Generalized Adiabatic Polaron Hopping: Meyer-Neldel Compensation and Poole-Frenkel Behavior

David Emin

Department of Physics and Astronomy, University of New Mexico Albuquerque, New Mexico USA 87131
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The commonly employed adiabatic treatment of polaron hopping is extended to treat the continuous alteration of a carrier wave function with the atoms' movements and a carrier's long-range interaction with a polar surrounding. These features, respectively, introduce carrier-induced softening of the atoms' vibrations and a hopping activation energy that depends on hopping distance. The Meyer-Neldel compensation effect results from carrier-induced softening of vibrations. Poole-Frenkel behavior emerges for electric-field driven polaron hopping in ionic and polar media.

Polaron hopping, characterized by a very low thermally activated mobility, has been observed in crystals as well as in many disordered materials [1]. Nonetheless, several widely observed transport phenomena in these materials have not been explained as being general features of polaron hopping. Here the Meyer-Neldel compensation rule [2] and Poole-Frenkel behavior [3] are shown to emerge from an extended treatment of adiabatic polaron hopping.

The Meyer-Neldel compensation rule states that the temperature-independent prefactor of an Arrhenius diffusion constant increases exponentially with the activation energy [2]. This effect acts to compensate for the decrease of the temperature-dependent factor with increasing activation energy: $D \propto \exp(E/\kappa T_0) \exp(-E/\kappa T)$, where E is the hopping activation energy, κ is the Boltzmann constant, and T and T_0 are the ambient and Meyer-Neldel temperatures, respectively. Thus, the diffusion constant, $D \propto \exp[-(E/\kappa)(1/T - 1/T_0)]$, falls or rises with increasing activation energy depending on whether $T < T_0$ or $T > T_0$. The Meyer-Neldel-compensation effect is observed for thermally activated hopping diffusion. This paper addresses the emergence of the Meyer-Neldel effect for electronic polaron hopping.

Poole-Frenkel behavior refers to the activation energy of the electrical conductivity or drift mobility decreasing in proportion to the square root of the electric-field strength F. Frenkel showed that such behavior results from an applied electric field enhancing the classical (over-the-barrier) carrier emission from an isolated Coulomb trap (e.g., donor) [3]. However, quantum-mechanical electron tunneling dominates classical carrier emission at high fields to yield an emission rate that rises exponentially with the square of the electric-field strength, F^2 [4]. Nonetheless, the electrical conductivity and drift mobility are observed to increase exponentially with $F^{1/2}$ at very high fields in many ionic and polar solids. This Letter shows how Poole-Frenkel behavior emerges for polaron hopping in such materials.

Polaron hopping is usually described as a thermally assisted transition of a charge carrier between two localized electronic states [1,5–7]. When the temperature is high enough for atomic motion to be treated as classical (typically $\kappa T > h\nu/3$, where ν is the characteristic phonon frequency) [7], the thermally activated polaron hopping rate becomes Arrhenius. Then, as depicted in Fig. 1, a hop can occur when, amidst atoms' thermal vibrations, the energies of the initial and final electronic states occasionally come into coincidence with one another. The hopping activation energy is the minimum energy required to achieve such a coincidence.

Original treatments of polaron hopping ignore carrier-induced shifts of the stiffnesses of atoms' vibrations [5,6]. Nonetheless, the full adiabatic theory shows that electrons' response to the motion of atoms generally alters the stiffnesses of their vibrations and thereby affects polaron hopping [8]. In particular, the lowering of atomic stiffness
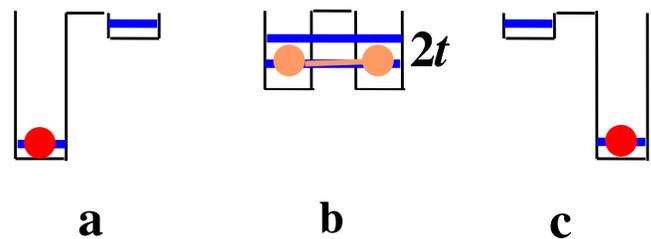

FIG. 1 (color online). (a) Displacements of atoms' equilibrium positions produce a potential well for a carrier (red dot) that localizes it at a site. (b) Amidst atoms' vibrations a coincidence configuration is occasionally achieved. The carrier is then shared between sites (paired orange dots). Two coincident energy levels are split by twice the electronic transfer energy t. Carrier-induced softening occurs as the intersite motion of a charge carrier reduces the stiffness of the associated atomic vibrations. (c) A hop is completed when a carrier settles on another site as atoms' vibration energy is dissipated to surrounding atoms. The thickness of the (blue) bars representing carrier energy levels indicates their variations due to thermal atomic vibrations.

associated with a hop is shown to produce Meyer-Neldel compensation. In addition, an applied electric field is shown to team with the long-range (Fröhlich) electron-phonon interaction [9] to produce Poole-Frenkel behavior for polaron hopping in ionic and polar media.

Adiabatic hopping occurs when the electron-transfer energy t is large enough so as to not limit a carrier's intersite hopping [1]. In these instances a carrier readily adjusts to changing atomic positions to effect a hop. The adiabatic jump rate in the Arrhenius hopping regime is

$$
\begin{aligned}
R_{\text{adiabatic}} &= \nu \exp[-(F_c - F_g)/\kappa T] \\
&= \nu \exp[-(F_c^{\text{vib}} - F_g^{\text{vib}})/\kappa T] \exp(-E/\kappa T), \quad (1)
\end{aligned}
$$

where F_g and F_c represent the free-energies with a charge carrier in its single-site ground-state and with the carrier shared between the sites of its minimum-energy-coincidence configuration, respectively. Similarly, the free-energy of atoms' vibrations in the electronic ground state and in the minimum-energy-coincidence configurations are denoted by F_g^{vib} and F_c^{vib}. The activation energy is the difference between the energies of these two configurations. For a three-dimensional medium it is given by [8]:

$$
E \cong \frac{V_S}{2R^3} + \frac{V_L}{2}\left(\frac{1}{R} - \frac{1}{\sqrt{R^2 + S^2}}\right). \quad (2)
$$

Here V_S and V_L respectively denote the combinations of material constants that govern the strengths of the short-range (deformation-potential-like) and long-range electron-phonon interactions while S measures the separation between the centroids of the two localized states of radii R involved in the hop, $S > 2R$ (both expressed in units of an interatomic separation a). The lowering of the activation energy from a carrier's spreading out over two sites, $-t$, is neglected in Eq. (2) since it is often ignorable for stable polaron formation: $t \ll (V_S/R^3 + V_L/R)/(1 + 1/R^2)$ [8,10,11]. The contribution to the activation energy from the short-range interaction does not depend on separation S since the ground-state and coincidence-configuration energies only depend on the volume contacted by the self-trapped carrier [5,8]. By contrast, the contribution to the activation energy arising from the long-range electron-phonon interaction falls with decreasing separation S as the net Coulomb interaction of a coincident-carrier with surrounding ions approaches that of a carrier in its ground state [8,12]. Thus, the long-range contribution to the activation energy vanishes as $S \to 0$ and approaches $V_L/2R$ as $S \to \infty$.

It is now shown that the Meyer-Neldel compensation rule emerges upon extending the treatment of polaron hopping to include the effects of carrier-induced softening produced by a carrier passing through a coincidence configuration. Carrier-induced softening occurs because a carrier's wave function changes as atoms move [13]. As such, carrier-induced softening is especially large at a coinci-

dence configuration since a carrier shifts between sites when its energy is changed by only the intersite tunnel splitting $2t$ (illustrated in Fig. 1). Thus the lowering of the free-energy of atoms' vibrations due to carrier-induced softening at a coincidence is much larger than that of the ground state, discussed in Ref. [8].

Carrier-induced softening at a coincidence is found by expanding the adiabatic energy to second-order in atomic displacements about the coincidence point [8,13]. Ultimately, the term in the exponential of Eq. (1) becomes

$$
\begin{aligned}
&\frac{F_g^{\text{vib}} - F_c^{\text{vib}}}{\kappa T} \\
&\cong \frac{\int dr[\Psi_+^*(r)\Psi_-(r)]\int dr'[\Psi_+^*(r')\Psi_-(r')]^* I(r - r')}{t}, \quad (3)
\end{aligned}
$$

where the general expression for the lowering of classical vibrations' free energy due to carrier-induced softening, the final term of Eq. (16) of Ref. [8], is applied to a coincidence with $\Psi_\pm(r)$ representing the even and odd pair of electronic wave functions of the two states of a coincidence. The electron-phonon interaction function $I(r - r')$ is defined in Eq. (19) of Ref. [8].

Expressing these two wave functions as combinations of local electronic states,

$$
\Psi_\pm(r) = \frac{\Phi(r) \pm \Phi(r - s)}{\sqrt{2}}, \quad (4)
$$

enables the free-energy to be rewritten as

$$
\begin{aligned}
&\frac{F_g^{\text{vib}} - F_c^{\text{vib}}}{\kappa T} \\
&= \frac{\int dr|\Phi(r)|^2 \int dr'|\Phi(r')|^2[I(r - r') - I(r - r' - s)]}{2t}.
\end{aligned}
\quad (5)
$$

It is expeditious to now note that integrals involving the local electronic states and the electron-phonon interaction function provide definitions of the energies involved in the hopping activation energy given in Eq. (2) [8]:

$$
\int dr|\Phi(r)|^2 \int dr'|\Phi(r')|^2 I(r - r') \equiv \frac{V_S}{R^3} + \frac{V_L}{R}, \quad (6)
$$

and

$$
\int dr|\Phi(r)|^2 \int dr'|\Phi(r')|^2 I(r - r' - s) \equiv \frac{V_L}{\sqrt{R^2 + S^2}}. \quad (7)
$$

Introducing the relations contained in Eqs. (6) and (7) into Eq. (5) yields

$$
\frac{F_g^{\text{vib}} - F_c^{\text{vib}}}{\kappa T} = \frac{E}{t}, \quad (8)
$$

where E is defined by Eq. (2).

Incorporating Eq. (8) into Eq. (1) gives the Meyer-Neldel result with $T_0 \equiv t/\kappa$:

$$R_{\text{adiabatic}} = \nu \exp\left[-\frac{E}{\kappa}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]. \qquad (9)$$

The adiabatic approach requires that $E > t$, $\kappa T > h\nu/3$. It fails when t is so small that the hopping becomes non-adiabatic $E > \kappa T > h\nu/3 > t$. Prior adiabatic treatments focus on the vanishing of nonadiabatic transitions with increasing t while implicitly ignoring softening [5,6].

To provide a more restrictive but clearer physical picture of the origin of the Meyer-Neldel effect, consider the double-well adiabatic potential for hopping between two sites with the short-range electron-phonon interaction of Holstein's Molecular-Crystal Model [6]. The adiabatic potential as a function of the difference between the two local deformation parameters $\eta\sqrt{2}$ is $V = k\eta^2/2 - (2kE\eta^2 + t^2)^{1/2}$. This potential consists of two near-harmonic wells of depth $\approx E$ centered at $\eta \approx \pm(2E/k)^{1/2}$ separated by a barrier centered at $\eta = 0$. A thermally activated hop corresponds to the passage of a particle over the barrier. With a carrier confined to a site, atomic vibrations correspond to a particle moving near a minimum characterized by the stiffness $\partial^2 V/\partial\eta^2 \approx k$. By contrast, the hopping of a carrier corresponds to the passage of the particle over the barrier with negative curvature $\approx -k(2E/t - 1)$. Thus the activation-energy E determines the magnitude of the negative curvature and the softening it produces. The reduction of atomic vibrations' free-energy caused by an excited state's experiencing the barrier-region's negative curvature is $-\kappa T(\Delta k/2k) = \kappa T(E/t)$, yielding Eq. (8).

In the presence of an applied electric field the activation energy, the minimum energy required to produce a coincidence, is reduced to [7]

$$E_F(S) = \frac{[4E(S) - qFaS\cos\theta]^2}{16E(S)}, \qquad (10)$$

where q is a carrier's charge, F is the magnitude of the electric-field driving the hop, and θ is the angle between the applied field and the jump direction. The S dependence of $E(S)$, given in Eq. (2), results from the long-range electron-phonon interaction that characterizes ionic and polar materials. Thus, the applied electric field and the long-range electron-phonon interaction act in tandem to produce a range of activation energies corresponding to a distribution of potential sites for adiabatic hops.

In the absence of an applied field $E(S)$ rises toward its maximum as $S \to \infty$. Application of an electric field shifts the maximum for field-assisted hops, those for which $\cos\theta > 0$, to a finite value of S. The condition governing the maximum is found by analyzing the requirement that $\partial E_F(S)/\partial S = 0$:

$$\frac{\partial E(S)}{\partial S} = \frac{qFa\cos\theta/2}{[1 + \frac{qFaS\cos\theta}{4E(S)}]} \cong \frac{qFa\cos\theta}{2}, \qquad (11)$$

where typically $4E(S) \gg qFaS\cos\theta$. Evaluation of $\partial E(S)/\partial S$ from Eq. (2) yields

$$\frac{\partial E(S)}{\partial S} = \frac{V_L S/2}{(R^2 + S^2)^{3/2}} \cong \frac{V_L}{2S^2}, \qquad (12)$$

for $S \gg R$. Equations (11) and (12) show that the activation energy for a hop in the field direction, $\cos\theta > 0$, peaks at $S_m \equiv \sqrt{V_L/qFa\cos\theta}$. Expressing $E_F(S)$ as a Taylor series expanded about S_m, evaluating the associated derivatives, and then summing the series yields

$$E_F(S) \cong E(\infty) - \sqrt{V_L qFa\cos\theta}\left[1 + \frac{(S - S_m)^2}{2SS_m}\right]. \qquad (13)$$

Poole-Frenkel behavior occurs when upon increasing the electric field, the broad peak centered on S_m comes to encompass the system's characteristic hopping distances, $(S - S_m)^2 < 2SS_m$. Jump rates then become

$$R(F, \theta) \propto \nu \exp\left[-\frac{E(\infty) - \sqrt{V_L qFa\cos\theta}}{\kappa}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]. \qquad (14)$$

These rates imbue high-field-driven polaron hopping with Poole-Frenkel behavior in that they increase exponentially with the square root of the electric-field strength.

Meyer-Neldel and Poole-Frenkel behaviors are widely observed. For example, time-of-flight measurements of the drift mobility are in accord with Eq. (14) for polaron hopping among a high density of polar molecular dopants imbedded in polymers [14,15]. Consistent with the attribution $T_0 \equiv t/\kappa$, T_0 falls from 700 to 300 K as the average intermolecular separation is increased from 1 to 2 nm. Furthermore, with $V_L \equiv (q^2/a)(1/\varepsilon_\infty - 1/\varepsilon_0)$ and $\varepsilon_0 \gg \varepsilon_\infty \approx 2.5$ for a polar molecular solid [8], the constant governing the polaron contribution to Poole-Frenkel behavior, $(V_L qa)^{1/2}/\kappa \approx 3$ K(cm/V)$^{1/2}$, is close to the observed value, 4 K(cm/V)$^{1/2}$ [14,15]. In addition, $E(\infty) \approx V_L/2R = 0.6$ eV agrees with the observed value for a molecular radius of 0.5 nm.

In summary, Meyer-Neldel compensation emerges for adiabatic polaron hopping when account is taken of the increase of the entropy of atoms' vibrations produced by the phonon softening (proportional to E) that accompanies a hop. Poole-Frenkel behavior results for electric-field enhanced hopping upon inclusion of the long-range electron-phonon interaction characteristic of ionic and polar materials. Both of these widely observed effects emerge from an expanded treatment of adiabatic polaron hopping.

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