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Simone Fratini, S. Ciuchi. Dynamical mean field theory of small polaron transport. 2003. hal-00000442

HAL Id: hal-00000442

<https://hal.science/hal-00000442>

Preprint submitted on 24 Jun 2003

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Dynamical mean field theory of small polaron transport

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(Dated: June 24, 2003)

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 formulae are found. The scaling properties of the resistivity are analysed, and a simple interpolation formula is proposed in the nonadiabatic regime.

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:

$$\rho = \rho_0 e^{\Delta/k_B T} \quad (1)$$

where the prefactor ρ_0 is weakly temperature dependent. Contrary to what happens in semiconductors, the activated behaviour 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}

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

was introduced in the late fifties to study such a behaviour, 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 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 reviews³. 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 "metallic-like" resistivity^{3,4,5} $\rho \propto (T/W) \exp(-\hbar\omega_0/k_B T)$. 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 characterised 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 to⁶ $\rho \sim T^{3/2}$.

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 narrow-band solids. However, strong deviations from pure Arrhenius behaviour are often reported⁷, possibly indicating the onset of the coherent transport regime. In some cases, the low temperature exponential law described above has also been identified unambiguously⁸.

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 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 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.¹⁰, where an analytical expression for the spectral function $A_e(\nu)$ was given

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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 non adiabatic case^{10,11}.

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,¹² 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)¹⁰. The resistivity at low (but finite) density can then be derived through an expansion in the fugacity⁹, yielding

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

In the above formula, the denominator is the current-current correlation function, and the numerator is proportional 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.¹⁷ The constant $\zeta = e^2 a^2 / \hbar v$ has the dimensions of resistivity, a being the lattice spacing, v the volume of the unit cell. In the following, we shall implicitly report the results for the dimensionless product $\rho x \zeta$, which is inversely proportional to the drift mobility, and assume $\hbar = k_B = 1$.

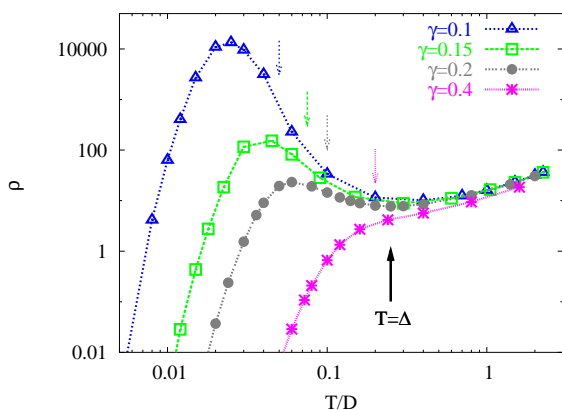


FIG. 1: Resistivity vs. temperature at $\lambda = 1.5$, for different values of the adiabaticity parameter. Short arrows mark the temperature $T = \omega_0/2$ below which phonon quantum effects acquire importance. The long upward arrow is the gap $T = \Delta$.

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.^{10,11}

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 $\gamma \rightarrow 0$, the problem is generally studied within a simplified “two-site” molecular model^{1,13}, 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 behavior³

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

This semi-classical description holds provided that the transitions to higher (antibonding) electronic states can be neglected, which corresponds to^{1,14}

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

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

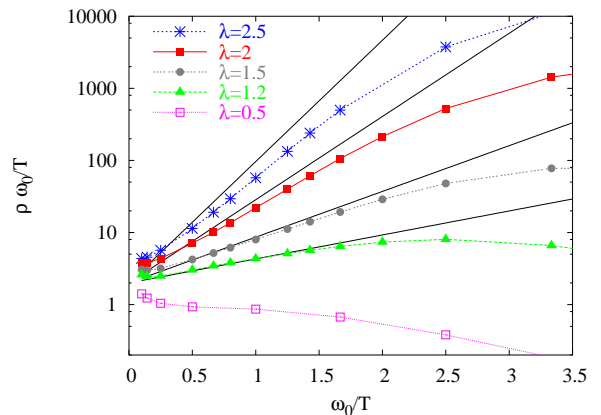


FIG. 2: Arrhenius plots of resistivity divided by T/ω_0 for fixed $\gamma = 0.2$, at various λ . The DMFT data are compared with the semi-classical formula (3) with $\Delta = [E_P(\lambda) - D]/2$ (straight lines) — see text.

To illustrate the accuracy of the semi-classical 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

$E_P(\lambda) = D\lambda + D/(8\lambda) + \dots$ is the adiabatic polaron energy, calculated e.g. in ref.¹⁰ [see Fig. 2, full lines — the slight 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 sizeable 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 shall see below, this behavior is quite general and is not restricted to the adiabatic case).

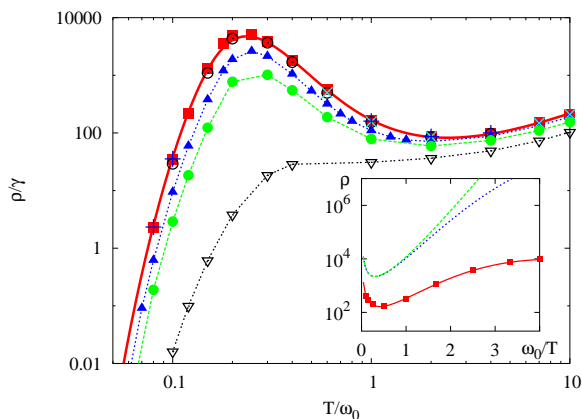


FIG. 3: Resistivity vs. temperature at $\alpha^2 = 10$. The data points correspond respectively to $\gamma = 4$ (+), 2 (squares), 1 (x), 0.5 (open circles), 0.2 (triangles), 0.15 (filled circles), 0.1 (open triangles) and were divided by γ to evidence the nonadiabatic scaling property (5). Inset: Arrhenius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

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

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

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. To do so, we choose to separate arbitrarily the “coherent” part ρ_C and the “activated” part ρ_H by *enforcing* Matthiessen’s rule $\rho^{-1} = \rho_C^{-1} + \rho_H^{-1}$. Introducing $y = T/\omega_0$, the DMFT data are well described by

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

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

with a temperature dependent activation gap

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

and with $A = 3.82$, $B = 4.77$, $c = 0.37$, $\delta = 0.26$.¹⁷ Note that the form of the prefactors in eqs. (6)-(7) is constrained by the scaling relation (5). The resulting curve for ρ is plotted in Fig. 3 for $\alpha^2 = 10$ (full line).¹⁸

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 $\gamma \rightarrow \infty$,^{1,14} treating the band parameter D as a perturbation. This yields the nonadiabatic textbook formula^{1,15}

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

valid at $T \gtrsim \omega_0$, with $B' = (2^7/\pi)^{1/2}$ [a generalization to lower temperatures was given in ref.¹, eq. (97)]. Since the effective expansion parameter which rules the perturbative treatment is η_2 itself, eq. (9) holds for $\eta_2 \ll 1$, a condition opposite to eq. (4).^{14,19}

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. We infer that this ubiquitous phenomenon is deeply related to the occurrence of a resistivity maximum — i.e. of the very presence of small polarons — as it takes place both in the adiabatic and nonadiabatic regimes.

In the same inset, we have also drawn the resistivity given by eq. (9) (dashed line), and its low temperature generalization (dotted line). Compared to the DMFT results, we see that the perturbative formulae 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 $D \rightarrow 0$, 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 sizeable phonon dispersion $\Delta\omega_{ph} \neq 0$, yielding eq. (9). However, especially in narrow band materials, the optical phonons often exhibit rather weak dispersions. Obtaining a finite result when $\Delta\omega_{ph} \rightarrow 0$ requires to treat the *electron* dispersion (i.e. the finite bandwidth, $D \neq 0$) nonperturbatively. This can be achieved by the DMFT, as is testified by the finiteness of our results.²⁰

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 formulae are found. First of all, a broad intermediate temperature regime emerges, regardless of the adiabaticity parameter γ , where the resistivity is still semiconducting-like, 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. Secondly, in the nonadiabatic regime, the DMFT results obey a simple scaling property, which is not compatible with the standard polaronic formulae of Holstein. Accordingly, large quantitative discrepancies arise in the predicted resistivity, which could result in wrong estimates when extracting microscopic parameters from the experiments.

Finally, we would like to point out that the adiabatic procedure which was successfully applied to study polaronic systems at finite density (half filling) within the DMFT scheme,¹⁶ is not suitable at low densities, where it is not able to reproduce the correct activated behavior (3). The reason is that the cooperative mechanism which leads to polaron localization at half filling — the presence of a bimodally distributed random field — ceases to be effective at low electron densities, where the phonons are *not* renormalized. In the latter case, polaron localization is a single-particle effect, the carriers being self-trapped in their own local deformation. The relative importance of the two different mechanisms of polaron trapping can be modulated by the density. The existence of an experimentally observable density crossover in polaronic systems will be the subject of future investigation.

We acknowledge M. Capone for a critical reading of the manuscript.

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¹⁷ We specialize here to a Bethe lattice with semicircular density of states, which is representative of three-dimensional systems, and use the prescription given in [A. Chattopadhyay *et al.*, Phys. Rev. B **61**, 10738 (2000)]. However, since the Kubo formula involves averages over the whole density of states, the results should not depend dramatically on the shape of N_ϵ .
¹⁸ The location of the resistivity maximum (for any α^2 in the nonadiabatic regime) is in good agreement with the value given in ref.⁵ $T_b \simeq \omega_0/(2 \log \alpha^2)$, 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).
¹⁹ Remarkably, at $\alpha^2 = 10$, the scaling property (5) holds for $\gamma \gtrsim 0.5$ which, taking $T \approx \omega_0$, corresponds to $\eta_2 \lesssim 1$. Note, however, that the low temperature coherent regime is not ruled by eq. (4), which relies on the analysis of incoherent hopping processes.
²⁰ 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 broaden-

ing of the peaks is of electronic origin, then $\Delta\omega_{el} \propto D$. In practical cases, where both the electrons and the phonons disperse, it is likely that the transport properties are de-

termined by the larger of $\Delta\omega_{el}, \Delta\omega_{ph}$.