Dynamical Mean-Field Theory of Transport of Small Polarons

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We present a unified view of the transport properties of small polarons in the Holstein model at low carrier densities, based on the dynamical mean-field theory. The nonperturbative nature of the approach allows us to study the crossover from classical activated motion at high temperatures to coherent motion at low temperatures. Large quantitative discrepancies from the standard polaronic formulas are found. The scaling properties of the resistivity are analyzed, and a simple interpolation formula is proposed in the nonadiabatic regime.

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In the common wisdom, polaronic transport in solids is synonymous of activated conductivity. When electrons are strongly coupled to bosonic degrees of freedom (phonons, excitons, etc.), self-trapped states are formed. If the size of the polaron is comparable with the lattice spacing, the motion is then dominated by hopping processes: the particle has to overcome a potential barrier Δ and loses its quantum coherence at each hop, giving rise to an activated law of the form

$$\rho = \rho_0 e^{\Delta/k_B T}, \tag{1}$$

where the prefactor ρ_0 is weakly temperature dependent. Contrary to what happens in semiconductors, the activated behavior here is not related to the number of thermally excited carriers, but rather to the mobility of the individual carriers.

The Holstein model [1,2]

$$H = -t\sum_{\langle i,j\rangle}(c_i^\dagger c_j + c_j^\dagger c_i) + \hbar\omega_0\sum_i a_i^\dagger a_i - g\sum_i c_i^\dagger c_i(a_i^\dagger + a_i)$$

was introduced in the late 1950s to study such a behavior, as was being measured in some transition metal oxides. In this model, tight-binding electrons interact locally with molecular deformations, whose natural vibration frequency is ω_0 (t is the hopping parameter; g is the electron-phonon coupling constant). Although this is a rather crude idealization of a real solid, the Holstein model captures the essential physical phenomena involved in small-polaron transport. The situation is in fact more complex than indicated by the simple formula (1) and is summarized in several reviews [3]. Three regimes of temperature can be identified.

At low temperatures, the polarons behave as heavy particles in a band of renormalized width W and are weakly scattered by phonons. For small enough W, all the states in the band are equally populated, leading to a "metalliclike" resistivity [3–5] $\rho \propto (T/W) \times \exp(-\hbar\omega_0/k_B T)$. The exponential law comes from the thermal occupation of the optical phonons, which are assumed to be the main source of scattering. Upon increasing the temperature, the mean free path is rapidly reduced until the picture of coherent motion breaks down, typically around some fraction of $\hbar\omega_0/k_B$. Hopping motion then becomes more favorable, leading to an activated behavior of the form (1). The crossover from coherent to hopping motion is thus characterized by a maximum in the resistivity. Eventually, at temperatures higher than the activation energy, the polaron states are thermally dissociated and the residual electrons are strongly scattered by thermal phonons. In this case, the equipartition principle leads to $\rho \sim T^{3/2}$ [6]. This theoretical scenario, which neglects electronic correlations, is in principle restricted to systems with low carrier densities. At higher densities, many-body effects should certainly be taken into account [7,8]. However, the inclusion of electronic correlations leads to a similar coherent-to-hopping crossover [8].

On the experimental side, the largest amount of work has been devoted to the activated regime, which is often observed around room temperature, and resistivities of the form (1) have been measured in a variety of lightly doped narrow-band solids [3]. However, strong deviations from pure Arrhenius behavior are often reported [9], possibly indicating the onset of the coherent transport regime. In a few cases, the low temperature exponential law described above has also been identified [10]. Observations of this kind are rare since the exponential behavior is easily destroyed by the presence of other scattering mechanisms such as disorder, acoustic phonons, etc.

The main purpose of this work is to shed some light on the crossover from activated to coherent transport, for which a reliable theoretical description is still lacking. To do this, we calculate the resistivity of independent

Holstein small polarons in the framework of the dynamical mean-field theory (DMFT). This approximation is suitable whenever the physics is ruled by local phenomena, as is the case in the present problem, where it allows one to take into account the quantum nature of the phonons ($\omega_0 \neq 0$) and the finite bandwidth effects ($t \neq 0$) on the same footing. Since the theory does not require any "small parameter," it is able to go beyond the traditional approaches usually applied to the problem and gives reliable results in the regime $k_B T \sim \hbar\omega_0$ of interest here. Moreover, it yields a unified view of the different regimes of polaronic transport, acting as a testing ground of the validity of previous approaches.

The DMFT solution of the Holstein model for a single polaron was presented in Ref. [11], where an analytical expression for the spectral function $A_\epsilon(\nu)$ was given in terms of a continued fraction. The polaron formation *at zero temperature* can be described by introducing two independent dimensionless parameters. The first is the adiabaticity ratio $\gamma = \omega_0/D$ (D is the unrenormalized half bandwidth) according to which an adiabatic ($\gamma \ll 1$) and nonadiabatic regime ($\gamma \gg 1$) can be defined. The mechanism of polaron formation is fundamentally different in the two regimes, leading to different definitions of the dimensionless electron-phonon coupling. Being $E_P = g^2/\omega_0$ the energy of a polaron on a single lattice site, a well-defined polaronic state is formed for large $\lambda = E_P/D$ in the adiabatic case, and for large $\alpha^2 = E_P/\omega_0$ in the nonadiabatic case [11,12].

The corresponding transport properties can be calculated through the appropriate Kubo formula, which relates them to the current-current correlation function of the system at equilibrium. In DMFT, due to the absence of vertex corrections [13], the latter is fully determined by the spectral function $A_\epsilon(\nu)$, which is known *exactly* in the limit of vanishing density (single polaron problem) [11]. The resistivity at low (but finite) density can then be derived through an expansion in the fugacity [14],

$$\rho(T) = \frac{k_B T}{x\zeta\pi} \frac{\int d\epsilon N_\epsilon \int d\nu e^{-\nu/T} A_\epsilon(\nu)}{\int d\epsilon N_\epsilon \phi_\epsilon \int d\nu e^{-\nu/T} [A_\epsilon(\nu)]^2}. \quad (2)$$

In the above formula, the denominator is the current-current correlation function, and the numerator is proportional to the carrier concentration x, which was explicitly taken out (the exponential weights in the integrals reflect the Boltzmann nature of the carriers). N_ϵ and ϕ_ϵ are, respectively, the density of states and the current vertex of the periodic lattice. The constant $\zeta = e^2 a^2/\hbar v$ has the dimensions of conductivity, a being the lattice spacing, and v being the volume of the unit cell. In the following, we implicitly report the results for the dimensionless product $\rho x \zeta$, which is inversely proportional to the drift mobility, and assume $\hbar = k_B = 1$.

The results for the resistivity are illustrated in Fig. 1 for fixed $\lambda = 1.5$ in the adiabatic case. The three regimes discussed in the introduction can be clearly identified—the resistivity first rises exponentially (coherent regime), then decreases exponentially (activated regime), and eventually increases again as a power law (residual scattering regime). This is true for all the data sets except at $\gamma = 0.4$, where the polaron formation has shifted to higher values of λ, as expected when moving away from the adiabatic limit [11,12].

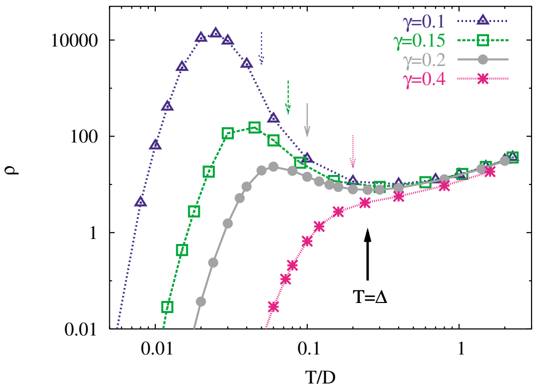

FIG. 1 (color online). Resistivity vs temperature at $\lambda = 1.5$, for different values of the adiabaticity parameter. Short arrows mark the temperature $T = \omega_0/2$ below which phonon quantum effects acquire importance. The long upward arrow is the gap $T = \Delta$.

Let us focus on the activated regime, $\omega_0 \lesssim T \lesssim \Delta$, where the polaron transport is dominated by incoherent hopping processes. In the adiabatic limit $\gamma \to 0$, the problem is generally studied within a simplified "two-site" molecular model [1,15], where the (classical) lattice degrees of freedom are seen to move "adiabatically" in the double-well energy curve determined by the electronic (bonding) state. At each jump, the system has to overcome a barrier $\Delta = E_P/2 - t$, leading to an Arrhenius-type behavior [3]

$$\rho = 2(T/\omega_0)\exp[\Delta/T]. \quad (3)$$

This semiclassical description holds provided that the transitions to higher (antibonding) electronic states can be neglected, which corresponds to [1,16]

$$\eta_2 \equiv \frac{D^2}{\omega_0\sqrt{2E_P T}} = [2\lambda\gamma^3(T/\omega_0)]^{-1/2} \gg 1. \quad (4)$$

Note that this does not coincide with the usual adiabaticity condition $\gamma \ll 1$ relevant for polaron formation.

To illustrate the accuracy of the semiclassical prediction, we show in Fig. 2 Arrhenius plots of the resistivity at fixed $\gamma = 0.2$, varying the coupling strength λ. First of all, our results indicate that the correct generalization of the two-site result (3) to infinite lattices is obtained by letting $\Delta = [E_P(\lambda) - D]/2$, where $E_P(\lambda) = D\lambda + D/(8\lambda) + \cdots$ is the adiabatic polaron energy, calculated, e.g., in Ref. [11] [see Fig. 2, full lines—the slight

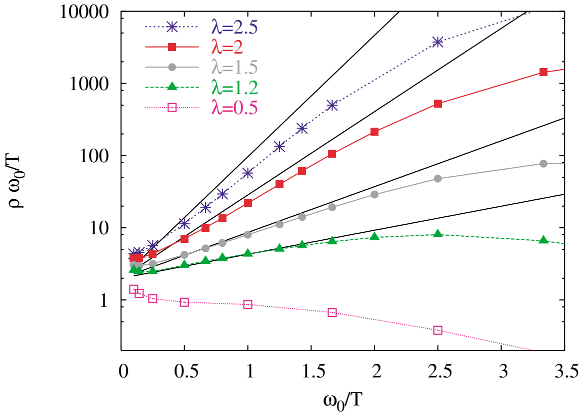

FIG. 2 (color online). Arrhenius plots of resistivity divided by T/ω_0 for fixed $\gamma = 0.2$, at various λ. The DMFT data are compared with the semiclassical formula (3) with $\Delta = [E_P(\lambda) - D]/2$ (straight lines)—see text.

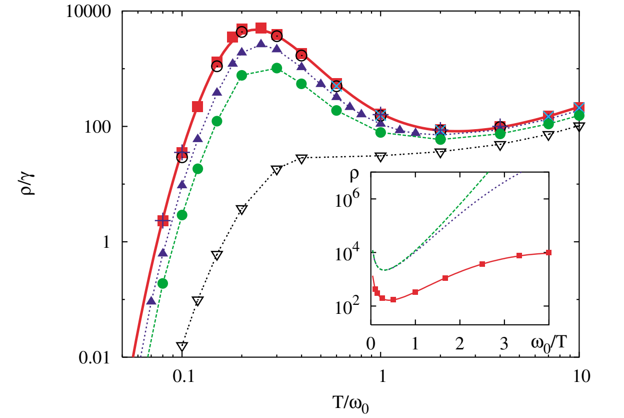

FIG. 3 (color online). Resistivity vs temperature at $\alpha^2 = 10$. The data points correspond, respectively, to $\gamma = 4$ (+), 2 (squares), 1 (×), 0.5 (open circles), 0.2 (triangles), 0.15 (filled circles), 0.1 (open triangles) and were divided by γ to evidence the nonadiabatic scaling property (5). Inset: Arrhenius plot of ρ at $\gamma = 2$, compared with the perturbative formulas—see text.

discrepancy at the highest values of λ is related to the breakdown of the condition (4)]. This suggests that the activated behavior arises from the thermal promotion from the ground state to the electron continuum, which differs from the Landau-Zener mechanism involved in the two-site model. In particular, the reduction of the activation gap by finite bandwidth effects is much stronger in the present case.

When the temperature is lowered below $T \approx \omega_0$, the quantum nature of the phonons can no longer be neglected. The lattice zero point fluctuations are then expected to induce delocalization of the trapped carriers, resulting in an enhancement of the polaron mobility. This phenomenon is a precursor of the coherent regime and has a sizable influence on the transport properties in a wide range of temperatures between the resistivity maximum T_b and the phonon frequency ω_0, which is in principle experimentally accessible. The enhancement of the mobility is signaled by a marked downturn from the Arrhenius behavior (see the right-hand side of Fig. 2) and takes place in the whole polaronic regime $\lambda \gtrsim 1$ (as we see below, this behavior is quite general and is not restricted to the adiabatic case).

In order to discuss the nonadiabatic case, where the polaron formation is ruled by the parameter α^2, the resistivity data are illustrated in Fig. 3 for different values of γ, and fixed $\alpha^2 = 10$. We again recognize the three regimes of polaron transport (coherent, activated, residual scattering). The presence of such a "peak-dip" structure is therefore independent of the adiabaticity ratio γ and *exists whenever the carriers are of polaronic nature.* At large γ, the resistivity obeys the following scaling property:

$$\rho(T, \alpha^2, \gamma) = \gamma f(T/\omega_0, \alpha^2) \tag{5}$$

as shown in Fig. 3. Although the numerical integrals involved in Eq. (2) do not lead to an analytical expression for $\rho(T)$, one can take advantage of the above scaling to derive a tractable interpolation formula valid in the nonadiabatic regime. Two limiting behaviors can be identified: the "coherent" part ρ_C at low temperatures and the "activated" part ρ_H at high temperatures. The total resistivity can be obtained by summing $\rho^{-1} = \rho_C^{-1} + \rho_H^{-1}$. (This corresponds to the assumption that the tunneling and hopping transition probabilities are additive, as obtained in Ref. [1] for $t \to 0$, and generalized in Ref. [16] using a perturbative expansion around the nonadiabatic limit.) Letting $y = T/\omega_0$, the DMFT data are well described by

$$\rho_C(y) = A\gamma\alpha^4 y e^{\alpha^2 - 1/y}, \tag{6}$$

$$\rho_H(y) = B\gamma y^{3/2} \exp[\Delta(y)/2y] \tag{7}$$

with a temperature dependent activation gap:

$$\Delta(y) = \alpha^2(1-\delta)\frac{\tanh c/y}{c/y} \tag{8}$$

and with $A = 3.82$, $B = 4.77$, $c = 0.37$, $\delta = 0.26$. Note that the form of the prefactors in Eqs. (6) and (7) is constrained by the scaling relation (5). The resulting curve for ρ is plotted in Fig. 3 for $\alpha^2 = 10$ (full line), and we have verified that it agrees with the DMFT data for any value of α^2 at large γ. The location of the resistivity maximum at large γ agrees with the value $T_b \simeq \omega_0/(2\ln\alpha^2)$ given in Ref. [5], while it fundamentally contradicts Holstein's estimate of Ref. [1]. The latter is based on the assumption that the polaron bandwidth is reduced with increasing temperature, which is a drawback of the perturbative approach (any narrow feature in the excitation spectrum, such as the polaron band, should rather get *broadened* by thermal effects).

Let us focus on the activated regime, as was done previously in the adiabatic case. The problem of polaron transport in this case is generally addressed from the "atomic" limit $\gamma \to \infty$ [1,16], treating the band parameter D as a perturbation. At temperatures $T \gtrsim \omega_0$, this yields the nonadiabatic textbook formula [1,17]

$$\rho(T) = B' \gamma^2 \alpha y^{3/2} \exp[\alpha^2/2y] \tag{9}$$

with $B' = (2^7/\pi)^{1/2}$, while at lower temperatures, the gap becomes temperature dependent and can be written in the form of Eq. (8) with $c = 0.25$ and $\delta = 0$ [see Ref. [1], Eq. (97)]. Since the expansion parameter which rules the perturbative treatment is η_2 itself, Eq. (9) should hold for $\eta_2 \ll 1$, a condition opposite to Eq. (4) [16].

The inset of Fig. 3 shows an Arrhenius plot of the resistivity in the activated regime for $\alpha^2 = 10$ and $\gamma = 2$. As in the adiabatic case, a marked downturn appears below $T \approx \omega_0$, indicating the onset of phonon quantum fluctuations. In the same inset, we have also drawn the perturbative result Eq. (9) (dashed line), and its low temperature generalization (dotted line). Compared to the DMFT results, we see that the perturbative formulas wildly overestimate both the absolute value of the resistivity and the activation energy—the slope of the curve—*within the activated regime*. Besides, a closer look at Eq. (9) shows that it does not obey the scaling formula (5). The disagreement is surprising, in view of the fact that the chosen parameters ($\eta_2 \approx 0.01$) lie well inside the range of validity of the perturbative approach.

The large discrepancy comes from the narrow-band character of the polaronic excitation spectrum. In the limit $D \to 0$, the electron states are essentially independent on different sites. This, together with the fact that the phonons are assumed to be local and dispersionless, prevents any transfer of energy between sites (the spectral function is a distribution of delta peaks) and makes the transition probabilities singular. Holstein healed the singularity by introducing *ad hoc* a sizable phonon dispersion $\Delta\omega_{\mathrm{ph}} \neq 0$, yielding Eq. (9). However, especially in narrow band materials, the optical phonons often exhibit rather weak dispersions. Obtaining a finite result when $\Delta\omega_{\mathrm{ph}} \to 0$ requires to treat the *electron* dispersion (i.e., the finite bandwidth, $D \neq 0$) nonperturbatively. [A simple calculation shows that, if $A(\nu)$ is a collection of peaks of width $\Delta\omega$, the resistivity is reduced by a factor of $\Delta\omega/\omega_0$ relative to Holstein's result. The observed scaling behavior (5) is recovered by noting that, if the broadening of the peaks is of electronic origin, then $\Delta\omega_{\mathrm{el}} \propto D$. In practical cases, where both the electrons and the phonons disperse, it is likely that the transport properties are determined by the larger of $\Delta\omega_{\mathrm{el}}, \Delta\omega_{\mathrm{ph}}$.]

In summary, we have applied the DMFT to study the transport properties of small polarons. The different behaviors expected by standard polaron theory—coherent, activated, and residual scattering regime—are recovered within a unified treatment, although notable deviations from the commonly accepted formulas are found. First of all, a broad intermediate temperature regime emerges, regardless of the adiabaticity parameter γ, where the resistivity is still semiconductinglike, but is strongly influenced by phonon quantum fluctuations. This regime, comprised between the resistivity maximum T_b and the phonon frequency ω_0, should be easily detected experimentally as a downturn in the Arrhenius plots of the resistivity. Second, in the nonadiabatic regime, the DMFT results obey a simple scaling property, which is not compatible with the standard polaronic formulas of Holstein. Accordingly, large discrepancies arise in the predicted resistivity, which could quantitatively modify our interpretation of the experiments.

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