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Hopping conduction in high electric fields: Three issues

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ABSTRACT

Three issues concerning phonon-assisted hopping in molecularly doped polymers are considered. The first issue is whether Arrhenius jump rates in the vicinity of room temperature arise from single-phonon or small-polaronic hopping. It is concluded that Arrhenius hopping only occurs above low temperatures through small-polaronic hopping. Second, hopping in molecularly doped polymers is compared with small-polaronic hopping of other systems. Small-polaronic hopping typically occurs between similar chemical structures whose energies are relatively insensitive to their surroundings. Thus, disorder energies experienced by carriers are often modest, values of several hundredths of an eV are common. Nonetheless, the effects of large electric fields on carrier mobilities differ significantly among disordered systems. Data reported for molecularly doped polymers is unlike that for either transition-metal-oxide or chalcogenide glasses. In no case is high-field transport well understood. Finally, I stress that steady-state flow is driven by differences in sites' quasielectrochemical potentials (QECPs). With disorder, differences of QECPs are not simply related to the driving emf. Solution of the (nonlinear) stochastic equations for the QECPs shows that bottlenecks produced by disorder result in nonohmic conduction. Solving the linearized stochastic (disordered resistor network) equations underestimates bottleneck effects. Linearization is inappropriate when intersite differences in the QECPs exceed κT.

Keywords: small polarons, nonohmic conduction, phonon-assisted hopping, disordered semiconductors, multiphonon hopping, molecularly doped polymers

2. INTRODUCTION

Early studies of electronic transport in solids viewed electron carriers as always moving freely and being only occasionally scattered by a defect, impurity or by motion of a solid's atoms (phonon scattering). However, about forty years ago it became evident that situations occur in which this view of electronic motion fails to apply. In particular, cases were discovered in which mobilities are extremely low, << 1 cm^2/V-sec, and rise with increasing temperature. These circumstances are described by a complementary picture in which electronic carriers are each usually confined at a site and only occasionally move to another nearby site. This type of transport is termed hopping transport.

Carriers execute hopping transport in some crystals. Holes in alkali halides (e.g., KCl) were found to move very slowly with rates that increase with increasing temperature. A localized hole in KCl occupies a severely localized state that bridges a pair of adjacent Cl anions that are displaced toward one another from their carrier-free equilibrium positions. Carriers in some transition-metal oxide crystals (e.g., LaMnO$_3$ and MnO) were also found to have mobilities that are very low and rise with rising

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temperature. In these instances carriers are thought to move been metal cations about which surrounding oxygen ions relax. Hopping-type transport was also found to occur between the molecules of some molecular crystals (e.g., sulphur). In all cases mobilities remain very low, << 1 cm^2/V-sec even at the highest temperatures measured (usually >> 300 K). At "high enough" temperatures, usually > 100-200 K, the hopping rates are Arrhenius with activation energies between about 0.1 and 1.0 eV.

Although hopping is found in some crystals, it is commonly observed in disordered materials. For example, transition-metal oxide glasses and chalcogenide glasses manifest hopping transport at temperatures up to the glass transition temperature. As in crystals, the hopping at high enough temperatures is Arrhenius with hopping activation energies being between a few tenths of an electron volt and an electron volt.

Hopping conduction is also found in another type of system, doped semiconductors. For example, silicon can be doped with very low densities (10^{15} cm^{-3}) of both shallow donors and shallow acceptors, e.g., phosphorus and boron, respectively. Electrons find it energetically favorable to leave donors and reside on acceptors. The donor sites that yield electrons become positively charged and the acceptor sites that receive electrons become negatively charged. If there are more donor sites than acceptor sites, some of the donors will retain their electrons and remain neutral. When the density of partially occupied donors is low enough, carriers hop between donors with very low mobilities that rise with increasing temperature. This hopping impurity conduction has activation energies between 10^{-4} and 10^{-3} eV and is observed when the temperature is low enough (<< 10 K). At higher temperatures carriers readily free themselves from the shallow impurities and move through the solid with high itinerant-type mobilities.

A theory of single-phonon-assisted hopping was developed by Miller and Abrahams to describe the low-temperature hopping of carriers between shallow impurites of doped semiconductors.[1] They also initiated study of the steady-state transport of carriers amongst sites that are positionally and energetically disordered. In particular, they approximated the set of master equations that describe hopping transport by a circuit of ohmic resistors whose dispersion of values depicts the inequivalence of different hops.

In Section 3 of this paper I describe why the single-phonon jump rate calculated by Miller and Abrahams in their studies of low-temperature shallow-impurity hopping is inappropriate to "high temperature" hopping. In Section 3, I also describe the properties of the small-polaronic hopping that typifies hopping observed above cyrogenic temperatures. In Section 4 results of extensive studies of high-temperature hopping in many systems are summarized. It is suggested that mobilities measured in small electric fields are often insensitive to disorder. By contast, the high-field mobilities may be sensitive to the stochastic processes via which carriers are driven to hop through disordered material by an applied electric field. Section 5 considers the interplay between high-field transport and disorder. By means of an illustrative example, it is shown that the resistance-network model of hopping in disordered materials underestimates the gradients of electrochemical potential that develop when carriers are driven to hop through tortuous paths of a disordered material. This underestimation becomes increasingly significant as the EMFs experienced by a carrier are raised above the thermal energy, κT. The neglected effect contributes an electric-field dependence to the steady-state carrier mobility. The resistance-network approach is seen to fail at low temperatures, with large disorder and with high electric fields.

3. PHONON-ASSISTED JUMP RATES

Our discussion of hopping transport begins by describing the mechanism by which a carrier executes a phonon-assisted hop.[2-4] First, consider a carrier severely localized about a site in a solid. The energy of the localized carrier depends on the positions of the surrounding atoms. Thus, as the positions of atoms are altered, so the energy of the localized electron is changed.

A transition of an electron between two localized states of different energy can occur when the pattern of atomic displacements about the two sites changes so as to bring the two electronic states into degeneracy with one another. Such transitions conserve energy as the net change of vibrational energy in the transition compensates the change of electronic energy. Such transitions are termed "phonon-assisted."

Since atoms are generally not static, the degeneracy of electronic levels associated with a phonon-assisted electronic transition is transitory.[2-4] To hop between sites a carrier must move between sites within the duration of the ephemeral degeneracy (a time interval determined by the Heisenberg uncertainty principle that necessarily vanishes as $\hbar$ vanishes). The time required for electrons to move between two sites is $\hbar/t$, where t is the electronic transfer energy associated with the two sites. If this electronic transfer time is shorter than the duration of an electronic degeneracy ("coincidence event"), carriers can usually follow the atomic motion and negotiate a hop. In these instances electronic transfer is not the rate-limiting portion of the jump process. Such hops are termed "adiabatic."

However, when the electronic transfer energy linking the two sites becomes very small (typically less than a phonon energy), the electron's intersite motion is too slow for it to reliably complete a hop. The phonon-assisted jump rate is then limited by the smallness of the electronic transfer energy. In particular, the rate for such a "nonadiabatic" phonon-assisted hop is reduced from its adiabatic value by a factor that is proportional to the square of the electronic transfer energy. This effect tends to limit hops to sites that are not too distant from one another.

In the "semiclassical regime," where the atomic motion may be treated as classical, the rates for such transitions are thermally activated with an activation energy equal to the minimum strain energy required to bring initial and final electronic states into "coincidence." This activation energy depends on the difference between electronic energies of final and initial states, Δ. The semiclassical phonon assisted jump rate is:

$$R(\Delta) = \{\nu \exp[-(4E_A + \Delta)^2/16E_A\kappa T]\}\, P, \tag{1}$$

where ν is the characteristic phonon frequency. Here P is the adiabaticity factor; it is near unity ($1 \geq P \geq 1/2$) when t is large enough for the hop to be adiabatic. However when t is small enough for the hops to be nonadiabatic, $P \ll 1$ and P is proportional to t^2.

It is useful to rewrite $R(\Delta)$ in Eq. (1) as the product of three factors:

$$R(\Delta) \cong [\nu \exp\text{-}(E_A/\kappa T)\, P] \exp(-\Delta/2\kappa T) \exp(-\Delta^2/16E_A\kappa T). \tag{2}$$

The factor in Eq. (2) that is enclosed with square brackets is the jump rate in the limit of vanishing disorder energy. The second factor in Eq. (2) is a "thermodynamic factor" that ensures detailed balance; that is, the ratio of the rate for a hop to the rate for the reverse hop is just $\exp(-\Delta/2\kappa T)/\exp(\Delta/2\kappa T) = \exp(-\Delta/\kappa T)$. The third factor causes the hopping rate to fall as the magnitude of the difference in the electronic energies of initial and final states, $|\Delta|$, is raised. The range of disorder energies for which the third factor is appreciable increases with the electron-lattice coupling strength, measured here by E_A. Thus, rates for hops between sites of disparate energies are only appreciable if the electron-lattice coupling strength is sufficiently large. Stated alternatively, hopping tends to become isoenergetic as the electron-lattice coupling strength is made sufficiently small.

Typical values of the change of the energy of a severely localized electron with a change of atoms' positions, the electron-lattice interaction force, F, are 2-6 eV/A. With an interatomic stiffness constant, k, (of the order of 10 eV/A^2) one finds that the force of a severely localized electron on surrounding atoms induces net atomic displacements of F/k. These net displacements, termed small-polaronic displacements, are typically a few tenths of an Angstrom. These carrier-induced displacements lower the carrier's energy by $F(F/k) = F^2/k$, typically from several tenths of an eV to 1-2 eV. The strain energy associated with displacing atoms by F/k is $(k/2)(F/k)^2 = F^2/2k$. The minimum strain energy associated with forming a coincidence E_A is $\cong F^2/4k$. Thus, the activation energies for high-temperature hopping are usually several tenths of an eV.

The study of phonon-assisted hopping is complicated by the fact that the semiclassical approach is only applicable at sufficiently high temperatures for the fluctuations of a carrier's energy due to atomic vibrations to greatly exceed a characteristic phonon energy: $F\sqrt{(2\kappa T/k)} \gg h\nu$.[5] Expressed differently, the validity of the semiclassical approach is that $8E_A\kappa T \gg (h\nu)^2$. As the temperature is reduced below that at which the semiclassical approach is applicable, phonon-assisted rates fall with decreasing temperature but in a nonArrhenius manner.[6]

At very low temperatures an Arrhenius temperature dependence can be regained, albeit with an activation energy that is smaller than the high-temperature semiclassical activation energy. In this low-temperature regime phonon-assisted hops occur with the absorption of the minimum of vibrational energy. Then a hop upward in energy is activated with the activation energy Δ. A hop downward in energy concomitantly tends toward temperature independence.

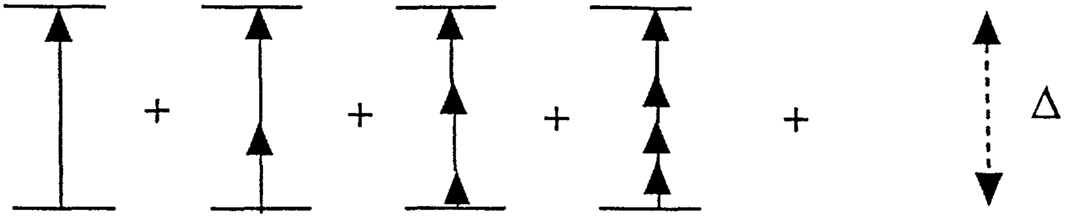

Fig. 1. The low-temperature hop of a carrier upwards in energy by an amount Δ occurs with the absorption of the minimum amount of vibrational energy. This vibrational energy can be delivered to the carrier by the absorption of varying numbers of phonons. Here the absorption of one, two, three and four acoustic phonons is explicitly shown.

As illustrated in Fig. 1, the upward hop of a carrier can occur with the absorption of a single phonon (energy conservation permitting) or with the absorption of multiple phonons of lower energy. The contribution of n-acoustic-phonon processes to the net rate is proportional to $[3\gamma(\Delta/h\nu)^2]^n/n!(2n-1)!$, where γ is the ratio of an electron energy to a phonon energy, a large number.[6] For electrons and holes in common group IV semiconductors γ ranges between 63 and 242. Thus, a low-temperature hop will only be dominated by the process in which only a single phonon is absorbed when the disorder energy is so small that $\Delta << h\nu$. The rate for a low-temperature hop that occurs with the absorption of a single low-energy acoustic phonon was calculated by Miller and Abrahams and applied to the case of cryogenic hopping between shallow impurities in doped group IV semiconductors. They estimate disorder energies in these cases to be between 10^{-4} and 10^{-3} eV.[1] The preexponential factor of the Miller-Abrahams rate is $\nu\{(t/\Delta)^2[3\gamma(\Delta/h\nu)^2](\Delta/h\nu)\}$.[1,6] This factor is much less than a vibration frequency, ν, since, as discussed above, $3\gamma(\Delta/h\nu)^2 << 1$ and $\Delta << h\nu$, while $t << \Delta$ is required for hopping transport.

While conservation of energy generally requires low-temperature hops to involve some acoustic phonons, one can consider hops between states whose energy corresponds to the energy of one (or just a few) optical phonons.[5] Here the results are similar to those described above. That is, low-temperature hops upward in energy are activated with the energy Δ, while hops downward in energy have temperature independent rates. Studies of hops involving both optical and acoustic phonons find similiar results.[7]

As the temperature is raised high enough so that the hopping may be treated semiclassically, the rates found for a well-localized carrier coupled to an optical phonon are also described by Eqs. (1) and (2). Indeed, the semiclassical rates are also obtained when a carrier is coupled sufficiently strongly to a number of vibrational modes.[8]

It is instructive to consider the complement to semiclassical small-polaronic hopping. This circumstance occurs when a carrier is not strongly coupled to any vibrational mode.[5] Specifically, one can consider hopping when the electron-lattice coupling with all modes is so weak that the semiclassical condition is not fulfilled even though the temperature exceeds the phonon temperature: e.g., $8E_A\kappa T <$

$(h\nu)^2$. This condition defines the high-temperature weak-coupling regime. Then even high-temperature hopping involves the absorption or emission of a number of phonons comparable to the minimum number of phonons consistent with the requirement of energy conservation. For a hop upward in energy the weak-coupling rate is proportional to the product of the Bose factors for the absorption of these phonons. For example, a hop in which n optical phonons of energy $h\nu$ are absorbed to produce a transition of energy $\Delta = n\,h\nu$, gives a rate proportional to $[\exp(h\nu/\kappa T) - 1]^{-n}$. This rate is Arrhenius at low temperatures, $R(\Delta) \propto \exp(-nh\nu/\kappa T) = \exp(-\Delta/\kappa T)$. However, at high temperature, $\kappa T > nh\nu/2$, the rate rises algebraically with temperature $R(\Delta) \propto T^n$.

In summary, observations of thermally activated jump rates at high temperatures are attributable to semiclassical (small-polaronic) hopping. The preexponential factors of these semiclassical rates are constrained to never exceed the characteristic vibrational frequency, ν.

4. "HIGH-TEMPERATURE" HOPPING CONDUCTION

High-temperature, semiclassical, hopping conduction has been observed in many different types of disordered solid. Small-polaronic hopping in transition-metal oxide glasses (e.g., vanadium phosphate glasses) occurs between transition-metal cations immersed in environments composed of high densities of cations and anions.[9] In chalcogenide (S, Se and Te) glasses, holes move between lone-pair orbitals of chalcogen atoms (e.g., from Te to Te atom) amidst other covalently bonded atoms (i.e., As, Si, Tl and Ge).[10] In molecularly doped polymers carriers move between dopant molecules immersed in polymers.[11]

In transition-metal oxide and chalcogenide glasses steady-state mobilities are determined from measuring the thermoelectric power and the conductivity as functions of temperature.[3,9,10] Taken together, these measurements permit one to determine the mobility. In chalcogenide glasses the conductivity is often high enough so that the Hall mobility can also be measured. In many circumstances the activation energy of the mobilities changes little as the glass composition is altered. In these cases a significant fraction of the glass is composed of a "dominant constituent" through which hopping occurs. Many examples of this behavior are found for the hopping of holes between As-Te regions of complex glasses of As, Te, Se, Ge and I. These observations lead to a picture in which carriers at room temperature experience disorder energies that are comparable to κT, several hundredths of an eV. Whatever sites exist with significantly higher energies are not visited by the carriers. Sites of significantly lower energies trap and hold carriers sufficiently well that they do not contribute to dc transport. Thus, except at compositions corresponding to percolation thresholds, energetic disorder does not manifest itself strongly in these glasses' high-temperature transport. In other words, activation energies for high-temperature hopping are local parameters that are not significantly affected by their environments.

In both transition-metal oxide and chalcogenide glasses the concentration of hopping sites is often sufficiently high that hopping is adiabatic. That is, carriers primarily move between sites that are sufficiently close together that the electronic transfer energies connecting them never falls significantly below hν. In these case the preexponential factor of the mobility is $(e/\kappa T)\nu\langle s\rangle^2$, a number between about 0.1 and 1 cm^2/V-sec, where $\langle s\rangle$ is the average intersite separation.

Despite having these transport properties in common, the limited data available on the mobility in large electric fields seems to differentiate between hopping in these different disordered solids. Specifically, small-polaron hopping in crystals is predicted to result in a mobility with a field dependence that varies roughly as

$$\mu(E) \cong \nu\langle s\rangle \exp(-E_A/\kappa T)\ [2 \sinh(eE\langle s\rangle/2\kappa T)/E] \exp[-(eE\langle s\rangle)^2/16E_A\kappa T]. \quad (3)$$

Such behavior is consistent with observations of trap-free hopping of holes in SiO_2.[12]

Transition-metal-oxide glasses usually contain densities of low-mobility (small-polaronic) carriers that are high enough to saturate any traps that may exist. High-field transport measurements indicate mobilities that are consistent with the form of Eq. (3).[9] However, the argument of the sinh is usually about an order of magnitude larger than expected if E is the applied electric field and $\langle s\rangle$ is the average intersite separation. Nonohmic conduction is only observed in fields above about 10^5 V/cm.

Chalcogenide glasses also manifest evidence of small-polaronic carriers. However, the carrier densities are lower than those of transition-metal-oxide glasses.[9] Furthermore, both steady-state and transient measurements suggest the presence of significant densities of traps. Drift mobilities are reported to rise exponentially as $\exp(eE\langle s\rangle/2kT)$ above field strengths of about 10^3 V/cm. As in the case of the transition-metal-oxide glasses the values of argument of the exponential are about an order of magnitude larger than would be expected if E were the applied field strength and $\langle s\rangle$ were actually the average intersite separation.

Mobilities ascribed to the motion of carriers between "dopants" molecules immersed in polymers have been deduced from time-of-flight experiments. These mobilities are reported to be of the form[11]

$$\mu(E) = \mu_0 \exp(-E_A/\kappa T) \exp[\gamma\sqrt{E}(1/\kappa T - 1/\kappa T_0)]. \quad (4)$$

As in the other disordered systems described above, the effect of the electric field on the activation energy is large in that $\gamma\sqrt{E}$ is $\gg eE\langle s\rangle$. However, the variation of the activation energy with the electric field is weak, varying only as the square root of the field strength. Furthermore, unlike the findings for other disordered systems, the activation energy of molecularly doped polymers appears to be independent of the average interdopant separation. The field-independent activation energy, E_A, can be sizeable: values of about 0.6 eV are reported for both DEH and DEASP immersed in both polycarbonate and polystyrene.[13,14] In these experiments γ/κ is about 4 $K(cm/V)^{1/2}$ and T_0 falls from about 700 K to about 300 K as the average intersite separation is raised from about 10 A to about 20 A. Finally, as indicated by Eq. (4), the mobility falls with increasing field when $T > T_0$.

Unusual values are often found for the temperature-independent prefactor. For example, while hopping distances of the order of 10 A are consistent with preexponential factors of the mobility being up to about 1-5 cm^2/V-sec, values up to 10^3 cm^2/V-sec are reported for μ_0, the zero-field preexponential factor extrapolated from the high-field measurements.

In summary, the high-field hopping in ordered systems agrees reasonably with theory. However, the high-field transport reported for disordered hopping systems depends sensitively on the system (and perhaps on the measurement technique). In no case have the observations been explained satisfactorily.

5. HOPPING CONDUCTION IN DISORDERED SOLIDS IS A NONLINEAR PROBLEM

Hopping transport in disordered media is usually viewed as being analogous to charge transport through a network of inequivalent resistors. Sites that can be occupied by a charge carrier are then represented by nodes of a resistor network. Here the validity of this resistor-network picture is critically assessed.

To begin, consider the current that flows directly between a pair of sites. The current that flows between sites i and j is generally given by:

$$I_{ij} = q\,[P_i\,(1 - P_j)\,R_{ij} - P_j\,(1 - P_i)\,R_{ji}], \tag{5}$$

where q is a carrier's charge, P_i and P_j are the probabilities of sites i and j being occupied, and R_{ij} is the rate with which a carrier hops from site i to site j. To proceed the occupation probability of a site is now related to its quasi-electro-chemical-potential (QECP) by the defining relation

$$P_i \equiv 1/\{\exp[\beta(E_i - \mu_i)] + 1\}, \tag{6}$$

where $\beta \equiv 1/\kappa T$. In equilibrium, the QECPs of all sites reach a common value, the electro-chemical potential. Next, with full generality the rate for a phonon-assisted hop from a state of energy E_i to one of energy E_j is written as

$$R_{ij} = \exp[-\beta(E_j - E_i)/2]\; r_{ij}(|E_j - E_i|), \tag{7}$$

where $r_{ij}(|E_j - E_i|)$ only depends on $(E_j - E_i)$'s magnitude. Detailed balance is ensured since $R_{ij}/R_{ji} = \exp[-\beta(E_j - E_i)]$. Combining Eqs. (5)-(7) yields another expression for the current that flows between a pair of sites:

$$I_{ij} = (q/2)\,\mathrm{sech}[\beta(E_i-\mu_i)/2]\,\mathrm{sech}[\beta(E_j-\mu_j)/2]\,r_{ij}(|E_j - E_i|)\,\sinh[\beta(\mu_i-\mu_j)/2]. \tag{8}$$

Equation (8) demonstrates that the driving force for flow between sites i and j is the difference of the two sites' QECPs, $\mu_i - \mu_j$.

To determine the steady-state current flowing between sites requires finding the QECPs. As in conventional circuit analysis, the QECPs are found by requiring 1) that the sum of the currents passing through each node be zero and 2) that the net difference of QECPs between ends of a sample equal the applied emf. With Eq. (8) these boundary conditions yield coupled nonlinear equations for the QECPs.

When the difference of QECPs in Eq. (8) becomes arbitrarily small, Eq. (8) reduces to Ohm's law: $I_{ij} = G_{ij}(\mu_i - \mu_j)$, where the conductance is given by

$$G_{ij} = (\beta q/4)\,\mathrm{sech}[\beta(E_i-\mu)/2]\,\mathrm{sech}[\beta(E_j-\mu)/2]\,r_{ij}(|E_j - E_i|), \tag{9}$$

and μ is the electrochemical potential. Much discussion of low-temperature hopping conduction employs a simplified version of Eq. (9) in which $\mathrm{sech}[\beta(E-\mu)/2]$ is replaced by $2\exp[-\beta|E-\mu|/2]$ and $r_{ij}(|E_j - E_i|)$ is replaced by $r_0 \exp(-\beta|E_j - E_i|/2)$, where r_0 is a constant:[1,15]

$$G_{ij} = (\beta q r_0)\exp[-\beta|E_i-\mu|/2]\exp[-\beta|E_j-\mu|/2]\exp(-\beta|E_j - E_i|/2). \tag{10}$$

This linearization scheme replaces the hopping system by a network of inequivalent conductances.

The replacement of the hopping system with a resistor network is only appropriate at sufficiently high temperatures for the transformation of Eq. (8) to Eq. (9) to be valid: $2\kappa T >> \mu_i - \mu_j$. Thus, while the resistor network has been used as a basis for discussing hopping conduction in the limit that $T \rightarrow 0$,[15] the network approach itself requires high enough temperatures. Alternatively put, the resistor-network approach requires the applied field to be sufficiently small for drops of QECP to be dwarfed by $2\kappa T$. In an ordered system this requirement is that $2\kappa T >> eEs$, where s is the intersite separation. For a field of 10^6 V/cm and hops of 10 A, eEs is 0.1 eV. Thus, even in an ordered system the resistor network would only be a valid representation of high-field hopping at very high temperatures. Furthermore, as will be discussed below, bottlenecks that occur for steady-state flow in a disordered system enhance some differences of QECP. Thus the resistor-network approach is prone to breakdown when the temperature is low, electric fields are high and disorder becomes significant.

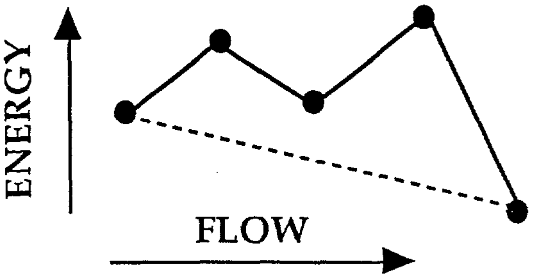

Fig. 2. Nearest-neighbor hopping along a chain of five sites (numbered sequentially from 0 to 4) is considered. The sites' energies are such as to produce two energy maxima (at sites 1 and 3) separated by an energy minimum (at site 2): $E_0 < E_1 > E_2 < E_3 > E_4$. The difference between the energies of the two peaks is $\Delta \equiv E_3 - E_1$ and the end sites are taken to be equivalent to one another. Thus, with the applied emf of qV, $E_0 = 0$ and $E_4 = -qV$ as illustrated by the dashed straight line.

To understand the implication of using the resistor-network approximation, the five-site model of Fig. 2 is studied. The QECPs can be calculated through use of the coupled nonlinear equations. These results are then compared with those obtained with the resistor-network model.

The calculation uses standardly employed approximations: sech[$\beta(E_i-\mu_i)/2$] is replaced by 2 exp[-$\beta|E_i-\mu_i|/2$] and $r_{ij} = r_0 \exp[-\beta|E_j - E_i|/2]$. The QECPs of the five sites are: $\mu_0 = 0$, $\mu_4 = -qV$ and

$$\beta\mu_1 = \ell n\left[\frac{1 + 2\,e^{\beta\Delta} + e^{-\beta qV}}{2(e^{\beta\Delta} + 1)}\right],$$

$$\beta\mu_2 = \ell n\left(\frac{e^{\beta\Delta} + e^{-\beta qV}}{e^{\beta\Delta} + 1}\right), \tag{10}$$

$$\beta\mu_3 = \ell n\left[\frac{e^{\beta\Delta} + e^{-\beta qV}(e^{\beta\Delta} + 2)}{2(e^{\beta\Delta} + 1)}\right].$$

As expected, in the high-temperature limit, $\kappa T > \Delta$ and qV, the drops in QECP are uniform: $\mu_i = -iqV/4$ over the five sites. However, in the low-temperature limit the drop in QECP approaches being across only the downward-hop side of the highest peak: $\mu_0 = \mu_1 = \mu_2 = \mu_3 = 0$ and $\mu_4 = -qV$ for $\Delta > 0$ and $\mu_0 = \mu_1 = 0$ and $\mu_2 = \mu_3 = \mu_4 = -qV$ for $\Delta < 0$.

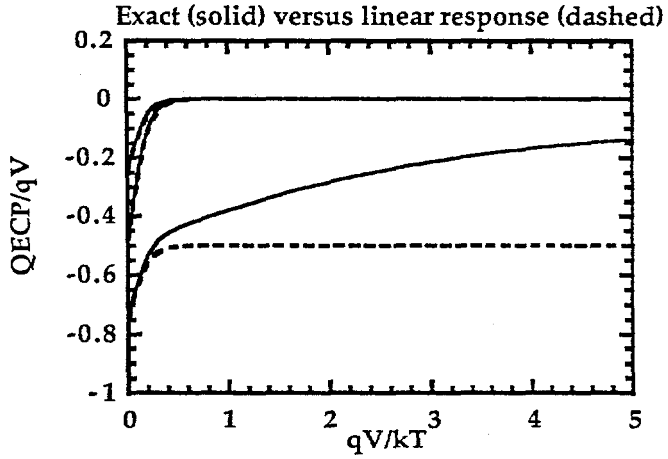

Fig. 3 The QECPs in units of qV are plotted against qV/κT. In the high temperatures limit the QECP is dropped uniformly across the five sites. Then QECP/qV is -0.25, -0.50 and -0.75 for the sites labelled as 1, 2 and 3. With decreasing temperature for Δ > 0 the drop of the QECP shifts to between sites 3 and 4.

This result contrasts with that obtained if a resistance network is assumed [obtained by replacing exp(-βqV) by 1 - βqV in Eqs. (10)]:

$$\mu_1 = -qV/2[\exp(\beta\Delta) + 1],$$

$$\mu_2 = -qV/[\exp(\beta\Delta) + 1],$$

$$\mu_3 = -qV[\exp(\beta\Delta) + 2]/2[\exp(\beta\Delta) + 1]. \qquad (11)$$

Thus, within the resistance-network approximation the drop of QECP falls equally over both sides of the highest peak: $\mu_0 = \mu_1 = \mu_2 = 0$, $\mu_3 = -qV/2$ and $\mu_4 = -qV$ for $\Delta > 0$; $\mu_0 = 0$, $\mu_1 = -qV/2$ and $\mu_2 = \mu_3 = \mu_4 = -qV$ for $\Delta < 0$. The differences between the results of the resistance network and the full hopping problem becomes most marked when $\kappa T < qV$.

Thus, the resistor-network model shows that the QECPs are increasingly shifted as the temperature is lowered, the applied emf is increased and the disorder is increased. However, the resistor-network model underestimates the charge redistribution that occurs as a result of carriers encountering a transport-limiting bottleneck: passing over site 1 for $\Delta < 0$ or over site 3 for $\Delta > 0$. The significance of this underestimation increases with reduced temperature, increased electric field and enhanced disorder. Finally, as illustrated in Fig. 4, it is noted that the full calculation of the QECPs results in a field-dependent mobility rather than the field-independent mobility that results from a self-consistent linear-response calculation.

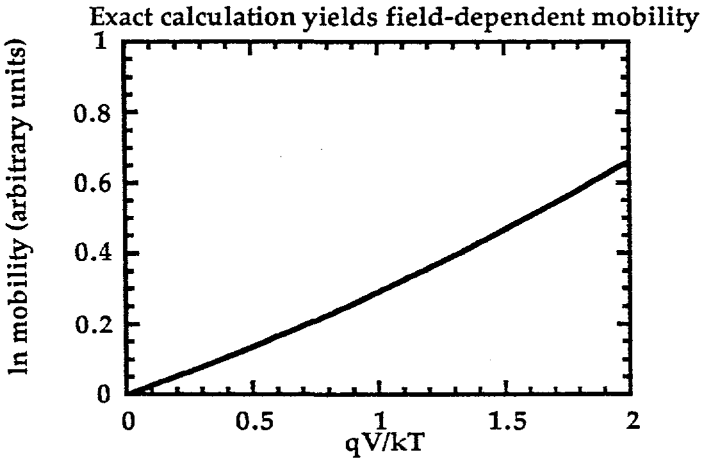

Fig. 4. Mobility of steady-state carriers increases with increasing applied field.

6. CONCLUSIONS

Three main conclusions are drawn from this work. First, observation of thermally activated hopping rates for electronic transport at all but cyrogenic temperatures implies small-polaronic hopping. Thus, transport calculations that attempt to describe such phenomena should employ small-polaron jump rates. Second, while the field dependences of small-polaron hopping observed in ordered systems are consistent with the existing theory, no theory exists that explains the observed non-Ohmic mobilities in disordered systems. Indeed, the field-dependences of measured mobilities in disordered solids are not universal. Measurements of high-field conduction in different classes of disordered material appear to differ significantly from one another. Third, hopping transport in disordered materials driven by high electric fields is not adequately described by a disordered resistor network. The redistribution of carriers that results from carriers in steady-state motion encountering bottlenecks is not adequately described by a resistor network. Full (nonlinear) treatment of charge redistribution in steady-state flow produces field-dependent contributions to carriers' mobilities. Thus, calculation of field-dependent steady-state mobilities can not generally employ a resistor-network approximation.

7. ACKNOWLEDGEMENT

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