Non Metallic Transport in Molecular Solids versus Dimensionality

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Path integral techniques and Green functions formalism are applied to study the (time) temperature dependent scattering of a polaronic quasiparticle by a local anharmonic potential in a bath of diatomic molecules. The electrical resistivity has been computed in any molecular lattice dimensionality for different values of electron-phonon coupling and intermolecular forces. A broad resistivity peak with non metallic behavior at temperatures larger than $\simeq 100K$ is predicted by the model for sufficiently strong polaron-local potential coupling strengths. This peculiar behavior, ascribed to purely structural effects, is favoured in low dimensionality.

**Keywords**: Path Integrals, Polarons, Anharmonicity

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I. INTRODUCTION

A considerable amount of theoretical work has been devoted to investigate the condition of polaron formation and the polaronic features in real materials. While there is growing evidence that fundamental properties such as the polaron size, effective mass and ground state energy are essentially similar in any dimension, it is still unclear to which extent transport properties in polaronic systems (markedly the electrical resistivity behavior versus temperature) depend on the lattice structure and dimensionality. Besides being conceptually relevant this question has become actual in connection with the discovery of unusual effects in underdoped high $T_c$ superconductors. Infact the presence of local lattice distortions with polaron formation has been envisaged in the high $T_c$ systems and signs of enhanced anharmonicity for some in- and out of plane oxygen modes have been detected in underdoped compounds by several groups. In this paper we focus on the problem of the interaction between a polaronic quasiparticle moving through a molecular lattice and a local structural instability modelled by a double well potential in its two state configuration. In particular we derive the effective interaction strenghts arising from this peculiar scattering mechanism and we study the effects on the electrical resistivity both of the intermolecular forces and of the lattice dimensionality.

II. THE MODEL

Our analysis starts from the following $\tau$ dependent Hamiltonian where $\tau$ is the time which scales as an inverse temperature according to the Matsubara Green’s function formalism:

$$H_0(\tau) = \bar{\epsilon}(g)\hat{c}^\dagger(\tau)\hat{c}(\tau) + \sum_{q} \omega_q a_q^\dagger(\tau)a_q(\tau) + H_{TLS}(\tau)$$
\[
\begin{pmatrix}
H_{TLS}(\tau) = \begin{pmatrix}
0 & \lambda Q(\tau) \\
\lambda Q(\tau) & 0
\end{pmatrix}
\end{pmatrix}
\]
\[
H_{int}(\tau) = -2\lambda Q(\tau)\hat{c}(\tau)\hat{c}(\tau)
\]
\[
Q(\tau) = -Q_o + 2Q_o \tau_o (\tau - t_i).
\]

\[\text{(0.1)}\]

\(H_0(\tau)\) is the free Hamiltonian made of: a) a polaron created (destroyed) by \(\hat{c}(\tau)\) in an energy band \(\epsilon(g)\) whose width decreases exponentially by increasing the strength of the overall electron-phonon coupling constant \(g\), \(\epsilon(g) = D\exp(-g^2)\); b) a lattice of diatomic molecules whose phonon frequencies \(\omega_q\) are derived analytically for a linear chain, a square lattice and a simple cubic lattice through a force constant model; c) a local anharmonic potential shaped by a Two Level System (TLS) in its symmetric ground state configuration. \(Q(\tau)\) is the one dimensional space-time hopping path followed by the atom which moves between two equilibrium positions located at \(\pm Q_o\). \(\tau_o\) is the bare hopping time between the two minima of the TLS and \(t_i\) is the instant at which the \(i\)th-hop takes place. One atomic path is characterized by the number \(2n\) of hops, by the set of \(t_i\) \((0 < i \leq 2n)\) and by \(\tau_o\).

In the last of eqs.(1), we assume that the class of \(\tau\)-linear paths yields the main contribution to the full partition function of the interacting system. The closure condition on the path is given by: \((2n - 1)\tau_s + 2n\tau_0 = \beta\), where \(\beta\) is the inverse temperature and \(\tau_s\) is the time one atom is sitting in a well. The interaction is described by \(H_{int}(\tau)\) with \(\lambda\) being the coupling strength between TLS and polaron, \(\lambda Q(\tau)\) is the renormalized (versus time) tunneling energy which allows one to introduce the \(\tau\) dependence in the interacting Hamiltonian [15].

Following a method previously developed [16] in the study of the Kondo problem, we multiply \(\lambda Q(\tau)\) by a fictitious coupling constant \(s\) \((0 \leq s \leq 1)\) and, by differentiating with respect to \(s\), one derives the one path contribution to the partition function of the system

\[
\ln\left(\frac{Z(n, t_i)}{Z_0}\right) = -2\lambda \int_0^1 ds \int_0^\beta d\tau Q(\tau) \lim_{\tau' \rightarrow \tau^+} G(\tau, \tau')_s
\]

\[\text{(0.2)}\]

where, \(Z_0\) is the partition function related to \(H_0\) and \(G(\tau, \tau')_s\) is the full propagator for polarons satisfying a Dyson’s equation:

\[
G(\tau, \tau')_s = G^0(\tau, \tau') + s \int_0^\beta dy G^0(\tau, y) \lambda Q(y) G(y, \tau')
\]

\[\text{(0.3)}\]

The polaronic free propagator \(G^0\) can be derived exactly in the model displayed by eqs.(1) [17]. We get the full partition function of the system by integrating over the times \(t_i\) and summing over all possible even number of hops:
\[ Z_T = Z_0 \sum_{n=0}^{\infty} \int_0^\beta \frac{dt_2}{\tau_0} \cdots \int_0^{t_2-\tau_0} \frac{dt_1}{\tau_0} \exp \left[ -\beta E(n, t_i, \tau_0) \right] \]

\[ \beta E(n, t_i, \tau_0) = L - (K^A + K^R) \sum_{i>j}^n \left( \frac{t_i - t_j}{\tau_0} \right)^2 \quad (0.4) \]

with \( E(n, t_i, \tau_0) \) being the one path atomic energy. \( L \), which is a function of the input parameters, is not essential here while the second addendum in eq.(4) is not local in time as a result of the retarded polaronic interactions between successive atomic hops in the double well potential. \( K^A \) and \( K^R \) are the one path coupling strengths containing the physics of the interacting system. \( K^A \) (negative) describes the polaron-polaron attraction mediated by the local instability and \( K^R \) (positive) is related to the repulsive scattering of the polaron by the TLS. Computation of \( E(n, t_i, \tau_0) \) and its derivative with respect to \( \tau_0 \) shows that the largest contribution to the partition function is given by the atomic path with \( \tau_0 = 0 \). The atom moving back and forth in the double well minimizes its energy if it takes the path with the highest \( \tau_0 \) value allowed by the boundary condition, that is with \( (\tau_0)_{\max} = (2nK_B T)^{-1} \). This result, which is general, provides a criterion to determine the set of dominant paths for the atom at any temperature. Then, the effective interaction strengths \( < K^A > \) and \( < K^R > \) can be obtained as a function of \( T \) by summing over \( n \) the dominant paths contributions:

\[ < K^A > = -\lambda Q_0^2 B^2 \exp(2\sum_q A_q) \sum_q A_q \omega^2_q \tilde{f} \]

\[ < K^R > = -\beta \lambda Q_0^3 B^3 \exp(3\sum_q A_q) \sum_q A_q \omega^2_q \tilde{f} \quad (0.5) \]

with: \( B = (n_F(\bar{\epsilon}) - 1)\exp(-g \sum_q \tanh(\beta \omega_q/2)) \) and \( A_q = 2g\sqrt{N_q(N_q + 1)}. \)

\( N_q \) is the phonon occupation factor and \( n_F(\bar{\epsilon}(g)) \) is the Fermi distribution for polarons. \( \tilde{f} = \sum_{n=1}^{N} (\tau_0)_{\max}^4 \) and \( N \) is the cutoff on the number of hops in a path. The particular form of \( (\tau_0)_{\max} \) suggests that many hops paths are the relevant excitations at low temperatures whereas paths with a low number of hops provide the largest contribution to the partition function at high temperatures. Since the effective couplings which determine the resistivity depend on \( (\tau_0)_{\max}^4 \), hence on \( N^{-3} \) (through \( \tilde{f} \)), a relatively small cutoff \( N \simeq 4 \) ensures numerical convergence of eqs.(5) in the whole temperature range. On the other hand the non retarded term \( L \) in eq.(4) has a slower \( 1/N \) behavior, therefore a larger cutoff should be taken at low temperatures where computation of equilibrium properties such as specific heat is strongly influenced by many hops atomic paths between the minima of the double well excitations.

The lattice Hamiltonian is made of diatomic sites whose intramolecular vibrations can favor trapping of the charge carriers [18]. The intramolecular frequency \( \omega_0 \)
largely determines the size of the lattice distortion associated with polaron formation [19] while the dispersive features of the phonon spectrum controlled by the first ($\omega_1$) and second ($\omega_2$) neighbors intermolecular couplings are essential to compute the polaron properties both in the ground state and at finite temperatures [20]. The range of the intermolecular forces is extended to the second neighbors shell since these couplings remove the phonon modes degeneracy (with respect to dimensionality) at the corners of the Brillouin zone thus permitting to estimate with accuracy the relevant contributions of high symmetry points to the momentum space summations [21].

Then the characteristic frequency $\bar{\omega}$, which we choose as the zone center frequency, is: $\bar{\omega}^2 = \omega_0^2 + z\omega_1^2 + z_{nnn}\omega_2^2$, $z$ is the coordination number and $z_{nnn}$ is the next nearest neighbors number. Hereafter we take frequencies values which are appropriate to systems with rather sizeable phonon spectra.

We turn now to compute the electrical resistivity due to the polaronic charge carrier scattering by the impurity potential with internal degree of freedom provided by the TLS. Assuming $s$ wave scattering, one gets [22,23]

$$\rho = \rho_0 \sin^2 \eta$$

$$\rho_0 = \frac{3n_s}{\pi e^2 v_F^2 (N_0/V)^2 \hbar}$$

(0.6)

where, $n_s$ is the density of TLS which act as scatterers, $v_F$ is the Fermi velocity, $V$ is the cell volume, $N_0$ is the electron density of states, $e$ is the charge and $\hbar$ is the Planck constant. The phase shift $\eta$ to the electronic wave function at the Fermi surface is related to the effective interaction strengths $<K^A>$ and $<K^R>$.

The input parameters of the model are six that is, the three molecular force constants, $g, D$ and the bare energy $\lambda Q_0$. $Q_0$ can be chosen as $\approx 0.03\AA$ consistently with reported values in the literature on TLS's which are known to exist in glassy systems [24–27], amorphous metals [28], A15 compounds and likely in some cuprate superconductors [29–31]. In these systems the origin of the TLS's is not magnetic. The bare electronic band $D$ is fixed at 0.1eV.

Let’s start by studying (Fig.1) the resistivity behavior in a 3D lattice as a function of the overall electron-phonon coupling $g$. $\lambda$ is fixed at 700meVÅ$^{-1}$ which means a bare tunneling energy of $\approx 35meV$ and the molecular force constants are $\omega_0 = 60meV$, $\omega_1 = 50meV$ and $\omega_2 = 20meV$, respectively. At low temperatures $\rho(T)$ approaches the unitary limit for any of the four $g$ values thus displaying the peculiar effect of the anharmonic potential with internal degree of freedom. At $T \approx 150K$, $\rho$ develops a $g$-dependent broad peak which softens and finally disappears by increasing $g$ in the strong coupling regime. We note that at $g > 1$ the polaron energy becomes smaller than the atomic tunneling energy hence polaron scattering by the TLS is essentially diagonal. On the contrary, in the intermediate coupling regime ($g$ in
the range 0.5 - 1) the incoming polaron can release a sufficiently high amount of energy, off diagonal scattering by the impurity potential prevails and a broad resonance peak emerges. At weaker $g$ the polaronic picture would lose any validity.

Next we turn to consider the effect of the lattice dynamics on the $\rho$ versus $T$ behavior. In Figs.2 and 3, the normalized resistivities are reported on for the 1D and 2D molecular lattices, respectively. Let’s set $g = 1$ which ensures both polaron formation and presence of the resonance peak also in 1D and 2D systems while the tunneling energy (as in Fig.1) is in the range of the values estimated by EXAFS investigations in high $T_c$ systems with double site distributions for the apical oxygen atoms $[29,32]$. By taking $\omega_0 = 60meV$ and $\omega_1 = 50meV$ we choose for the first neighbors intermolecular coupling model a characteristic phonon energy $\bar{\omega} \simeq 0.1eV$. This choice allows us: i) to treat correctly the ground state polaron properties versus dimensionality $[21]$, ii) to reproduce the sizable phonon energy of c-axis polarized mode due to apex oxygen vibrations coupled to the holes in the Cu-O planes of $YBa_2Cu_3O_{7-\delta}$. In underdoped compounds (whose c-axis resistivity displays the unusual non metallic behavior) this mode appears enhanced in energy $[33]$. Although our simple cubic lattice does not account for the details of the structural effects of $YBCO$ we are therefore in the appropriate range of parameters to capture the main features of the lattice polarons scattered by local instabilities in those compounds. The role of the second neighbors couplings is emphasized in Figs.2 and 3 by varying $\omega_2$ which however should not exceed $\omega_1$. Increasing $\omega_2$ the polaron spreads in real space and becomes lighter. Accordingly the height of the peak decreases. We also note that the strength of the intermolecular forces influences the position of the peak versus temperature which results from a balance between competing attractive and repulsive interactions (eqs.(5)). At fixed parameters, the height of the 1D peak is roughly twice as much that of the 2D one. Comparing the dotted 2D curve ($\omega_2 = 20meV$) with the corresponding case ($g = 1$ plot) in Fig.1, one sees that the 3D peak is further reduced and its absolute value lies below the residual resistivity value.

The dynamics of the TLS and its coupling to the charge carrier strongly affect the transport in any dimensionality as Figs.4 make evident. When $\lambda$ is small (i.e. below $300meV \AA^{-1}$ in 1D) polaron and TLS are weakly coupled, off diagonal scattering is unlikely to occur and the conductivity is metallic-like. Increasing $\lambda$, the atomic tunneling energy becomes of order of the polaron energy and the conditions for resonant scattering are established. Note that by varying $\lambda$ the resistivity peak does not shift versus temperature while the $\lambda$ threshold value for the appearance of metallic conductivity is larger in higher dimensionality. This means that 3D systems can sustain a larger degree of anharmonicity (than low dimensional systems) and still exhibit metallic transport properties while trapping of the charge carrier by the anharmonic impurity potential is favoured in 1D. It is this trapping
which causes the broad resistivity peak and non metallic transport at \( T \) larger than \( \simeq 100K \) in 1D.

We investigate further the effect of the molecular forces (Figs.5) by *increasing* the *intramolecular* energy and *decreasing* the *intermolecular* energies with respect to Figs.4. The 1D peak (compare Fig.5(a) and Fig.4(a)) is reduced for any \( \lambda \) value whereas the 2D and 3D peaks are here larger than in Figs. 4(b) and 4(c) respectively. The reason is the following: in 1D, the intramolecular coupling is determinant because of the low coordination number; as a result, by enhancing \( \omega_0 \) the carriers become lighter and the absolute resistivity is reduced. On the contrary in 2D and mostly in 3D, long range effects are more effective hence, the stronger \( \omega_0 \) (with respect to Figs.4) is more than balanced by the weaker \( \omega_1 \) and \( \omega_2 \); as a result, the characteristic 2D and 3D phonon frequencies are smaller, polaron becomes less mobile and the resistivity peaks are accordingly higher.

### III. Conclusion

The path integral formalism has been applied to study the time retarded interacting problem of a polaron scattered by a local anharmonic potential in a lattice of diatomic molecules. I have derived the full partition function of the system and obtained analytically the effective coupling strengths as a function of temperature. The electrical resistivity has been computed in any lattice dimensionality for a large choice of input parameters. Strength of the overall electron-phonon coupling (\( g \)), strength of the polaron-local potential coupling (\( \lambda \)) and strength of the molecular forces interfere, giving rise to a rich variety of resistivity behaviors versus temperature. As a main feature, when the conditions for resonant scattering between polaron and local double well potential are fulfilled, a broad resistivity peak shows up in the 100-150K range. However, the shape of the peak essentially depends on the dynamics of the local potential (tuned by \( \lambda \)) and, for sufficiently low atomic tunneling energies, metallic conductivity conditions are recovered. Generally, in 3D the resistivity maximum is less pronounced than in low dimensionality and, for sufficiently strong intermolecular couplings, the height of the peak lies below the residual resistivity value, being therefore hardly visible in experiments. On the other hand, in 1D and 2D, the maximum can easily become larger than the residual resistivity by a factor \( \simeq 3 - 4 \) for realistic choices of tunneling energies and lattice force constants. Then, non metallic resistivities can be expected in low dimensional polaronic systems with local lattice instabilities at least for temperatures above \( \simeq 100K \). As a final remark one should add that, while the *intramolecular* energies have been varied throughout the paper as apparently independent parameters, their values for real systems can be obtained (for instance) by a least squares fitting procedure to experimentally known
FIG. 1. Electrical Resistivity normalized to the residual ($T = 0$) resistivity for four values of electron-phonon coupling $g$. The bare TLS energy $\lambda Q_0$ is 35meV. The force constants which control the phonon spectrum in the 3D lattice are: $\omega_0 = 60\text{meV}, \omega_1 = 50\text{meV}, \omega_2 = 20\text{meV}$

FIG. 2. 1D Electrical Resistivity as a function of the second neighbors intermolecular force constant. $g = 1$. $\lambda Q_0$, $\omega_0$ and $\omega_1$ are as in Fig.1
FIG. 3. 2D Electrical Resistivity as a function of the second neighbors intermolecular force constant. $g = 1$. $\lambda Q_0$, $\omega_0$ and $\omega_1$ are as in Fig.1

FIG. 4. Electrical Resistivities for six values of the polaron-TLS coupling $\lambda$ in units $meV\AA^{-1}$. $g = 1$. $\omega_0 = 60meV$, $\omega_1 = 50meV$, $\omega_2 = 30meV$. (a) one dimension; (b) two dimensions; (c) three dimensions.
FIG. 5. Electrical Resistivities for six values of the polaron-TLS coupling $\lambda$ in units $\text{meV} \, \text{A}^{-1}$. $g = 1$, $\omega_0 = 80 \text{meV}$, $\omega_1 = 40 \text{meV}$, $\omega_2 = 20 \text{meV}$. (a) one dimension; (b) two dimensions; (c) three dimensions.

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[1] Emin D, Holstein T, (1976) Phys. Rev. Lett. 36, 323
[2] De Raedt H, Lagendijk A, (1983) Phys. Rev. B 27, 6097; ibid., (1984) 30, 1671
[3] Kabanov V V, Mashtakov O J, (1993) Phys. Rev. B 47, 6060
[4] Kipidakis G, Soukoulis C M, Economou E N, (1995) Phys. Rev. B 51, 15038
[5] de Mello E, Ranninger J, (1997) Phys. Rev. B 55, 14872
[6] Kalosakas G, Aubry S, Tsironis G P, (1998) Phys. Rev. B 58, 3094
[7] Kostur V N, Allen P B, (1997) Phys. Rev. B 56, 3105
[8] Alexandrov A S, Mott N F, (1994) Rep. Prog. Phys. 57, 1197
[9] Yarlagadda S, cond-mat/0010198
[10] Devreese J T, (1996) Encyclopedia of Applied Physics 14, 383-409 (Wiley-VCH Publishers, Inc.)
[11] Romero A H, Brown D W, Lindenberg K, (1999) Phys. Rev. B 60, 14080
[12] Voulgarakis N K, Tsironis G P, (2001) Phys. Rev. B 63, 14302
[13] see Anharmonic properties of High $T_c$ Cuprates (1995) edited by Mihailović D, Ruani G, Kaldis E, Müller K A, (World Scientific, Singapore)
[14] Palles D, Poulakis N, Liarokapis E, Conder K, Kaldis E, Müller K A, (1996) Phys. Rev. B 54, 6721
[15] Zoli M, (1991) Phys. Rev. B 44, 7163
[16] Hamann D R, (1970) Phys. Rev. B 2, 1373
[17] Zoli M, (1999) Proceedings of the 6th International Conference on: Path Integrals from $\text{peV}$ to $\text{TeV}$ - 50 Years after Feynman's paper, World Scientific Publishing p.478
[18] Holstein T, (1959) Ann. Phys. (N.Y.) 8, 325
[19] Alexandrov A S, Kornilovitch P E, (1999) Phys. Rev. Lett. 82, 807
[20] Zoli M, (2000) J.Phys.:Condens. Matter 12, 2783
[21] Zoli M, (2000) Phys. Rev. B 61, 14523
[22] Mahan G D, (1981) Many Particle Physics, Plenum Press, N Y
[23] Yu C C, Anderson P W, (1984) Phys. Rev. B 29, 6165
[24] Anderson P W, Halperin B I, Varma C H, (1971) Philos. Mag. 25, 1
[25] Philipps W A, (1972) J.Low Temp.Phys. 7, 351
[26] Fessatidis V, Mancini J D, Massano W J, Bowen S P, (2000) Phys. Rev. B 61, 3184
[27] Zawadowski A, von Delft J, Ralph D C, (1999) Phys. Rev. Lett. 83, 2632
[28] Cochrane R V, Harris R, Strom-Olsen J, Zuckerman M J, (1975) Phys. Rev. Lett. 35, 676
[29] Mustre de Leon J, Conradson S D, Batistic I, Bishop A R, (1991) Phys. Rev. B 44, 2422
[30] Saiko A P, Gusakov V E, (1999) JETP 89, 92
[31] Menuschenkov A P, Klementev K V, (2000) J.Phys.:Condens.Matter 12, 3767
[32] Haskel D, Stern E A, Hinks D G, Mitchell A W, Jorgensen J D, (1997) Phys. Rev. B 56, R521
[33] Timusk T, Homes C C, Reichardt W in [3] p.171
[34] Zoli M, (1991) J.Phys.:Condens. Matter 3, 6249
\[ \rho(T)/\rho(T=0) \]
\( \rho(T)/\rho(T=0) \)

![Graph showing the temperature dependence of density ratio](image)
$\rho(T)/\rho(T=0)$
