Quantum−Classical Transition Analogy of the Diffusion−Mobility Relation for Hopping and Band Transport Systems: Molecules to Materials
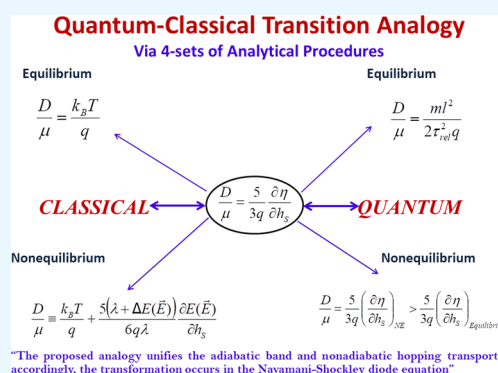
Karuppuchamy Navamani*

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: We propose a quantum−classical transition analogy for Einstein's diffusion−mobility (D/μ) relation to reveal electron−hole dynamics in both the degenerate and nondegenerate molecular and material systems. Here, one-to-one variation between differential entropy and chemical potential $(\Delta\eta/\Delta h_s)$ is the proposed analogy, which unifies quantum and classical transport. The degeneracy stabilization energy on D/μ decides whether the transport is quantum or classical; accordingly, the transformation occurs in the Navamani−Shockley diode equation.

Quantum-Classical Transition Analogy
Via 4-sets of Analytical Procedures

Equilibrium $\quad$ $\frac{D}{\mu} = \frac{k_B T}{q}$ $\qquad$ Equilibrium $\quad$ $\frac{D}{\mu} = \frac{ml^2}{2\tau_{rel}^2 q}$

CLASSICAL ← $\frac{D}{\mu} = \frac{5}{3q}\frac{\partial\eta}{\partial h_S}$ → *QUANTUM*

Nonequilibrium $\quad$ $\frac{D}{\mu} \equiv \frac{k_B T}{q} + \frac{5(\lambda + \Delta E(\vec{E}))}{6q\lambda}\frac{\partial E(\vec{E})}{\partial h_S}$

Nonequilibrium $\quad$ $\frac{D}{\mu} = \frac{5}{3q}\left(\frac{\partial\eta}{\partial h_S}\right)_{NE} > \frac{5}{3q}\left(\frac{\partial\eta}{\partial h_S}\right)_{Equilibrium}$

"The proposed analogy unifies the adiabatic band and nonadiabatic hopping transport; accordingly, the transformation occurs in the Navamani-Shockley diode equation"

1. INTRODUCTION

The diffusion−mobility ratio (D/μ) is the fundamental transport relation for all classes of systems, from molecules to materials. Einstein's relation works well in classical nondegenerate systems at equilibrium and quasi-equilibrium conditions.[1] Numerous reports show that there is a deviation in Einstein's relation for degenerate systems.[2−5] In fact, all high-performance (conducting) devices are manufactured by degenerate systems, which are normally electron/hole rich and have high transporting ability without carriers' energy loss. The quantum-level understanding of charge transport in molecular and material systems in both the cases of equilibrium and nonequilibrium is crucial for next-generation semiconductor technology. To get the complete picture of charge transport mechanisms in different electronic systems, we propose here the entropy-ruled D/μ relation, $\frac{D}{\mu} = \frac{5}{3q}\frac{\Delta\eta}{\Delta h_s}$. Here, q, η, and h_s are the electric charge, chemical potential, and differential entropy, respectively. Charge transport in molecular systems generally follows the Gaussian diffusion function. Moreover, the shape of the existing degeneracy states (by the external field) in the material system (i.e., periodic) also seems to be the Gaussian or Lorentzian width. The Gaussian-like transport is referred to as normal diffusion transport. In principle, the differential entropy (h_s) is derived from the Gaussian function, $\Phi(x) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{x^2}{2\sigma^2}\right)$; hence, the differential entropy is expressed as $h_s(x) = -\int\Phi(x)\cdot\ln\Phi(x)dx = \ln(\sigma\sqrt{2\pi e})$.[6] The

entropy-ruled D/μ relation was derived from the generalized Einstein relation with the conjunction of differential entropy-dependent carrier density equation.[2,6] This relation mainly elucidates chemical potential over the degeneracy strength (i.e., $\Delta\eta/\Delta h_s \equiv \sigma\cdot\Delta\eta/\Delta\sigma$) or vice versa on transport, which decides the typical electron−hole dynamics (quantum or classical or intermediate) in molecular devices. Here, σ is the Gaussian disorder width or Gaussian variance. Note that the molecular transport is generally studied by the Gaussian disordered model, which leads to normal diffusion transport.[2] In principle, the Gaussian variance (σ) increases with the existing degeneracy levels (or the production of new states by orbital splitting process, e.g., Stark and Zeeman effect), which depends on the amplitude of external field and doping concentrations. In this report, the introduced term $\Delta\eta/\Delta h_s$ is the quantum−classical transition analogy of the D/μ relation for the entire characteristic range of molecular and material systems. Moreover, this analogy is related to the degeneracy stabilization potential of a concerned molecule, $V_{DS} = \Delta\eta/(q\cdot\Delta h_s)$. The degeneracy stabilization potential is defined as the required minimum potential to maintain the existing

degeneracy levels during charge transport. That is, the existence of degenerate states by an applied field is continuously sustained (or stabilized) without any collapse at a certain chemical potential value in a given quantum system. For high degenerate limits, the transport will be delocalized (i.e., band model), and the localization transport (or hopping mechanism) is normally anticipated in disorder with non-degenerate or weakly degenerate molecules. Thus, the proposed analogy here is so named quantum—classical transition analogy (or band-hopping transition analogy), which will suit both the equilibrium and the nonequilibrium transport for wide temperatures.

It is a unique analogy of diffusion—mobility ratio to explain both the Einstein transport regime, i.e., (i) $\frac{D}{\mu} = \frac{k_B T}{q}$, and non-Einstein transport regimes of (ii) $\frac{D}{\mu} > \frac{k_B T}{q}$ (diffusion-dominant transport) and (iii) $\frac{D}{\mu} < \frac{k_B T}{q}$ (diffusion-limited transport). One-to-one variation between η and h_s or vice versa is the key factor to determine the typical transport of one among the above three D/μ transport regimes. Here, $\frac{D}{\mu} = \frac{5}{3q}\frac{\Delta\eta}{\Delta h_s} \equiv \frac{5}{3q}\frac{\sigma\cdot\Delta\eta}{\Delta\sigma}$, since $h_s = \ln(\sigma\sqrt{2\pi e})$. The production of degenerate states (i.e., in terms of differential entropy changes) with respect to the chemical potential in the given molecular solids decides whether the transport is mobility-dominant or diffusion-dominant. The typical transport is mainly correlated with our entropy-ruled $(\mu/D) = 0.6q\cdot dh_s/d\eta \equiv 0.6q\cdot d\sigma/(\sigma\cdot d\eta)$. For highly degenerate situations, mobility is the dominant parameter in the molecular devices rather than the diffusion coefficient due to large variation in σ, even at small η changes (η can be tuned by applied bias/field and doping). In such cases, the required degeneracy stabilization energy for orbital splitting is small enough; hence, it is referred to as mobility-dominant (i.e., bandlike) or diffusion-limited transport. The large production of degenerate electronic levels in the materials due to the applied field or by appropriate potential doping naturally facilitates the delocalized transport behavior, which leads to high field-response mobility. In this high-degeneracy case, even at lower bias, the expected quantum characteristic features are high. Here, the existing degenerate states are stabilized by only infinitesimal potential, which is the class of quantum materials. According to our analogy, quantum systems principally have minimum degeneracy stabilization potential $(V_{DS} = \Delta\eta/(q\cdot\Delta h_s))$. That is, the quantum features in a given system maximally appear with a minimum V_{DS}. If the required degeneracy stabilization energy (or chemical potential) is more, at which the transport will be diffusion-dominant. Highly doped molecular systems have a large chemical potential which is more favored for the diffusion process. In some cases, even at large applied bias conditions, the existing degeneracy levels in the molecular or material systems will be a minimum which in turn towards the low mobility or insulator regimes. The intriguing point here is that the μ belongs to an intrinsic nature (electronic structure) of the systems and the D is driven by η (or charge density gradient). Here, the parameter η is a direct consequence of charge density, which can be modified by a few external agents like gate voltage, doping, and temperature. Thus, our analogy of μ/D unifies the band and hopping transport models via the parameters h_s and η. The parameter h_s is responsible for band transport due to the existence of continuum degeneracy levels

(closely packed orbitals due to the large electronic coupling) and the parameter η helps to drift/activate the electron—hole transfer (in terms of density flux) from one to the next consequential electronic state (HOMO for hole and LUMO for electron transport). The electron—hole dynamics in the random site energy landscape (disordered) can be examined by diffusion transport through the mean squared displacement approach.[7] If the energy gap between the existences of degeneracy levels is in the order of $k_B T$ at which Einstein's relation is valid for a particular molecular device. This is referred to as the thermally activated hopping mechanism; therefore, the Marcus theory of charge transfer rate is more suitable for molecular transport in high-temperature regions ($T > 150$ K).[7] Moreover, in the cases of nonequilibrium at a finite temperature, the value of the D/μ ratio deviates from Einstein's original value, i.e., $D/\mu > k_B T/q = g k_B T/q$, where g always be greater than unity. Here, g is the enhancement factor, which is a dimensionless quantity. On the other hand, in periodic systems, the energy difference between the degeneracy levels is dominated by the electronic part (i.e., quantum) rather than the thermal energy (classical). Here, the expected electron energy will be in the order of $\hbar^2 k^2/2m$. In such materials (delocalized band), the electronic-level interactions are large enough, which reveals the large electronic coupling and too lesser reorganization energy. The large weightage of electronic interactions leads to quantum transport via a linear superposition principle, which can be quantified by the chemical potential shifting. For classical systems, the vibronic interactions will be dominant rather than electronic energy.

In this paper, we mainly propose the quantum—classical transition analogy of Einstein's diffusion—mobility relation, which unifies the delocalized band and hopping (localized) transport and also elucidates the crossover nature between them. Through this analogy, one can explain both the Einstein transport and non-Einstein transport regimes; accordingly, we classify the typical transport (hopping-dominant or band-like or intermediate). Importantly, here we generalize the entropy-ruled charge transport method for molecular and material systems at a wide temperature range. Using this entropy-ruled method, four sets of analytical procedures are proposed to explore the charge transport mechanism in both the quantum and classical molecular and material systems under equilibrium and nonequilibrium cases.

2. MODEL

In principle, the activity (a)—chemical potential (η) relation in the molecular species can be expressed as[8,9]

$$\eta = k_B T(1 + \ln a) = k_B T\left(1 + \ln\left(\frac{n}{n_o}\zeta\right)\right) \tag{1}$$

Here, n_0, n, and ζ are the initial and final electron densities and the activity coefficient for electron transfer reactions, respectively.

According to our earlier model,[6] the charge carrier density is given by

$$n_{h_s} = n_0 \exp\left(\frac{3h_s}{5}\right) \tag{2}$$

Through the Marcus theory of electron transfer reactions within the molecular specimens, the activity coefficient (ζ) is generally described as[8,9]

$$\zeta = \exp\left[\frac{(\lambda + \Delta E(\vec{E}))^2}{4\lambda k_B T}\right] \tag{3}$$

where λ and $\Delta E(\vec{E})$ are the reorganization energy and site energy difference, respectively. Inserting eqs 2 and 3 into eq 1, we get the explicit form of chemical potential

$$\eta = k_B T\left(1 + \frac{3}{5}h_s + \frac{(\lambda + \Delta E(\vec{E}))^2}{4\lambda k_B T}\right) \tag{4}$$

Therefore, the activity can be expressed as

$$a_{d=3} = \exp\left(\frac{3}{5}h_s + \frac{(\lambda + \Delta E(\vec{E}))^2}{4\lambda k_B T}\right) \tag{5}$$

Here, the charge hops from one site to the next electronic site of the potential energy surface (or barrier height) of the disordered systems. The barrier height is generally described by the relative chemical potential and hence the minimum required energy for charge hopping across the barrier is η. The above relations are more appropriate for studying the electron transfer kinetics in molecular solids. On the other hand of inorganic materials, the traversing chemical potential gives rise to the quantum flux (in terms of electronic level shift), which is mainly responsible for chemical, magnetic, and quantum transport properties. For example, the Landau level shift in the materials is observed under magnetic field circumstances, which can be quantified by the chemical potential. In principle, the changes in carrier density with respect to the chemical potential provide information on the thermodynamic density of states (TDOS) or electronic compressibility in the systems. That is, the total interactions are well-adjusted by the single energy parameter, which is the chemical potential. Thus, the electronic transport in the materials is ruled by the chemical potential, which generally includes the kinetic, exchange, and correlation terms. Through the doping process, one can usually modify the carrier concentration in the systems (for both molecules and materials), which is directly associated with the chemical potential. According to the dopant concentrations, the magnitude of chemical potential will be varied, which makes a potential difference in different sites in the system and leads to the diffusion process. Here, the charge density gradient (in terms of chemical potential variation) is mainly responsible for diffusion current.

Based on the above ground, we unify the diffusion−mobility relation for both the molecular (disordered) and material (periodic) systems in equilibrium and nonequilibrium cases. According to the entropy-ruled method,[8] the governing relation for the diffusion−mobility ratio is

$$\frac{D}{\mu} = \frac{5}{3q}\frac{\Delta\eta}{\Delta h_s} \tag{6}$$

In this relation, $\Delta\eta/(q \cdot \Delta h_s)$ is the degeneracy stabilization potential, which is the deterministic factor for unifying both the delocalized band and the hopping transport. In this relation (eq 6), $\Delta\eta/\Delta h_s$ is the quantum−classical transition analogy of Einstein's D/μ relation, which can be valid for the entire temperature ranges, from equilibrium to nonequilibrium situations.

2.1. Four Sets of Analytical Procedures. Using the quantum−classical transition analogy of $\Delta\eta/\Delta h_s$, we have proposed here the four sets of analytical procedures for

hopping and band transport at different thermodynamic conditions.

2.1.1. Analytical Set 1. For disordered dominant transport under equilibrium cases of $\zeta \to 1$ (see refs 8 and 9), eq 1 is reduced to

$$\eta = k_B T\left(1 + \ln\left(\frac{n}{n_0}\right)\right) \tag{7}$$

Inserting eq 2 in eq7 and taking the differentiation will give

$$\frac{\partial\eta}{\partial h_s} = \frac{3}{5}k_B T \tag{8}$$

Substituting eq 8 into eq 6 then gives

$$\frac{D}{\mu} = \frac{5}{3q}\frac{\partial\eta}{\partial h_s} = \frac{k_B T}{q} \tag{9}$$

The above relation shows the validity of the Einstein relation at high-temperature ranges ($T > 150$ K) with equilibrium cases. Here, we retain the original Einstein relation.

2.1.2. Analytical Set 2. In the case of disordered hopping transport with nonequilibrium ($\zeta > 1$), the variation of chemical potential with respect to the degeneracy-coupled energy fluctuations can be described as

$$\frac{\partial\eta}{\partial h_s} = \frac{\partial\eta}{\partial E(\vec{E})}\frac{\partial E(\vec{E})}{\partial h_s} = \frac{3}{5}k_B T + \frac{(\lambda + \Delta E(\vec{E}))}{2\lambda}\frac{\partial E(\vec{E})}{\partial h_s} \tag{10}$$

The applied electric or magnetic field modifies the site energy fluctuation in the given molecular devices. Based on eq 10, the reformulation of Einstein's diffusion−mobility relation for nonequilibrium systems is

$$\frac{D}{\mu} \equiv \frac{k_B T}{q} + \frac{5(\lambda + \Delta E(\vec{E}))}{6q\lambda}\frac{\partial E(\vec{E})}{\partial h_s} \tag{11}$$

In the cases of nonequilibrium at a high-temperature range of $T > 150$ K, the value of the D/μ ratio deviates from Einstein's original value, i.e., $D/\mu > k_B T/q = g k_B T/q$, where g always be greater than unity. In this regime, the energy flux is observed, which depends on the value of $\frac{\partial E(\vec{E})}{\partial h_s}$, see eq 11. Interestingly, we preserve the original Einstein's relation from eq 11, while the electric field-assisted energy fluctuations along the molecular sites will be zero, $\frac{\partial E(\vec{E})}{\partial h_s} \to 0$.

2.1.3. Analytical Set 3. The anticipated degeneracy stabilization energy for an ideal periodic (i.e., ordered) system is in the order of $\frac{\hbar^2 k^2}{2m}$, where k and m are the wave vector and effective mass of an electron, respectively. In this quantum regime, the dynamics of the delocalized electron in the Fermi surface can be equated by

$$\frac{\partial\eta}{\partial h_s} \to \frac{3}{5}E_F \equiv \frac{3}{10}m v_F^2 \tag{12}$$

where v_F is the Fermi velocity. On the other hand of localized disordered systems, the Fermi energy term is replaced by the thermal energy (see eq 8). In the disordered systems, the charge transport can be studied by the thermally activated hopping mechanism. It is to be noted that the Fermi energy is principally equated with the $k_B T_F$. Comparing eqs 9 and 12

$$\frac{D}{\mu} = \frac{5}{3q}\frac{\partial \eta}{\partial h_s} = \frac{E_F}{q} = \frac{mv_F^2}{2q} \equiv \frac{m}{q}\left(\frac{l^2}{2\tau_{rel}^2}\right) \quad (13)$$

Since $l = v_F\tau_{rel}$, here l is the mean free path and τ_{rel} is the relaxation time. In order to validate, we herein revisit the Boltzmann approach using an entropy-ruled charge transport method for periodic (i.e., ordered) materials in an equilibrium state and is expressed as

$$\mu = \frac{q(dn/d\eta)v_F^2\tau_{rel}}{2n} \equiv \frac{3}{10}q\left(\frac{dh_s}{d\eta}\right)v_F^2\tau_{rel} \quad (14)$$

The governed mobility expression (eq 14) is the quite general form for most of the quantum systems, which is originally developed from an entropy-ruled method with conjunction of the Boltzmann approach.[5,8,10] Comparing eqs 6 and 14, we get

$$D = \frac{v_F^2\tau_{rel}}{2} = \frac{l^2}{2\tau_{rel}} \quad (15)$$

Here, the differential entropy is $h_s = \ln(\sigma\sqrt{2\pi e})$ and hence

$$dh_s = \frac{d\sigma}{\sigma} \approx \frac{\sigma_f - \sigma_i}{\sigma_f} \to 1 \quad (16)$$

In our study, the satisfying condition for delocalized band transport is $\sigma_f \gg \sigma_i$, which usually occurs in high-degeneracy cases even at small perturbation. That is, the existence of continuum degeneracy levels leads to the state of equilibrium; the degeneracy levels are equally distributed in the energy scale of $\frac{\hbar^2 k^2}{2m}$. Here, the relative chemical potential is the changes of energy during the particle flux (dE/dN), which is directly proportional to the Fermi energy[11,12]

$$d\eta = \frac{dE}{dN} \equiv \frac{3}{5}E_F \quad (17)$$

Substituting eqs 16 and 17 into eq 6, the diffusion−mobility relation becomes

$$\frac{D}{\mu} = \frac{E_F}{q} = \frac{mv_F^2}{2q} \equiv \frac{ml^2}{2\tau_{rel}^2 q} \quad (18)$$

Now, we explicitly get the same relation as eq 13. The above D/μ relation (eq 18) is more appropriate for continuum band transport. For localized hopping cases, the diffusion equation (15) will be replaced by

$$D = \frac{\langle x^2(t)\rangle}{2t} \quad (19)$$

where $\langle x^2(t)\rangle$ and t are the mean squared displacement and simulation time, respectively. Using eqs 15 and 18, one can preserve the original band mobility as

$$\mu = \frac{q\tau_{rel}}{m} \quad (20)$$

Using eq 14, the extent of the diffusion-based mobility for Dirac materials (e.g., monolayer graphene) is

$$\mu_{Dirac} = \frac{qv_F^2\tau_{rel}}{E_F} \equiv \frac{qv_F\tau_{rel}}{\hbar k_F} \to \frac{ql}{\hbar k_F} \quad (21)$$

Since, $D = v_F^2\tau_{rel}/2$.

2.1.4. Analytical Set 4.
For periodic systems with nonequilibrium cases, the D/μ ratio is described as

$$\left(\frac{D}{\mu}\right)_{NE} = \frac{5}{3q}\left(\frac{\partial\eta}{\partial h_s}\right)_{NE} > \frac{5}{3q}\left(\frac{\partial\eta}{\partial h_s}\right)_{equilibrium} \quad (22)$$

In this case,

$$\left(\frac{\partial\eta}{\partial h_s}\right)_{NE} \to b\frac{3}{5}E_F^{NE} \quad (23)$$

Here, b is the proportionality dimensionless constant, which is associated with the enhancement factor, $g \geq 1$. It is to be noted that the variation in differential entropy (dh_s) is the deciding factor for the deviation range from its electronic and thermal equilibrium value.

In principle, the carrier energy (E) must be in the order of η and hence $E \geq \eta$. That is, the required minimum energy for carrier kinetics, $E \equiv \eta$. Here, the parameter η is the energy difference between the adjacent sites. The average charge transfer energy (kinetic term) and Fermi energy are principally related by $E = \frac{3}{5}E_F$ (see ref 11). In such a way, one other simplified form of quantum−classical transition for Einstein's D/μ relation is $\frac{D}{\mu} = \frac{5}{3q}\frac{\Delta\eta}{\Delta h_s} \equiv \frac{1}{q}\frac{\Delta E_F}{\Delta h_s} \equiv \frac{1}{q}\frac{k_B\Delta T_F}{\Delta h_s}$, where T_F is the Fermi temperature. On the other hand of disordered solids, the charge hops over the barrier height, which is normally activated by the thermal energy, $k_B T$ (see eq 1 and 7). In such high-temperature limits, D/μ is equivalent to that of thermal energy, $k_B T/q$.

3. RESULTS AND DISCUSSION

Herein, our proposed analogy (i.e., quantum−classical transition analogy) is analytically verified and tested for dialkyl-substituted thienothiophene-capped benzobisthiazole (BDHTT-BBT) and methyl-substituted dicyanovinyl-capped quinquethiophene (DCV5T-Me) molecular solids at different electric field values. The presence of a benzobisthiazole unit along with the substituted dicyanovinyl-capped quinquethiophene in the BDHTT-BBT molecule naturally provides electron affinity property. Here, the benzobisthiazole unit provides the planar geometry in this molecule, which is responsible for strong $\pi-\pi$ interactions. The DCV5T-Me molecule has a crystalline nature due to the methyl-substituted thiophene rings, which support good charge transport properties. More details of the structure−property relation were presented in our earlier study.[6] The applied field naturally modifies the site energy disorder (i.e., $\Delta E\ (\vec{E})$), which has a direct impact on charge transport. It is to be expected that the enhancement of the D/μ relation is due to nonequilibrium, which is shown in Figures 1 and 2. Interestingly, one can reproduce the original Einstein relation from our analogy at a high-temperature range of nondegenerate or weakly degenerate limits, under equilibrium conditions. To show the validity of our analogy, we perform and extent the computational studies for electronic transport properties of BDHTT-BBT and DCV5T-Me molecular systems. For our calculations, the computed charge transport parameters (charge transfer integral, site energy, and reorganization energy) from quantum chemical calculations and molecular conformation (stacking angle, angular distribution) with structural kinetics information are taken from our previous study.[6] The molecular conformation is generally obtained through molecular
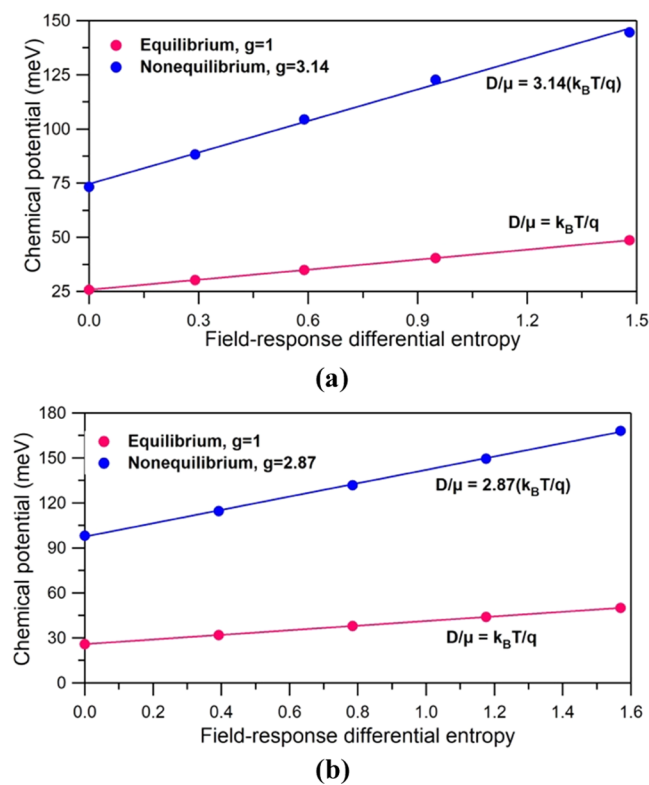
(a)

(b)

Figure 1. Chemical potential (η) with respect to the field-response differential entropy (h_s) for electron transport in (a) BDHTT-BBT and (b) DCV5T-Me molecules at different ΔE ($\vec{E}$) of 0, 20, 40, 60, and 80 meV. The η linearly increases with h_s, and hence the slope of η–h_s characteristic study is constant. The main observation is that the η–h_s relation is an analogy form of Einstein's mobility–diffusion (D/μ) relation.

dynamics simulation. In this work, we extent the kinetic Monte–Carlo simulations to calculate the diffusion–mobility ratio in BDHTT-BBT and DCV5T-Me molecules for both equilibrium and nonequilibrium cases (see Figure 1). It is observed that the results of equilibrium transport confirm the validity of Einstein's relation for both molecules. However, in the case of nonequilibrium, we observe a deviation (i.e., enhancement) in Einstein's relation from its original value of $k_B T/q$.

Comparably, the BDHTT-BBT molecule has a larger value of D/μ (=$3.14 k_B T/q$) under a nonequilibrium condition, which reveals that the field-response diffusion coefficient is dominant rather than field-response mobility. In this case, Einstein's relation deviates from its real value by 3.14 (i.e., $3.14 k_B T/q$), which is shown in Figures 1 and 2. That is, the required applied bias is more for BDHTT-BBT rather than the DCV5T-Me system to hop along the barrier. Here, it is anticipated that the probability of the Gaussian distribution width in this molecule (BDHTT-BBT) will be lesser than unity, $P_{GW} \cong dh_s = \frac{d\sigma}{\sigma} < 1$, since $h_s = \ln(\sigma\sqrt{2\pi e})$. This analysis reveals that the cooperative behavior between the chemical potential and differential entropy is the deterministic factor for the D/μ ratio.

Various reports clearly manifest that the D/μ relation influences the diode performance, which can be analyzed by the current density (J)–voltage (V) characteristic study with the aid of the diode ideality factor (N_{id}).[1,6,13,14] Here, the ideality factor has a direct correlation with the enhancement
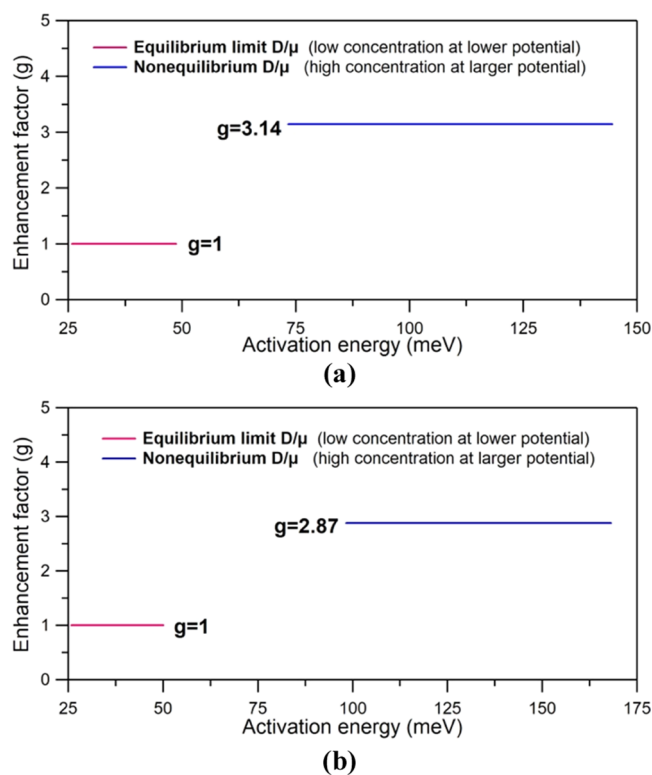

(a)

(b)

Figure 2. Using the quantum–classical transition analogy of the D/μ factor, the validity and limitations of Einstein's relation are studied in (a) BDHTT-BBT and (b) DCV5T-Me molecular solids. Here, we preserve the original Einstein's relation for both molecular systems under equilibrium cases (see eqs 7–9). The magnitude of deviation is equated by the enhancement parameter (g) in nonequilibrium limits, which influence the diode performance. The site energy disorder-coupled polaron movement (see eq 4) plays a vital role for the nonequilibrium D/μ factor, which reveals a diffusion enhancement rather than mobility. The plots show that there is a nonequilibrium, while the applied bias is strong enough.

parameter, g. According to an entropy-ruled method, the governing Navamani–Shockley (NS) diode equation for molecular quantum devices is given by[8,10]

$$J = J_0\left[\exp\left(qV\frac{3\Delta h_s}{5\Delta\eta}\right) - 1\right]$$

(24)

where J_0 is the saturation current density. Comparing eqs 12, 13, and 24, we can reform eq 24 as

$$J \sim J_0\left[\exp\left(qV\frac{\Delta h_s}{\Delta E_F}\right) - 1\right] \equiv J_0\left[\exp\left(qV\frac{\Delta h_s}{k_B \Delta T_F}\right) - 1\right]$$

(25)

In equilibrium condition ($\Delta h_s \to 1$), the Navamani–Shockley diode equation becomes

$$J = J_0\left[\exp\left(\frac{qV}{E_F}\right) - 1\right] \equiv J_0\left[\exp\left(\frac{qV}{k_B T_F}\right) - 1\right]$$

(26)

For equilibrium nondegenerate and most of the weakly degenerate cases of a high-temperature limit ($T \geq 150$ K) $\left(\frac{\Delta h_s}{k_B \Delta T_F} \to \frac{1}{k_B T}\right)$ (see ref 8), we preserve the original Shockley diode equation from eq 25. During the trap-free diffusion current of the Langevin mechanism, the calculated ideality

factor is close to unity, $N_{id} \rightarrow 1$ (see Figure 3). For instance, using current density−voltage characteristic study under
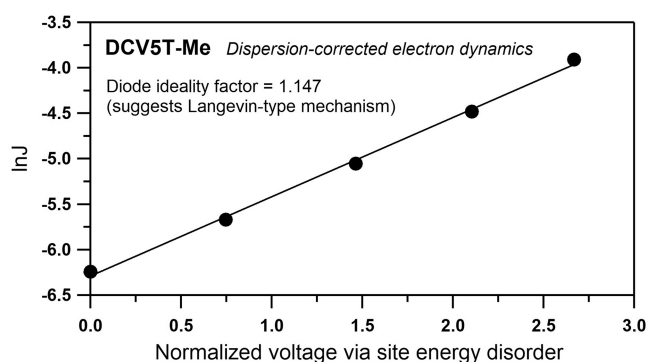

Figure 3. Logarithmic current density with respect to the normalized voltage at different site energy disorder (0, 20, 40, 60, and 80 meV) for electron transport in the DCV5T-Me molecule. In this calculation, the dispersion−correction is included. The ideality factor (N_{id}) is obtained from the logarithmic current density (ln J)−voltage (V) characteristic study. The numerical differentiation of this plot shows the validity of the *Navamani−Shockley* diode equation.

dispersion−correction, the calculated ideality factor for the DCV5T-Me molecule is 1.147, which suggests the Langevin transport (see Figure 3). Here, the expected D/μ relation is equal to 1.147 times the Einstein value, k_BT/q.

At a low temperature limit ($T \rightarrow 0$), the Navamani−Shockley diode current equation for quantum degenerate molecular devices is $J = J_0\left[\exp\left(qV\frac{\Delta h_s}{\Delta E_F}\right) - 1\right]$. Now, our analogy of the D/μ relation becomes quantum in nature and will be $\frac{D}{\mu} = \frac{5}{3q}\frac{d\eta}{dh_s} \equiv \frac{1}{q}\frac{dE_F}{dh_s}$. On the other hand, in the trap-assisted recombination mechanism (i.e., Shockley−Read−Hall (SRH) transport), the ideality factor will be close or equal to 2. Here, the Navamani−Shockley diode equation during the recombination process in quantum devices is explicitly described as

$$J = J_0\left[\exp\left(\frac{3}{10}qV\frac{\Delta h_s}{\Delta \eta}\right) - 1\right] = J_0\left[\exp\left(qV\frac{\Delta h_s}{2\Delta E_F}\right) - 1\right]$$

(27)

Now, the analogy turns out to be $\frac{D}{\mu} = \frac{10}{3q}\frac{d\eta}{dh_s} \equiv \frac{2}{q}\frac{dE_F}{dh_s}$. Here, the effective chemical potential with respect to the electron−hole dynamics at a particular electronic site in the studied organic semiconductor is $\Delta\eta_{reco} = \eta_e - \eta_h = 2\eta$, since $\eta_e = -\eta_h = |\eta|$. For disordered molecular solids (classical regime) at a high-temperature limit, the diode equations for the Langevin and SRH mechanisms are $J = J_0\left[\exp\left(\frac{qV}{k_BT}\right) - 1\right]$ and $J = J_0\left[\exp\left(\frac{qV}{2k_BT}\right) - 1\right]$, respectively. In such a high-temperature limit, as we discussed earlier, the original Einstein's relation will be retained from our proposed analogy.

Some of the interesting ongoing research reports suggest that Dirac-type electronic transport is observed in some organic systems at appropriate thermodynamic conditions.[15,16] This leads to a new dimension of electronic transport in synergetic nature between molecules and materials via the

structure−property relationship. In the Dirac-type quantum regime, the chemical potential is the sole parameter for the D/μ relation. Hence, one needs to investigate the D/μ ratio in two-dimensional (2D) Dirac materials for a thorough understanding via our quantum−classical transition analogy. Due to relativistic characteristic phenomena, 2D Dirac systems naturally follow the transport behavior of $(2 + 1)$D (i.e., normal 3D) materials. Herein, among the best examples of the Dirac system is graphene. In this regard, we have here analyzed the electronic transport (via diffusion−mobility relation) of graphene to generalize our model for all Dirac systems from molecules to materials. Recently, Chen et al. explored the modulation of quantum mechanical resonance through the chemical potential oscillation in monolayer graphene.[17] In this experiment, the characteristics of a graphene mechanical resonator were systematically investigated at 4.3 and 300 K temperatures for different bias conditions by using a magnetic field ($\vec{B}$) and a gate voltage (V_g). In this resonator, the distance between the gate electrode and graphene was 200 nm. Here, graphene acts as a metallic plate. The results reveal the chemical potential (η)-driven electron density (n) flux between the Landau levels (LLs), which is naturally tuned by V_g and applied $\vec{B}$. From this experimental data, using eq 2, we here further compute the relative differential entropy (h_s) at different electron densities (n) for different V_g-driven η values, which is presented in Figure 4.
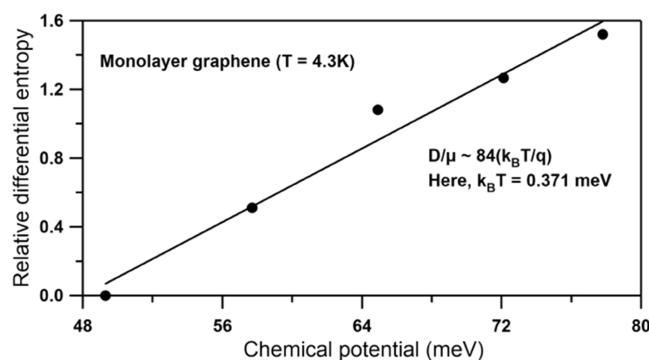

Figure 4. Chemical potential-driven differential entropy provides the diffusion−mobility ratio for monolayer graphene. The result shows a linear relationship between h_s and η. Here, the diffusion coefficient−mobility relation falls in the quantum regime and hence the mean free path is evolved instead of mean square displacement (since $D = l^2/(2\tau_{rel}) \equiv 2v_F^2\tau_{rel}/2$) instead of $D = \langle x^2(t)\rangle/2t$, which is responsible for the large enhancement in the D/μ ratio.

The present analysis here elucidates that the V_g-driven η significantly enhances the h_s and hence the expected orbital splitting (or degeneracy levels) will be more (compare Figures 1 and 4). In such a quantum limit, diffusion and mobility are associated with the mean free path and Fermi energy. On the other hand, for classical disordered systems, the diffusion and mobility are related with the mean squared displacement and temperature, respectively. Moreover, it was observed from an earlier report by Martin et al. that for each volt of variation by back-gate voltage (V_g), the electron density (n) changes in the order of 7×10^{10} cm^{-2} for monolayer graphene.[18] This experiment was performed at 0.3 K. Using this relation, we extend the V_g-tuned Fermi energy and μ/D relation, which is shown in Figure 5.
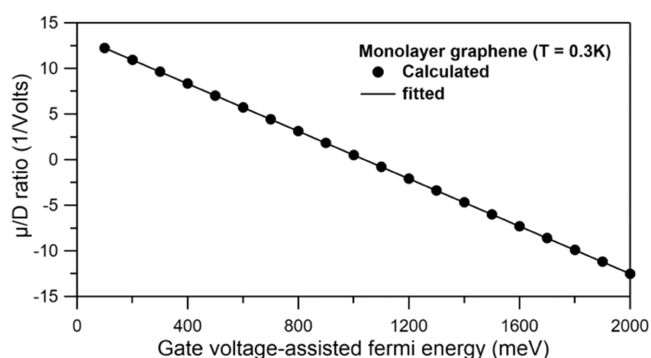
Figure 5. Inverse of the D/μ ratio linearly decreases with the gate voltage-driven Fermi energy, which describes the pure quantum nature of the D/μ relation. In this case, the synergy between Fermi energy and differential entropy is the deterministic factor for this basic transport relation.

The authors observed the carrier density flux changes when the magnetic field was turned on (i.e., 0 to 11 Tesla).[18] Here, the noted carrier density distribution follows the Gaussian-based disorder width (σ). At $\vec{B} = 11T$, the estimated σ magnitude was 6 times greater than that calculated at 0 T (i.e., $\sigma_{\vec{B}=11T} \cong 6\sigma_{\vec{B}=0T}$). In this situation, using our quantum—classical transition analogy, the calculated D/μ ratio value is around 40 mV (see Figure 5). The analysis clearly illustrates that the synergetic relation between the Fermi energy (chemical potential) and differential entropy determines the value of the D/μ ratio for all typical systems with a wide range of thermodynamic limits.

4. CONCLUSIONS

In summary, based on our developed four sets of analytical procedures, it is concluded that the proposed analogy $\left(\frac{D}{\mu} = \frac{5}{3q}\frac{d\eta}{dh_s}\right)$ is a unified form of all typical transport relations, from quantum to classical in both the cases of equilibrium and nonequilibrium. Our analogy (in terms of four sets of analytical procedures) is numerically verified and tested for dialkyl-substituted thienothiophene-capped benzobisthiazole (BDHTT-BBT) and methyl-substituted dicyanovinyl-capped quinquethiophene (DCV5T-Me) molecular solids, as well as for Dirac-type electron—hole dynamical systems (e.g., graphene) at different physical limits. According to the four sets of analytical procedures, the Navamani—Shockley diode current density equation will be transformed. Our study suggests that for the systems of large *degeneracy stabilization energy* (for large chemical potential), we anticipate the electric field-response diffusion coefficient is more dominant than mobility. On the other hand, for highly degeneracy cases (in terms of large differential entropy), the typical transport is dominated by the mobility (or field-response mobility) rather than the diffusion coefficient. Our analogy of Einstein's D/μ ratio (along with the four sets of analytical procedures) is a more suitable analogy for both the molecular (e.g., organic) and material (e.g., inorganic) systems in entire thermodynamic ranges, which is the unified transport analogy. This is a basic anatomy for designing novel electronic devices, which might lead to a new dimension in next-generation semiconductor technology.

AUTHOR INFORMATION

Corresponding Author

Karuppuchamy Navamani − *Department of Physics, Centre for Research and Development (CFRD), KPR Institute of Engineering and Technology, Coimbatore 641407, India;* orcid.org/0000-0003-1103-2393; Email: pranavam5q@gmail.com

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c08046

Notes

The author declares no competing financial interest.

REFERENCES

(1) Wetzelaer, G. A. H.; Koster, L. J. A.; Blom, P. W. M. Validity of the Einstein relation in disordered organic semiconductors. *Phys. Rev. Lett.* **2011**, *107*, No. 066605.

(2) Roichman, Y.; Tessler, N. Generalized Einstein relation for disordered semiconductors—implications for device performance. *Appl. Phys. Lett.* **2002**, *80*, 1948.

(3) Abou, B.; Gallet, F. Probing a nonequilibrium Einstein relation in an aging colloidal glass. *Phys. Rev. Lett.* **2004**, *93*, No. 160603.

(4) Fratini, S.; Ciuchi, S. Bandlike motion and mobility saturation in organic molecular semiconductors. *Phys. Rev. Lett.* **2009**, *103*, No. 266601.

(5) Navamani, K. Revisiting Einstein's diffusion-mobility relation for universal quantum materials: A generalized paradigm. *Europhys. Lett.* **2021**, *134*, 47001.

(6) Navamani, K.; Pati, S. K.; Senthilkumar, K. Effect of site energy fluctuation on charge transport in disordered organic molecules. *J. Chem. Phys.* **2019**, *151*, No. 224301.

(7) Troisi, A. Charge transport in high mobility molecular semiconductors: classical models and new theories. *Chem. Soc. Rev.* **2011**, *40*, 2347.

(8) Navamani, K. Continuum time-delayed electron hopping in the extended dynamical molecules and entropy-ruled Einstein relation for organic semiconductors. *J. Phys. Commun.* **2021**, *5*, No. 075012.

(9) Bazant, M. Z. Theory of Chemical kinetics and charge transfer based on nonequilibrium thermodynamics. *Acc. Chem. Res.* **2013**, *46*, 1144−1160.

(10) Navamani, K.; Rajkumar, K. Generalization on entropy-ruled charge and energy transport for organic solids and biomolecular aggregates. *ACS Omega* **2022**, *7*, 27102−27115.

(11) Ashroft, N. W.; Mermin, N. D. *Solid State Physics*; Cengage Learning: India Edition, 2011.

(12) Mahan, G. D. *Many-Particle Physics*, 3rd ed.; Kluwer Academic: 2000.

(13) Mendels, D.; Tessler, N. Drift and diffusion in disordered organic semiconductors: the role of charge density and charge energy transport. *J. Phys. Chem. C* **2013**, *117*, 3287−3293.

(14) Wetzelaer, G. A. H.; Blom, P. W. M. Diffusion-driven current in organic-semiconductor diodes. *NPG Asia Mater.* **2014**, *6*, No. e110.

(15) Ohki, D.; Yoshimi, K.; Kobayashi, A. Transport properties of the organic Dirac electron system α-(BEDT-TSeF)$_2$I$_3$. *Phys. Rev. B* **2020**, *102*, No. 235116.

(16) Pan, H.; Zhang, H.; Sun, Y.; Li, J.; Du, Y.; Tang, N. C$_4$N$_3$H monolayer: A two-dimensional organic Dirac material with high Fermi velocity. *Phys. Rev. B* **2017**, *96*, No. 195412.

(17) Chen, C.; Deshpande, V. V.; Koshino, M.; Lee, S.; Gondarenko, A.; MacDonald, A. H.; Kim, P.; Hone, J. Modulation of mechanical resonance by chemical potential oscillation in graphene. *Nat. Phys.* **2016**, *12*, 240−244.

(18) Martin, J.; Akerman, N.; Ulbricht, G.; Lohmann, T.; Smet, J. H.; Klitzing, K.; von Yacoby, A. Observation of electron-hole puddles in graphene using a scanning single-electron transistor. *Nat. Phys.* **2008**, *4*, 144−148.