cong(M_pc_s/4\pi\hbar)n_q(1+n_{q'})|r(\kappa,0)|^2. \quad (20)$$

Here $n_q=1/[\exp(\hbar c_s|q|/kT)-1]$, $\kappa\cong L(|q|+|q'|)/2$, and the wave vectors of the incident and reflected phonon, q and q', are given in terms of V and V' by the collision kinematics.

Introducing (20) into the Boltzmann equation for the polaron velocity distribution function, we obtain the transport relaxation rate as

$$1/\tau=(2\hbar/\pi M_pL^2)\int_0^\infty d\kappa\,\kappa|r(\kappa,0)|^2(\kappa T_c/T)\exp(\kappa T_c/T)[\exp(\kappa T_c/T)-1]^{-2}, \quad (21)$$

where $T_c=\hbar c_s/kL$ is a crossover temperature. Namely, for $T\ll T_c$ the reflection coefficient of phonons with thermal wave vector $q_{th}\sim T/LT_c\ll1/L$ is $|r(Lq_{th},0)|^2\sim T^2$, whereas the velocity change due to a reflected thermal phonon is $\Delta V\sim2\hbar q_{th}/M_p\sim T$ and the number of thermally excited modes is proportional to $q_{th}\sim T$; thus $1/\tau\sim T^4$. For $T\gg T_c$ phonons with $q\sim1/L$ and thermal occupation $n_q\sim T/T_c$ give the main contribution to transport relaxation. Therefore we have $1/\tau\sim T$ in the high-temperature limit. Since the change of the polaron velocity in a collision with a thermal phonon is inversely proportional to the polaron mass M_p, we have $1/\tau\sim1/M_p$ and the mobility $\mu=\tau/M_p$ is independent of M_p.

It is of interest to compare the foregoing results to those obtained in I. In the optical model (I) transport relaxation is also dominated by reflection in polaron-phonon encounters. As a result of the complete degeneracy of the underlying Einstein spectrum, however, the collision dynamics is determined mainly by the polaron kinetic energy, the reflectivity depending strongly on the polaron de Broglie wave vector, k_p; namely, $|r(k_p)|^2\sim\exp(-2\pi Lk_p)$. A significant consequence of this last result is that the effective relaxation time, i.e., $\langle\tau\rangle_{thermal}$ (not $\langle1/\tau\rangle_{thermal}^{-1}$!), increases for temperatures $T>T_m\sim(\hbar\omega_0\times\hbar^2/2M_pL^2)^{1/2}/k$, despite the increase in phonon population. In the present case, however, in which the underlying vibration spectrum is acoustic, the polaron is the "heavy" object in a collision, the dynamics is determined by the acoustic pho-

non energy, and $|r|^2$ depends only on the phonon wave vector q, even for $Lk_p \gg 1$. As a consequence, the transport relaxation time (and hence the mobility) shows the monotonically decreasing temperature dependence discussed above.

Finally, a remark about the conditions of the adiabatic approach (2) is in place. Qualitatively, we expect it to be valid, if the electronic binding energy, E_p, is large compared to the typical phonon energy of order $\hbar c_s/L$. With use of (4) and (5), this becomes equivalent to the strong-coupling requirement $(\pi/12)C^2/Mc_s^2 \gg \hbar\omega_D$ ($\omega_D \equiv \pi c_s/a$). Apart from a logarithmic prefactor, $(2/\pi)\ln(\pi L/a)$, of order unity, this condition coincides with Ref. 5 [cf. their Eq. (108)].

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