generalization on entropy-ruled charge and energy transport for organic solids and biomolecular aggregates

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abstract: herein, a generalized version of the entropy-ruled charge and energy transport mechanism for organic solids and biomolecular aggregates is presented. the effects of thermal disorder and electric field on electronic transport in molecular solids have been quantified by entropy, which eventually varies with respect to the typical disorder (static or dynamic). based on our previous differential entropy (hₐ)-driven charge transport method, we explore the nonsteady carrier energy flux principle for soft matter systems from small organic solids to macro-biomolecular aggregates. through this principle, the synergic nature of charge and energy transport in different organic systems is addressed. in this work, entropy is the key parameter to classify whether the carrier dynamics is in a nonsteady or steady state. besides that, we also propose the formulation for unifying the hopping and band transport, which provides the relaxation time−hopping rate relation and the relaxation time−effective mass ratio.

the calculated disorder drift time (or entropy-weighted carrier drift time) for hole transport in an alkyl-substituted triphenylamine (tpa) molecular device is 9.3 × 10⁻⁷ s, which illustrates nuclear dynamics-coupled charge transfer kinetics. the existence of nonequilibrium transport is anticipated while the carrier dynamics is in the nonsteady state, which is further examined from the rate of traversing potential in octupolar molecules. our entropy-ruled einstein model connects the adiabatic band and nonadiabatic hopping transport mechanisms. the logarithmic current density at different electric field-assisted site energy differences provides information about the typical transport (whether trap-free diffusion or trap-assisted recombination) in molecular devices, which reflects in the navamani−shockley diode equation.

1. introduction

the diffusion−mobility relation generally provides fundamental transport properties for all classes of materials, from classical to quantum systems. according to the generalized paradigm, diffusion mobility is directly related to the carrier density and thermodynamic density of states of the system. from our earlier studies, it has been emphasized that entropy is a key parameter to study the electric field coupled with disordered transport in molecular solids. the interesting fact is that the entropy-dependent charge density and diffusion coefficient relations are originally derived from the entropy-committed energy flux equation. this energy flux equation explains the entropy-mediated variation in energy flux under nonsteady-state conditions. here, the entropy-dependent charge density and diffusion relations are directly involved in charge transport calculations. moreover, previous reports also endorse the importance of entropy-driven charge separation efficiency in different organic−metal frameworks. the coupled effect of thermal and quantum flux on charge and energy transport can be quantified by appropriate entropy parameters (e.g., vibrational entropy, differential entropy, etc.). various typical interactions (including lattice dynamics) also play a vital role in

charge and energy transport in electronic devices. from our earlier reports, it is made clear that thermally coupled chemical potential is the primary tuning thermodynamic entity for optoelectronic properties, which is directly related to entropy. in this regard, the entropy-committed electronic transport in different organic−organic and organic−inorganic compounds is of great interest for novel electronic devices. with this motivation, modeling the entropy-ruled electronic transport method for universal quantum systems (from low- to high-dimensional systems) is our main focus for the next generation of semiconductor technology. among the various charge transport models and theorems, the einstein diffusion−mobility relation is the basis to study the electronic/charge transport properties of any system of interest (from molecules

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to materials). In principle, diffusion-based mobility is strongly associated with the intrinsic nature (electronic or band structure) of molecules/materials. Essentially, the diffusion–mobility ratio (or Einstein’s relation) elucidates the device performance, which has a direct relationship with current density ($J$)–voltage ($V$) characteristics. For instance, the enhancement of diode performance can be illustrated by the ideality factor, which is the main consequence of the diffusion–mobility relation.\(^7,8\)

The celebrated Einstein’s diffusion–mobility relation works perfectly well for most of the classical systems even at quasi-equilibrium. But over the last five decades, there are many experimental and theoretical reports on quantum systems that deviate from the original value of Einstein’s classical relation.\(^2\)\(^-\)\(^13\) The reason for the deviations is that the real materials are not truly classical, and even most of the molecular degenerate systems are quasi-quantum systems. In general, quasi-quantum systems have a weak disorder (due to various typical defects), electron–electron interactions, electron–phonon interactions, and various other interactions.\(^4\)\(^-\)\(^10\)\(^,\)\(^12\)\(^-\)\(^18\)

In such degenerate cases, the classical Einstein relation does not work, and essentially, it cannot explain the charge transport at low temperatures, where most of the phenomena are quantum in nature.\(^7\)\(^,\)\(^13\)\(^,\)\(^19\)\(^-\)\(^20\) The presence of disorder in the systems possibly drives them to reduce their symmetries for energy stability. The Einstein relation is valid for a non-interacting lower particle density system at high temperatures along with equilibrium or quasi-equilibrium conditions.\(^21\) In the context of diode functioning, Einstein’s original relation poorly explains the diffusion ideality factor.\(^4\)\(^,\)\(^11\)\(^,\)\(^17\) The effect of electric field-coupled energetic disorder is quite important in organic semiconductors, since various inevitable interactions, including electronic and nuclear degrees of freedom, control the charge transport.\(^14\)\(^-\)\(^16\)\(^,\)\(^24\)\(^-\)\(^28\) The transition from dynamic to static disordered transport is anticipated in molecular devices when the magnitude of the applied electric field increases.\(^3\) Also, real materials usually have several scattering processes arising from various interactions between the charge carriers and the lattice vibrations. These scattering processes lead the system to reach a nonsteady-state domain, where the classical Einstein equation (diffusion–mobility ratio) possibly takes a deviation from its original value of $k_B T / q$, where, $k_B$, $T$, and $q$ are the Boltzmann constant, temperature, and electronic charge, respectively. Recent reports also suggest the nonlinear electronic transport enhancement, which again confirms the deviation of the classical Einstein relation.\(^10\)^\(^,\)\(^29\)

In principle, the charge transport in vibronic-coupled disordered systems, like organic solids and biomolecules is estimated using the Master equation method or kinetic Monte-Carlo (KMC) simulations.\(^14\)\(^,\)\(^24\)\(^-\)\(^27\)\(^,\)\(^30\)\(^-\)\(^32\) The dynamic disorder due to structural kinetics gives rise to on-site potential flux, which drifts the carrier motion along the preferred hopping pathway.\(^24\)\(^,\)\(^28\)\(^,\)\(^33\) In such drift-diffusion cases, the properties can be numerically characterized by the drift disorder time.\(^25\)\(^,\)\(^26\)\(^,\)\(^34\)\(^,\)\(^35\) Here, the drift mobility takes a deviation from the equilibrium mobility (from Einstein’s relation), and the dynamical disorder in organic media results in a crossover mechanism from hopping to band-like transport.\(^16\)\(^,\)\(^25\)\(^,\)\(^26\)\(^,\)\(^28\)\(^,\)\(^36\)\(^-\)\(^39\)

It is to be noted from various dynamic disorder studies that there is a possibility of band-like transport in organic media due to dynamic localization,\(^4\)\(^,\)\(^25\)\(^,\)\(^28\)\(^,\)\(^40\) flickering resonance,\(^37\)\(^,\)\(^41\) orbital splitting (or degeneracy),\(^23\)\(^,\)\(^42\) coherent effect,\(^14\)\(^,\)\(^43\) and potential-induced drift force.\(^7\)\(^,\)\(^15\)\(^,\)\(^32\)\(^,\)\(^35\)\(^,\)\(^36\)\(^,\)\(^38\)\(^,\)\(^44\) In this scenario, the dynamic-to-static disorder conversion (or vice versa) effect needs to be included in charge transfer analysis in multisite electronic media (multiple local minima of potential energy surfaces) of the extended hopping molecular systems.\(^15\)\(^,\)\(^16\)\(^,\)\(^22\)\(^,\)\(^25\)\(^,\)\(^26\)\(^,\)\(^35\)\(^,\)\(^36\)\(^,\)\(^45\)\(^-\)\(^47\) To analyze the typical disorder effect on charge transfer kinetics, the entropy is effectively considered here for charge separation and drift-diffusion studies.\(^17\)\(^,\)\(^45\)\(^,\)\(^48\)\(^,\)\(^49\) Mendels and Tessler described the charge and energy transport during the drift-diffusion process in disordered degenerate semiconductors.\(^18\) They pointed out that the dependence of charge density on energy transport is an intensive matter in high-density devices (degenerate classes of materials), which leads to chemical potential-dependent drift-diffusion. Moreover, Navamani’s entropy-ruled Einstein relation clearly shows the traversing nature of chemical potential along the hopping sites, and its consequential effects on semiconducting properties.\(^7\) This shuttling chemical potential is strongly associated with differential entropy, which provides information about the degenerate weight on charge and energy transport in molecular solids.

From the above discussion, it is clear that there is no single complete theory that could explain both the charge and energy transport in the quantum domain. In this line, it is necessary to generalize entropy-ruled charge and energy transport theory for a wide range of nanosystems under different thermodynamic conditions. With this motivation (taking into account all of the above key issues), we derive a unified formalism to get a better understanding of charge and energy transport in different classes of molecular solids, from weak to strong degenerate regimes. In this paper, we have introduced an extended version of the entropy-ruled charge and energy transport method to study the drift-coupled diffusion transport. According to our proposed entropy-dependent diffusion and charge density expressions, one can explore both the charge and energy transport (i.e., drift-diffusion) at different magnitudes of the applied electric field for any molecular solids and devices. Here, effective entropy incorporates the effects of thermal disorder and degeneracy weightage on electron/hole kinetics in organic systems. The proposed method is the generalized one, which connects both the quantum and classical transport via two parameters, effective entropy and chemical potential. In this method, one-to-one variation between effective entropy and chemical potential describes well to determine the device performance, as well as to decide the typical transport type (i.e., quantum or classical or intermediate).

2. MODEL

The generalized charge and energy transport relation for organic semiconductors can be described as\(^1\(^,\)\(^5\)

\[
\frac{dE}{dt} = \frac{q^2}{\epsilon} D n
\]

(1)

where $\frac{dE}{dt}$ is the carrier’s energy transfer rate, $q$ is the electronic charge, $n$ is the electron density, $\epsilon$ is the electronic permittivity of the material, and $D$ is the diffusion coefficient. From the above generalized charge and energy transport relation (eq 1), the carrier energy rate directly depends on the charge diffusion coefficient and carrier density (electron or hole) in the concerned molecular devices. Here, the nonsteady-state energy transport (nonuniform potential flux) $\frac{dE}{dt} \neq 0$ is expected when...
diffusion takes place in molecular solids (see eq 1). That is, the existence of nonsteady energy flux is observed for both the cases of steady and nonsteady state diffusion transport in the molecules. The main corollary is that the particle flux (in terms of diffusion) causes the existence of nonsteady energy transport. According to our earlier model,\textsuperscript{2,4,5} the rate of traversing carrier’s energy flux (i.e., nonsteady energy transport) with respect to entropy changes in the conjugated molecular sites can be related by

\[
\frac{dE(\hat{E}, T)}{dt} = \frac{dE}{dt} \exp\left(\frac{h_S - \frac{S}{k_B}}{k_B}\right)
\]  

(2)

where \(S\) is the entropy that quantifies the amount of disorder change due to randomness by thermal fluctuation, defect states, and various interactions such as phonon scattering, and \(k_B\) is the Boltzmann constant. In molecular solids at high temperatures (\(T > 150\) K), the breakdown of the translational symmetry leads to a nonperiodic potential energy surface (PES). The energy difference between two adjacent local minima of PES of the molecule is the barrier height, which is the energetic disorder for the charge transport. If the disorder energy landscape is more, then the expected electronic interactions will be minimum, which leads to higher entropy (\(S\)). For ordered structures, on-site interactions/electronic couplings are large enough, and hence, the entropy is almost negligible. In our study, the entropy \(S\) mainly elucidates the thermal effect on electronic transport. On the other hand, the parameter \(h_S\) is the differential entropy, which provides the degenerate weightage on transport and it can be tuned by the applied bias or electric field. The field response on electronic transport (mobility) is described by \(h_S\). Here, the differential entropy mainly deals with the electronic degeneracy (or orbital splitting), which is usually associated with the Gaussian disorder width (\(\sigma\)). The existence of degenerate states due to the applied electric field (stark effect) or magnetic field (Zeeman effect) can be quantified by the disorder width, \(\sigma\). In principle, the existence of degeneracy levels is related by \(h_S \propto \ln Z\), where \(Z\) accounts for all possible existing electronic states. The charge transport in molecular solids is well approximated by the Gaussian disordered model.\textsuperscript{3} Thus, the parameter \(h_S\) is derived from the Gaussian function \(\Phi(\chi)\). Here, \(h_S = -\int \Phi(\chi) \ln \Phi(\chi) d\chi\), where \(\Phi(\chi) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{x^2}{2\sigma^2}\right)\). For large values of \(h_S\), the transport will be in higher order due to the existence of degeneracy, and hence, the charge transport is kinetically favored. In principle, the thermal entropy term \(S\) does not favor the charge transport, but the differential entropy term \(h_S\) supports the electronic transport, which is normally high for degenerate systems. In this regard, effective entropy is defined as \(h_{\text{eff}} = h_S - \frac{S}{k_B}\). The governing energy rate expression (eq 2) clearly describes that the presence of entropy (or entropy changes by thermal and electronic degeneracy) facilitates the variation in nonsteady energy transport. This is named the nonsteady energy flux equation, which helps to explore the synergic nature between the charge and energy transport (see eqs 1 and 2). It is to be noted that the carrier energy rate is directly proportional to the diffusion coefficient and the charge density. At zero applied electric field, the carrier energy rate might depend only on the diffusion property. On the other hand, when there is an applied bias, the drift-coupled diffusion is anticipated, which improves the traversing carrier energy rate in molecular devices. As reported in earlier studies,\textsuperscript{3,5–6} the effect of the applied electric field, doping, and other interactions (including thermal effect) on charge and energy transport can be quantified by entropy parameters \(S\) and \(h_S\). Based on eq 2, one can emphasize that the variation in nonsteady energy flux strongly depends on the change in entropy due to various internal and external interactions of the system. For homogeneous systems, the density gradient is negligible (i.e., \(dn/dx \rightarrow 0\)) and hence, the expected diffusive transport is a minimum but it can be improvised by the drift effect with the aid of an electric field or bias. Moreover, the amount of typical disorder (static or dynamic) also has a significant impact on drift-diffusion transport. Our entropy-dependent charge transport method provides nonlinear charge transport with the disorder or relative entropy.\textsuperscript{7} This nonlinear transport includes both drift and diffusion. The randomness of electronic sites possibly takes the system to a nonequilibrium state, which can be modified by the applied electric field. In this regard, the correlation between electron density due to the effective disorder in both equilibrium and nonequilibrium cases can then be expressed as follows\textsuperscript{3,26}

\[
n_{n_{h,S}} = n_0 \exp\left(\frac{3}{5}\left(h_S - \frac{S}{k_B}\right)\right)
\]

(3)

The \(\pi\)-electron density for charge transport can be quantified by eq 3. With respect to the thermal disorder and applied electric field, the carrier density accordingly contributes to the electronic transport, which can be estimated using parameters \(S\) and \(h_S\) respectively. According to the entropy changes, the charge redistribution is anticipated, which is mainly responsible for delocalization. In principle, the presence of disorder makes significant changes in electronic transport.\textsuperscript{,48,49} To achieve high performance in molecular devices (e.g., OPVs and OLEDs), we choose degenerate systems that have rich electron density. In principle, the differential entropy \(h_S\) is related by \(h_S = \ln(\sigma \sqrt{2\pi e})\). Here, \(\sigma\) represents the Gaussian disorder width, which provides information on the delocalization/localization property of the molecules. This is associated with \(h_S\), which is a direct consequence of degeneracy (for more details, see ref 3). As expressed in our earlier studies,\textsuperscript{3,4} \(h_S\) is calculated from the relation

\[
h_{\text{eff}} = \ln\left(\frac{(dE/dt)}{(dE/dt)_0}\right),
\]

which originated from the nonsteady energy flux principle (see eq 2). Moreover, numerous studies confirm that there is an enhancement of charge transport in organic semiconductors due to the effects of the non-Condor principle, dynamic localization, and orbital splitting, which are mainly responsible for degeneracy.\textsuperscript{16,24,25,28,34,35,38} In such degenerate cases, the charge transport deviates from the hopping regime and moves toward the band-like or intermediate regime. This crossover mechanism strongly underlies the nonequilibrium diffusion transport. Due to the presence of disorder (which includes thermal disorder, randomness in the electronic site, and degeneracy weight) in the materials, the charge transport property is modified. This disordered transport can be characterized by entropy-dependent charge and diffusion expressions. In this regard, the governing expressions of the entropy-modulated diffusion coefficient for disordered systems are as follows:\textsuperscript{3,4}
The above diffusion expression is in agreement with an earlier observation that was proposed by Bregg.\textsuperscript{48} Besides that, various studies confirm that the presence of entropy improves the charge diffusion process in organic solids, which is the direct evidence of our relation (see eq 4).\textsuperscript{6,12,48} Using eqs 1\textendash{}4, one can explicitly explain the synergy between charge and energy transport, which is named the nonsteady carrier energy flux principle. The first two expressions are related to the nonsteady energy transport and the latter two equations give the charge transport in molecular solids. These four sets of analytical expressions are dependable on relative entropy (or entropy changes). Here, entropy is the ruling parameter for both charge and energy flux with respect to effective interactions. The charge carrier flux in the form of a diffusion process directly enrolls the nonsteady-type energy distribution in the molecules. These four sets of equations expound on the nonsteady energy transport, which is here named ‘nonsteady carrier energy flux principle’ or ‘diffusion-adapted unsteady energy flux principle’ (see eqs 1 and 2).

Generally, diode functioning can be investigated by the ideality factor, which is associated with the enhancement parameter, \( g \geq 1 \). In principle, the Shockley diode equation (current density \( J \)\textendash{}voltage \( V \) characteristic relation) is naturally associated with the Einstein diffusion\textendash{}mobility ratio factor. Through the ideality factor value, the possible deviation in Einstein’s relation for different materials is incorporated. In this regard, the generalized form of Einstein’s relation can be written as follows:\textsuperscript{2,60}

\[
\frac{D}{\mu} = \frac{k_B T}{q} = \frac{n}{q \frac{\partial \eta}{\partial \eta}} = \frac{1}{q \frac{\partial \eta}{\partial \eta} \ln n}
\]  

(5)

where \( \eta \) is the chemical potential. The chemical composition, type, and position of the heteroatoms in the molecular solids and the external interactions (e.g., applied bias) decide the magnitude of chemical potential. According to our method, the chemical potential plays a vital role in molecular charge transport.

In the present study, we have developed a method to understand the drift-diffusive behavior in real molecular devices via the enhancement parameter \( g \), which is a function of entropy (includes temperature, randomness, and bias effects), chemical potential, and charge density. It has been noted that parameter \( g \) has a nonlinear dependence on \( n \), chemical potential, \( \eta \), and disorder. To obtain a clear insight into disorder-coupled electronic behavior in molecular solids, we propose the entropy-rulled Einstein relation for molecular systems. Inserting eq 3 in eq 5, the diffusion\textendash{}mobility ratio becomes (see ref 4)

\[
\frac{D}{\mu} = \frac{5}{3q \frac{\partial \eta}{\partial \eta}}
\]  

(6)

From the above relation (eq 6), it is observed that the diffusion\textendash{}mobility ratio is inversely proportional to the slope of effective entropy with respect to the chemical potential. This is known as the Navamani’s entropy-rulled method for diffusion mobility transport. This diffusion-based mobility transport (or modified Einstein \( D/\mu \) relation) is one of the key parameters in the current density \( f \)\textendash{}voltage \( V \) characteristic study, which is usually incorporated by the diode equation.\textsuperscript{21} In this regard, the performance of the normal Shockley diode equation for different molecular devices can be analyzed by the ideality factor in different applied bias situations. As described in the previous study, the Navamani\textendash{}Shockley (NS) diode equation for molecular quantum devices can be written as follows\textsuperscript{6}

\[
J = \frac{3q}{5} \frac{\partial \eta}{\partial \eta} \exp \left( \frac{3q}{5} \frac{\Delta h_{\text{eff}}}{\Delta \eta} \right) - 1
\]  

(7)

where \( J, J_0, V, \) and \( \Delta h_{\text{eff}}/\Delta \eta \) are the current density, saturation current density, applied voltage, and the variation of differential entropy with respect to the chemical potential, respectively. This NS diode equation (eq 7) is the modified version of the Shockley diode equation, which is suitable for both the quantum and classical systems of molecules. Here, the chemical potential can be adjusted by varying the applied electric field (or gate voltage) or by electrochemical doping. When there is a change in chemical potential or temperature or both, the effective entropy will be varying in the form of field-dependent degeneracy (in the form of \( h_s \) and thermal disorder (in the form of \( S \)). The thermal disorder and its consequences on asymmetric electronic levels resist the charge transport due to localization. To this extent, the density of states \( \frac{\partial \sigma}{\partial \eta} \) of conductivity \( \sigma \) relation, \( \sigma = q^2 T \frac{\partial \sigma}{\partial \eta} \) is redefined as follows

\[
\sigma_{h_s} = \frac{3q^2}{5} \frac{n_0 D_0 \frac{\partial h_{\text{eff}}}{\partial \eta}}{\partial \eta} \exp(h_{\text{eff}})
\]  

(8)

From this entropy-rulled conductivity expression (eq 8), it is observed that the presence of entropy in the molecular systems increases electronic transport. In principle, the chemical potential acts as a driving force to drift the electron/hole kinetics. Using our entropy-rulled method, we illustrate the charge transport mechanism in a new perspective with two parameters of effective entropy and chemical potential, giving a new direction to organic semiconductor technology. Our recent works on organic semiconductors clearly explain the physics of deviation in Einstein’s relation and its effect on device performance via the ideality factor.\textsuperscript{3,4} To this extent, the proposed method hereby further provides a deeper understanding of molecular charge transport by our entropy-rulled charge transport formalism. Importantly, the changes of effective entropy with respect to the chemical potential \( \frac{\Delta h_{\text{eff}}}{\Delta \eta} \) or vice versa is the key descriptor to explore both the quantum and classical features of charge and energy transport. Using this method, we can investigate the synergy of thermal and quantum flux in molecular devices under different physical conditions. Accordingly, the cooperative relation between charge and energy transport in the drift-diffusion mechanism is explicitly addressed in this paper. The degenerate weighted entropy \( h_s \) helps to make more charge separation from low- to high-dimensional excitonic systems, which is confirmed by various studies.\textsuperscript{6} The enhancement of entropy due to degeneracy increases the conductivity, and hence, it has direct consequences on field-effect transistors. However, diffusion-based electrical conductivity is limited while the thermal disorder is increased, which is in good corroboration with Troisi’s studies.\textsuperscript{16,24,40} In principle, the typical heterojunction of electronic devices decides the charge separation efficiency via the free energy difference. For molecular semiconductors, free energy is directly associated with the site energy difference.
The site energy is the energy of an electron or hole when it is localized at a particular molecular site. This site energy of the carrier can be modified by the applied electric field or electron–hole doping. As described in our earlier studies, the effect of the electric field-assisted site energy difference ($\Delta E_i$) on charge carrier dynamics can be characterized by entropy $h_s$. The charge separation in heterojunctions or interfaces of any quantum device depends dominantly on the electron’s or hole’s site energy difference rather than that of thermal energy, $\Delta E_i \gg k_i T$. In this regard, electronically weighed entropy $h_s$ is the crucial parameter to design ideal devices. As discussed above, $h_s$ originally provides the degeneracy weight on electronic transport (field response behavior), which can be tuned by gate voltage or external electric field. The dynamic disorder possibly enhances $h_s$, which in turn facilitates hopping to band-like transport. Also, various studies have shown that there is an intermediate transport between hopping and the band mechanism in different molecular solids, which is strongly associated with molecular packing, self-aggregation, dynamic disorder, etc.

The observed crossover in the charge transport equation in various disordered semiconductors demands generalization between localized hopping and the delocalized band transport mechanism. The electronic and nuclear degrees of freedom along with interfacial fluctuations give rise to a polaronic cloud in the material, which effectively determines the enhancement in electronic transport. Notably, the dynamically induced dielectric property is commonly observed in most disordered molecular semiconductors. Because of the on-site potential flux, the current density gradient is anticipated along hopping sites, which can be illustrated by the continuity equation. Therefore, the carrier dynamics in dynamical systems is polaron dominated. On the basis of the above, we generalize the hopping and band transport through the charge transfer rate ($K_{CT}$)–relaxation time ($\tau_{\text{rel}}$) relation as

$$\tau_{\text{rel}} = \frac{e m}{q n} K_{\text{CT}}$$

(9)

where $\tau_{\text{rel}}$ and $K_{\text{CT}}$ are the carrier relaxation time and charge transfer rate, respectively. Note that the above generalized hopping and band transport expression depends on the electric permittivity of the medium ($\varepsilon$), effective mass ($m$), electron density ($n$), and charge transfer rate ($K_{\text{CT}}$). Here, $K_{\text{CT}}$ is usually estimated by the semiclassical Marcus theory. Now, the effective mass of the carrier is $m = \gamma \tau_{\text{rel}}$. According to the typical disorder (static or dynamic) in organic molecular media, the carrier dynamics is characterized by the frictional coefficient, $\gamma$. In this connection, the charge transfer rate and the frictional coefficient are related as follows

$$\gamma = \frac{q^2 n}{\varepsilon K_{\text{CT}}}$$

(10)

These generalized hopping and band transport conjectures (eqs 9 and 10) agree well with earlier reports. In the present charge transport method, the polaronic nature can be studied from the electric permittivity of the medium ($\varepsilon$), which is in agreement with Troisi’s arguments based on the Hall effect measurement carried by Podzorov et al.

In this work, we have developed the carrier relaxation time ($\tau_{\text{rel}}$)–effective mass ($m$) ratio, i.e., $\tau_{\text{rel}} = \frac{D}{k_{B} T}$. The relaxation time decreases with temperature, due to thermal scattering. This relation connects both localized hopping and delocalized band transport. The electronic contribution for electron/hole dynamics in the devices is larger at the quantum limit of low temperature. In principle, the superposition of electronic states is disturbed when the temperature increases; therefore, the thermally assisted disorder breaks the symmetrical interactions. Using this model, one can describe the charge and energy transport in various thermodynamics limits for both adiabatic and nonadiabatic transport regimes. The proposed method and formalism are helpful for experimentalists to engineer the device’s performance as well as stability.

Besides that, the survival probability-correlated energy redistribution function can be helpful to study the nonequilibrium charge and energy transport. For molecular transport, the electron/hole hopping takes place by thermal activation. According to the earlier method, the potential redistribution function under nonequilibrium circumstances can be characterized as follows

$$V_d(t) = g(S, E, T) \frac{k B T}{q} (1 - \exp(1 - P(t)))^{16/15}$$

(11)

where $V_d(t)$ is the potential drift, $g$ (i.e., enhancement parameter) is a function of disorder, electric field, and temperature, and $P(t)$ represents the survival probability of charge in an initial electronic site. This expression deals with the drift-coupled diffusion transport under nonequilibrium conditions. The basic point is that $g$ is always greater than or equal to 1 and possibly increases with the electric field. At high temperatures, the thermal potential variation during the charge transport can be illustrated by eq 11.

Here, the drift potential expression dictates the $D/\mu$ values in a high electric field (when it becomes nonlinear), where the $g$ parameter is larger than unity. At weakly disordered (or quasi-equilibrium) and very low or zero field conditions, parameter $g \rightarrow 1$ in which the drift-like transport (eq 11) is reduced as

$$V_d(t) = \frac{k_{B} T}{q} (1 - \exp(1 - P(t)))^{16/15}$$

Thus, the field-enhanced diffusion mobility equation can be written as

$$\left(\frac{D}{\mu}\right)_{\text{non-equ}} = \left(\frac{D}{\mu}\right)_{\text{equ}} + V_d(t)$$

(13)

Here, the enhancement parameter ($g$) strongly depends on the drift potential and can be tuned by an electric field, disorder, and chemical potential. It is clear from this equation that even in quasi-equilibrium cases, the diffusion–mobility ratio deviates from the Einstein equation.

3. ANALYSIS AND APPLICATIONS

3.1. Drift-Diffusion Transport from Nonsteady- to Steady-State Regime. Using our method, one can predict the drift-diffusion behavior for any molecular device with a variety of intrinsic and external factors like weak to strong disorder, low or intermediate to high field effect, and linear to nonlinear regime transport behaviors. Interestingly, various earlier reports suggested the entropy effect on charge separation in organic photovoltaic cells in different molecular systems. Here, the Coulomb barrier is a key factor for

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electronic transport via charge separation and is strongly influenced by entropy for different molecular systems.\textsuperscript{48} These observations are clearly shown in our entropy-dependent diffusion, current density, and conductivity formalism for molecular semiconducting devices (see eqs 4–8). To obtain a clear picture of charge transport in organic layered devices, we revisit the previous experimental investigations, which explicitly provide hole transport in three different organic thin-film devices, P1, P2, and P3, at different bias voltages.\textsuperscript{54} These devices are originally fabricated by alkyl-substituted triphenylamine (TPA)-based molecules such as 2-(4-(5-(diphenylamino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene-malononitrile \((X1)\), 2-(4-(5-(4-(di-p-tolylamino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene)malononitrile \((X2)\), and 2-(4-(5-(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-1,3,4-oxadiazol-2-yl)benzylidene) malononitrile \((X3)\), respectively. Here, TPA derivatives have \(\pi\)-conjugation properties, playing a central role in enhancing the transport properties of semiconducting devices. Along with suitable side chains, the molecular packing of TPA in unit crystals can be modified; accordingly, the transport property is improved. The attachment of methyl and tert-butyl in the para-position of TPA leads to good optoelectronic properties as well as structural stability. The chemical structures of \(X1\), \(X2\), and \(X3\) molecules are given in the Supporting Information (see ref 54). It was reported that electronic device P3 has a large hole transporting ability compared to P1 and P2 devices. This is because the presence of tert-butyl-substituted \(X3\) derivative has notable electron-denoting and hyperconjugation properties. Therefore, we theoretically analyze the hole dynamics behavior in the P3 layered device. In principle, one can anticipate the state of nonequilibrium or quasi-equilibrium transport during the charge propagation along consequential hopping sites. In this paper, we reproduced the simulation results based on the previous study (see ref 54) to understand the transition from nonequilibrium to equilibrium transport via the quasi-equilibrium point in both the nonsteady- and steady-state dynamical regimes. The total charge propagation along multilayered hopping sites has been monitored at different voltages (see ref 54). To monitor the nonequilibrium hole transport in the P3 layered device, we have numerically tested the survival probability of the hole with time using Monte-Carlo (MC) simulations. The survival probability plot (see Figure 1) provides the nature of charge decay along the consequential layers in the P3 device, which can be modified by the bias voltage, doping, disorder, and other dynamical effects.

As described in the earlier study,\textsuperscript{34,36} the survival probability-correlated entropy variation is calculated by the relation \(S(t) = -k_B \ln [P(t)/P_0]\). Here, the survival probability follows the relation \(P(t) = P_0 \exp(-K_{CT} t)\). The thermal and site energetic disorder effect on the diffusion relation (see eq 4) is correlated to the entropy parameter \(S(t)\). Based on the typical disorder (static or dynamic) in terms of entropy, the diffusion trend is monitored (see Figure 2). The result shows that there is a transition from nonequilibrium to quasi-equilibrium diffusion in the nonsteady- to steady-state dynamics, respectively. In our simulation, it is assumed that the charge is initially localized at the first molecular site at one end of the molecular chain and then the charge propagates with time, along the consecutive sites toward the other end of the molecular chain. Here, nonsteady dynamical transport is expected up to a certain initial time range of simulation. This time range is referred to as the disorder drift time, \(t_d\) (see ref 26). As described in our earlier study, the “disorder drift time” gives information about how quickly the electron/hole transits from one localized site to the next site with respect to the dynamic disorder of the molecule.\textsuperscript{26,34} That is, this drift time correlates with the electron/hole dynamics and nuclear dynamics in the molecular media, which is the main consequence of the strength of interactions between electronic and nuclear degrees of freedom. At this disorder drift time, the electron/hole is influenced by the maximum drift effect by dynamic disorder. That is, until this time, the maximum probability of the charges is localized/distributed at the initial molecular site. The distribution of charges is not equal in the entire stacked system at or before drift time onset. This facilitates the transition from nonequilibrium to quasi-equilibrium transport, which is shown in Figure 2. In this case, the diffusion dynamics moves from the nonsteady state to the steady state. Notably, the cooperative behavior of nonsteady- and steady-state dynamics in nonequilibrium-to-equilibrium charge diffusion is found in the case of the P3 device, which leads to the drift-diffusion mobility of the P3 device (see Figure 2). However, in the case of P1 and P2 devices, the expected synergic behavior is minimal.

The existence of both steady and nonsteady dynamics-associated “nonequilibrium-to-equilibrium diffusion transition” is originated from electronic and nuclear degrees of freedom (or dynamic disorder). The disorder drift effect on carrier dynamics is mainly elucidated by parameter \(t_d\). It is to be noted that there is nonuniform diffusion dynamics in the nonsteady regime. In the present work, the changes in diffusion at the.
nonsteady regime, \(\frac{d\rho}{dt} \neq 0\), and invariance properties at the steady-state regime, \(\frac{d\rho}{dt} = 0\), are the significant observations here. Moreover, the nonequilibrium diffusion is observed until the time range of drift time \((t_d)\), and beyond that, the transport transits toward equilibrium. This drift time acts as a quasi-equilibrium point. The transition from nonequilibrium to equilibrium transport (via the quasi-equilibrium point) results in the deviation of Einstein’s diffusion–mobility ratio from its original value of \(\frac{\nu_0}{\eta}\). In this study, the disorder drift time \((t_d)\) acts as a conjunction parameter of both nonsteady and steady states on nonequilibrium-to-equilibrium transition transport. The rate of the average diffusion coefficient can be written as

\[
\left\langle \frac{dD}{dt} \right\rangle = \frac{D_{\text{non-equ}} - D_{\text{quasi-equ}}}{t_d} = \frac{D_{\text{non-equ}}}{t_d}
\]

(14)

\[
D_{\text{non-equ}} = \left\langle \frac{dD}{dt} \right\rangle t_d + D_{\text{quasi-equ}}
\]

(15)

According to eq 15, the Einstein’s diffusion–mobility relation can be described as

\[
\left( \frac{D}{\mu} \right)_{\text{non-equ}} = \frac{1}{\mu(t)} \left\langle \frac{dD}{dt} \right\rangle t_d + \left( \frac{D}{\mu} \right)_{\text{quasi-equ}}
\]

(16)

The first term on the right side of eq 16 is related to the drift kind of diffusive mobility, which is equivalent to the drift potential, \(V_{\text{drift}}\). The second term is related to the classical Einstein’s equation for pure diffusive transport (zero drift) and is normally observed at the equilibrium domain. As reported by earlier studies,21 Einstein’s original relation works well for the quasi-equilibrium state also. The above equation (eq 16) is the “nonequilibrium-assisted drift-diffusion transport” in both the regime of nonsteady and steady states for 2D and 3D organic semiconducting devices. In the steady-state limit, the \(D/\mu\) relation for the quasi-equilibrium state is \(\frac{D}{\mu} = \frac{k_B T}{\eta}\). Thus, eq 16 can be modified as

\[
\left( \frac{D}{\mu} \right)_{\text{non-equ}} = \frac{1}{\mu(t)} \left\langle \frac{dD}{dt} \right\rangle t_d + \frac{k_B T}{\eta}
\]

(17)

Here,

\[
\frac{1}{\mu(t)} \left\langle \frac{dD}{dt} \right\rangle t_d \propto \frac{dV}{dt} t_d
\]

The changes of diffusion \((D)\) and entropy \((S)\) at drift time \((i.e., t=td)\) and at nonequilibrium cases \((i.e., t=0)\) for two-dimensional \((2D)\) layered systems can be expressed as

\[
D_{\text{2D,non-equ}} = D_{\text{2D,t=t_d}}\exp\left(\frac{S(t_d)}{k_B T}\right)
\]

(18)

In this connection, to understand the density flux with respect to the entropy changes, we derive the entropy-dependent charge density relation for 2D systems and it is described as

\[
n_{\text{2D,non-equ}} = n_{\text{2D,t=t_d}}\exp\left(\frac{S(t_d)}{2k_B T}\right)
\]

(19)

By comparing eqs 18 and 19, it is defined that the entropy-ruled charge density flux is larger than the entropy-ruled diffusion flux while the carrier motion takes place from the nonequilibrium to equilibrium regime, i.e.,

\[
\frac{n_{\text{2D,non-equ}}}{n_{\text{2D,equ}}} = \frac{n_{\text{2D,non-equ}}}{n_{\text{2D,equ}}} \exp\left(\frac{S}{2k_B T}\right)
\]

For the P3 molecular device, the hole carrier drift time is 9.3 \(\times 10^{-5}\) s (see Figure 2). In this region, the charge transfer kinetics is anticipated under the steady-state dynamical regime. This drift time-correlated charge transfer was also analyzed for different organic systems in the earlier studies.26,35,36 From Figure 2, one can relate the nonequilibrated-to-equilibrated diffusive transport via the quasi-equilibrium point while the carrier dynamics moves from the nonsteady to steady state in the molecular devices. This variation intriguingly causes changes in Einstein’s original relation of \(D/\mu\).

3.2. Charge Dynamics-Correlated Potential Redistribution Analysis. The local chemical potential and dynamic disorder are key drifting factors for polaron hopping in molecular solids. The nonequilibrium diffusion–mobility relation (see eq 17) mainly emphasizes the importance of the potential distribution rate (along the consequential hopping sites), which helps to study drift-diffusion transport. In this regard, the potential distribution with simulation time is analyzed using the potential energy redistribution function (see eqs 11 and 12). This function is nonlinearly related to the survival probability of the charge carrier. To obtain physical insights into drift-diffusion synergic behavior with respect to the rate of traversing potential, we hereby extend the previous theoretical charge transfer kinetic investigation of octupolar derivatives.26 In our numerical study, octupolar derivatives are considered for charge carrier dynamical analysis. The chosen molecules are 2,4,6-tris[5-(3,4,6-triaryloxyphenyl)thiophene-2-yl]-1,3,5-triazene (octupolar 1b), 2,4,6-tris[5-(3,4,6-trithiophen-2-y1)-1,3,5-triazene (octupolar 1c), and 2,4,6-tris[5-(3,4,6-tridodecyloxyphenyl)-2,2′-bithiophene-5-y1]-1,3,5-triazene (octupolar 2), which were synthesized by Yasuda et al.38 The presence of the electron-rich thiophene ring at each peripheral arm and the triazene unit at the central core are responsible for both electron and hole transport. The coplanar nature of these molecules facilitates \(\pi\)-stacking properties, and hence, it possesses a hexagonal columnar arrangement even at room temperature. Due to strong \(\pi-\pi\) interactions, the electron/hole carrier can easily propagate along the columnar stacked molecular solids. The chemical structures of these molecular systems are given in the Supporting Information (also see ref 26). According to our proposed model, we numerically reproduce and perform the earlier charge transport calculation using KMC simulations. Along with the electron reorganization energy, the angle (i.e., the stacking angle or twist angle between adjacent molecules)-dependent effective charge transfer integral, \(J_{\mu}(\theta)\), and the site energy difference, \(\Delta E_{\text{g}}(\theta)\), are interpolated for 300 values and are given as the input to the KMC simulations to predict the electron kinetics in these molecules. Here, the molecular dynamics time step \((0.1\) ps) and temperature \((300\) K) are provided in the KMC simulations. The output of KMC describes the survival probability of the carrier at each site for different time scales of simulations. As described in the earlier studies,35 the survival probability–carrier energy redistribution relation provides equilibrium speed in the molecular system during the charge injection or transport. Based on our analysis,
it is suggested that the device performance can be illustrated by potential equilibrium speed, which depends on the conjugation length (or the number of layers). Using eq 11, the plotted potential distribution (see Figure 3) shows the existence of a nonequilibrium/quasi-equilibrium nature in these molecules during the charge propagation. In this regard, the rate of potential distribution (or rate of traversing potential) along the consequential hopping sites is calculated.

The performed KMC simulation yields the possibility of redistribution of the potential in the studied molecules with respect to the carrier dynamics. After a long enough simulation time, the equilibrium is attained. The fitted parameter “rate of traversing potential” (see Figure 3) determines the time gap between nonequilibrium/quasi-equilibrium and equilibrium transport, which essentially depends on on-site potential flux by dynamic disorder along with the locally induced electric field. This observation assures the possibility of nonlinear behavior in the drift-diffusion process and is responsible for the transition from nonsteady- to steady-state transport. The local and nonlocal interactions define the strength of charge localization or delocalization, which quantifies the charge density transfer (i.e., density flux) from site to site, as well explained by Wang and Beljonne.26 It has been noted that derivative octupolar 1c has a high rate of traversing potential of around $5.28 \times 10^{12}$ V/s for electron transport, which facilitates fast charge distribution speed in the entire molecular solids. In this case, the electron drifted by structural dynamics (dynamic disorder) is relatively significant. But in the case of electron transport in octupolar 1b, the calculated traversing potential rate ($6.83 \times 10^{12}$ V/s) is low, which stipulates the less density flux along the extended hopping sites due to strongly localized incoherent hopping transport.

The transition from hopping to band-like transport is expected while the structural oscillation frequency (dynamic disorder) is in the order of harmonic frequencies (see refs 3 and 24). Most of the dynamic disordered molecular system follows the intermediate transport between localized hopping and the delocalized band mechanism. In this context, the typical transport is characterized via the time scale of oscillation and its consequences on the frictional coefficient. The puddles of electron/hole propagation in the degenerate molecular media have identical similarities with the hydrodynamics principle (i.e., the collective motion of N-particles) in which the understanding of the frictional coefficient is highly solicited. In the present section, the transport behavior with respect to the frictional coefficient and oscillation frequency (structural fluctuation) for octupolar molecular media is explained. For instance, octupolar 1c has a low frictional coefficient, and hence, the calculated diffusion constant is relatively high (418 cm$^2$/s). Also, the estimated electron drift time due to structural dynamics is very less (∼35 fs), which confirms the dynamic disordered transport in the octupolar 1c molecule. In this case, the electronic and nuclear degrees of freedom perturb the localized charge. This is responsible for a higher rate of traversing potential (see Table 1). The fast fluctuations (dynamic) rely on a low frictional coefficient, facilitating hopping-to-band-like transport transition, which is in agreement with an earlier observation.26 Here, there is no significant loss in charge transfer kinetics (coherent) at each hopping step. On the other hand, the diffusion is significantly reduced in octupolar 1b molecules due to a high frictional

Table 1. Disorder Drift Time ($t_d$), Diffusion Coefficient ($D$), Rate of Traversing Potential ($dV/dt$), $\pi$–Electron Density ($n$), Frictional Coefficient ($\gamma$), and Nonequilibrium Diffusion–Mobility Relation (D/μ)$_{non-equ}$ for Electron Transport in the Octupolar Derivatives

| molecule   | $t_d$ (fs) (see ref 26) | $D$ (cm$^2$/s) | $dV/dt$ ($\times 10^{10}$ V/s) | $n$ ($\times 10^{13}$ cm$^{-3}$) | $\gamma$ ($\times 10^{16}$ eV s/cm$^2$) |
|------------|-------------------------|----------------|-------------------------------|-------------------------------|-----------------------------------|
| octupolar 1b | 252.13 | 90.3 | 6.83 | 0.42 | 2.857 |
| octupolar 1c | 34.70 | 418.0 | 528.4 | 7.00 | 0.617 |
| octupolar 2  | 135.34 | 67.1 | 176.8 | 14.56 | 3.845 |

\[ \text{Figure 3. Traversing potential along the consequential hopping sites during the electron transport in the octupolar derivatives. The potential flux confirms the nonequilibrium transport, which facilitates nonlinear behavior in quasi-equilibrium situations as well. The charge distribution speed from site to site is studied by kinetic Monte-Carlo simulations using eq 11, which is the direct consequence of the transporting ability.} \]
coefficient of $2.86 \times 10^{-6}$ eV s/cm². The static disorder is direct compliance of a large fractional effect on charge propagation along the molecular sites. This is well corroborated with the diffusion limited by disorder.16,22,24,40

3.3. Site Energy Fluctuation on Entropy-Ruled Electron Transport and Its Consequences on Non-steady Energy Transport. Generally, the charge transfer rate is directly associated with diffusion, mobility, conductivity, and current density. The carrier energy flux through the charge transfer kinetics is a consequence of the rate of traversing carrier energy, which can be tuned by the applied electric field through the site energy difference, $\Delta E(\mathbf{\vec{E}})$. Henceforth, the relationship between the charge transfer rate and the traversing energy rate along the consequential sites is important to understand the drift-coupled diffusion mechanism in molecular devices. That is, the charge and energy transport are basic criteria to understand the drift-diffusion relation. For this analysis, we have used the charge transport parameters of dialkyl-substituted thiophene-capped benzobithiazole (BDHTT-BBT) molecules from our previous work.3 In the present investigation, we have numerically calculated the charge transport quantities of the BDHTT-BBT molecule for different $\Delta E(\mathbf{\vec{E}})$ values (i.e., 0, 20, 40, 60, and 80 meV) through KMC simulations. In BDHTT-BBT, the benzobithiazole moiety is placed in the core region with an end substituent of dialkyl-substituted thiophene units. Benzobithiazole provides planarity and molecular stability, and hence, this molecular solid suits well for designing functional molecular semiconductors. Experimentally observed $\pi-\pi$ stacking distance in the BDHTT-BBT crystal structure is 3.52 Å. The delocalized $\pi$ orbital of this molecule improves electron/hole transfer kinetics, which motivates further investigation of the charge transport properties of the BDHTT-BBT molecule. The chemical structure of the BDHTT-BBT molecule is provided in the Supporting Information (also, see ref 3). The rate of traversing carrier energy in the stacked or conjugated BDHTT-BBT molecular solids reveals the existence of a nonsteady dynamical state of $\frac{dE}{dt} \neq 0$, which influences the nonlinear transport in dynamical systems (see Figure 4). Here, the energy traversing rate is calculated at a different set of $\Delta E(\mathbf{\vec{E}})$ values of 0, 20, 40, 60, and 80 meV using the energy redistribution function (see refs 3–5). The nonlinear behavior of charge transport parameters (like diffusion, conductivity, and current density) strongly depends on the differential entropy parameter, $h_s = \ln(\sqrt{2\pi}\sigma)$, where $\sigma$ is the Gaussian disorder width. Our results show that both the diffusion coefficient and logarithmic current density nonlinearly increase with the rate of traversing energy. This is the direct evidence of nonlinearity in the carrier network while the system is in the nonsteady-state regime. Therefore, here, the existence of nonlinear transport further question’s the validity of Einstein’s original relation to some extent of nonsteady-state electron and hole dynamics. Based on the above analysis along with the earlier investigations,3,4 it is to be noted that the entropy parameter is one of the best descriptors to explain both the validity and limitations of celebrated Einstein’s relation, $\frac{D}{\mu} = \frac{kT}{q}$. In this scenario, we recently developed the quantum-classical transition analogy of Einstein’s diffusion–mobility relation, which unifies the band and hopping transport and also elucidates the crossover nature between them.5 From this analogy, it is to be noted that the chemical potential and differential entropy are two authentic parameters to study any typical transport, essentially one can identify whether the transport is band or hopping or intermediate. According to this analogy, the chemical potential is generally associated with the reorganization energy (due to the presence of excess positive/negative charge), chemical structure, and the magnitude of electric field-assisted site energy disorder, $\Delta E(\mathbf{\vec{E}})$. For the BDHTT-BBT molecule, the computed reorganization due to the presence of an additional electron is 190 meV (see ref 3).

In this context, the chemical potential is computed at different $\Delta E(\mathbf{\vec{E}})$ values for electron transport in BDHTT-BBT molecules, which are summarized in Table 2.

To analyze the variation in differential entropy ($h_s$) with respect to the chemical potential ($\eta$), we have plotted $h_s$ versus $\eta$, which shows a linear response (see Figure 5). In principle, the electron density and chemical potential have a one-to-one correspondence with each other. The $\pi$–electron density with respect to the chemical potential for the BDHTT-BBT molecule is calculated for different $\Delta E(\mathbf{\vec{E}})$ values, which are given in Table 2. The results clearly show that the electron density increases in quadratic nature with the chemical potential (see Figure 4). Here, the $\pi$–electron density plot follows the relation $n(\eta) = 2.309 \times 10^{20} - 2.96 \times 10^{18} \eta + 2.841 \times 10^{16} \eta^2$. Generally, the change of electron density with respect to the chemical potential is the thermodynamic density of states (TDOS). In this analysis, the TDOS relation for the BDHTT-BBT molecule is $\frac{dn}{d\eta} = -2.96 \times 10^{18} + 5.682 \times 10^{16} \eta$, which linearly varies with the chemical potential.

According to Navamani’s entropy-ruled method,4 the charge transport quantities such as the diffusion–mobility relation, the density of states, conductivity, and current density are in direct relation with the factor $\frac{dn}{d\eta}$ (see eqs 6–8). A detailed explanation is provided in Section 2. In the present study, differential entropy $h_s$ linearly increases with the chemical potential. According to the entropy-ruled method,4 the mobility is directly proportional to $\frac{dn}{d\eta}$ (see eq 6). In this way, the mobility relation for the BDHTT-BBT molecular solid is $\mu(\mathbf{\vec{E}}) = 12.32 \times D(\mathbf{\vec{E}}) \cong 0.318 \frac{\rho(\mathbf{\vec{E}})}{E^2}$. For different applied electric fields via the site energy difference ($\Delta E(\mathbf{\vec{E}})$), the diffusion coefficient increases, which was shown in the previous study.3 By this procedure (entropy-ruled method, see

![Figure 4](https://doi.org/10.1021/acsomega.2c01118)

**Figure 4.** Electron density with respect to the chemical potential for the BDHTT-BBT molecule at different values of $\Delta E(\mathbf{\vec{E}})$. Closed circles represent the calculated electron density (by our model) and the solid line is a fitted plot.
Table 2. Chemical Potential ($\eta$), $\pi$-Electron Density ($n$), Thermodynamic Density of States ($\frac{dn}{dq}$), Differential Entropy ($h_d$), Mobility–Diffusion Ratio Factor ($\frac{dh_d}{d\eta}$), Mobility ($\mu$), and Conductivity ($\sigma$) for Electron Transport in the BDHTT-BBT Molecule at a Different Set of $\Delta E(E)$ Values of 0, 20, 40, 60, and 80 meV

| molecule       | $\Delta E(E)$ (meV) | $\eta$ (meV) | $n \times 10^{20}$ cm$^{-3}$ | TDOS, $\frac{dn}{dq}$ (eV$^{-1}$ cm$^{-3}$) | $h_d$ (ref 3) | $\frac{dh_d}{d\eta}$ (meV$^{-1}$) | $\mu$ (cm$^2$/V s) | $\sigma$ (S/cm) |
|----------------|----------------------|--------------|-------------------------------|-----------------------------------------------|---------------|-----------------------------------|-------------------|---------------|
| BDHTT-BBT      | 0                    | 73.3         | 1.64                          | 1.205 $\times 10^{10}$                        | 0.00          | 0.00                              | 0.068             | 1.072         |
|                | 20                   | 88.3         | 1.95                          | 2.057 $\times 10^{10}$                        | 0.290         | 2.053 $\times 10^{-2}$            | 0.082             | 2.055         |
|                | 40                   | 104.5        | 2.34                          | 2.978 $\times 10^{10}$                        | 0.589         | 3.053 $\times 10^{-1}$            | 0.087             | 3.353         |
|                | 60                   | 122.7        | 2.90                          | 4.012 $\times 10^{10}$                        | 0.949         | 3.053 $\times 10^{-1}$            | 0.100             | 5.216         |
|                | 80                   | 144.6        | 3.99                          | 5.256 $\times 10^{10}$                        | 1.480         | 3.053 $\times 10^{-1}$            | 0.124             | 8.454         |

Figure 5. Differential entropy linearly increases with the chemical potential for the BDHEE-BBT$^*$ molecule at different site energy fluctuation ($\Delta E(E)$) values of 0, 20, 40, 60, and 80 meV. Closed circles are theoretically computed chemical potential (using our model) at different $\Delta E(E)$-associated differential entropy, and the solid line is a fitted plot.

The ratio $\frac{dh_d}{d\eta}$ is the key factor to study (or measure) the fundamental transport quantities like diffusion mobility, the density of states, conductivity, and current density, which is indeed ideal for advanced semiconductor technology and devices. For instance, the diode $J$–$V$ characteristic study can be thoroughly analyzed using this single factor $\frac{dh_d}{d\eta}$. By tuning this factor through doping, applied bias, etc., one can improve the device performance, which can be easily studied by the Navamani–Shockley diode equation. Besides drift-coupled diffusion and its effect on mobility, other extended parameters (conductivity, current density, etc.) are precisely explored by the factor $\frac{dn}{dq}$ for both the quantum and classical systems at any thermodynamic limit. Henceforth, this factor essentially provides a generalized picture of the charge transport mechanism taking place in different systems of interest (from nondegenerate to degenerate materials), which might help explore the next-generation molecular semiconductors and their potential applications.

Furthermore, the synergy between the charge and energy transport in the molecules is fundamentally important in designing high-performance devices for novel applications of photovoltaics or light-emitting diodes. The earlier study carried out by Mendels and Tessler also confirms the direct relationship between the drift-diffusion process and the charge and energy transport in organic semiconductors. At this juncture, here, we have introduced the nonsteady carrier energy flux principle, which consists of four sets of analytical expressions of entropy-dependent charge density, diffusion, and energy flux rate (see eqs 1–4). According to the thermal and quantum flux in the system, typical entropy ($S$ or $h_S$) is taken into account in these expressions (eqs 1–4), which gives the nonsteady-state energy transport with respect to the carrier (electron/hole) dynamics in the given molecular solids. That is, the rate of energy flux under nonsteady-state conditions $\frac{dE}{dt} \neq 0$ (see eqs 1 and 2); the presence of a diffusion process might have occurred in the studied system. It is noted that diffusion transport is a key phenomenon for the existence of nonsteady carrier energy flux, which is also inevitably varying with the entropy (see eq 2). With respect to the magnitude of the carrier energy flux rate (or rate of traversing carrier energy along the consequential sites of BDHTT-BBT molecular solids), the diffusion coefficient and electron current density are anticipated in a given system (BDHTT-BBT), which is shown in Figure 6. We interestingly found that the diffusion coefficient and logarithmic current density ($\ln j$) exponentially increase with TDOS ($\frac{dn}{dq}$) and are directly proportional to $\frac{dh_d}{d\eta}$ (differentiation of eq 3 with respect to the chemical potential). In other words, the trends of TDOS-dependent diffusion and current density are observed in Figure 7 and also in Table 2. This gives information about the degeneracy weight on charge transport. According to our entropy-ruled method, diffusion is a basic transport quantity for other extended quantities like conductivity and current density. To obtain further insights, we have plotted the conductivity and current density for electron transport in the BDHTT-BBT molecule with different $\Delta E(E)$-driven diffusion coefficient values, which are shown in Figure 8.

It is to be noted that diffusion transport linearly influences the conductivity as well as the logarithmic current density ($\ln j$). In other words, the current density exponentially increases in the diffusion transport region.

With the energy redistribution function (see eq 12), one can obtain the energy flux during the charge transport, which is...
Electronic coupling, which reveals the large charge delocalization, nonlinearly correlated with the survival probability of the charge carrier. It has been observed that there is a nonlinear charge transport behavior in the extended molecular solids, which is a direct consequence of the rate of traversing carrier energy. Here, nonlinearity is mainly responsible for drift-coupled diffusion transport. In this nonsteady regime, the carrier dynamics-associated mean value of single-particle chemical potential is expressed as

$$
\eta(t) = \frac{\Delta E}{\Delta P(t)} = k_B T \left[ \ln(1 - \exp(-1)) \right]_{t \to \infty}
- \left[ \ln(1 - \exp(-1)) \right]_{t \to 0}
/ [P(t)_{\text{t} \to \infty} - P(t)_{\text{t} \to 0}]
$$

(20)

The above expression (eq 20) is named dynamically coupled single-particle chemical potential, which can be varied with the survival probability of the charge carrier at a particular initial site. In the present study, the single-particle (electron/hole) dynamics is characterized by the survival probability ($P(t)$) of the carrier in the concerned molecular solids. To this extent, the instantaneous dynamically coupled single-particle chemical potential can be described by $\eta(t) = \frac{1}{15}E_k(t)$. That is, the electron/hole transfer kinetics is in a direct relationship with the chemical potential. The Fermi energy—kinetic energy of a single electron relation is $E_k \approx \frac{1}{2}E_F$. For a high degenerate limit of $\eta \gg k_B T$, the diffusion—mobility ratio ($D/\mu$) is directly proportional to the chemical potential (or Fermi energy). On the other hand, in nondegenerate classical systems, $D/\mu$ is equivalent to that of thermal energy ($\sim k_B T$), instead of electronic contributions, which preserves the Einstein relation.

According to Navamani’s entropy-ruled method, $D/\mu$ is explicitly written as

$$
\frac{D}{\mu} = \frac{5}{3} \frac{\Delta \Delta E}{\Delta \Delta \sigma}
$$

The diffusion is influenced by the chemical potential (or charge density flux), and the mobility is strongly associated with the existence of degeneracy strength (or $h_0 = \ln(\sqrt{2\pi\sigma})$), where $\sigma$ is the Gaussian disorder width, which provides the populated degeneracy width. That is, the minimum required chemical potential to hop over the barrier height in disordered molecules determines the magnitude of diffusion coefficient. Here, chemical potential is the energy to help to drift the electron/hole hop in the disordered molecules. In principle, the existence of degeneracy levels reduces the barrier height, which leads to mobility-dominant transport over diffusive mechanism. The analysis suggests that the mobility is intrinsically dominant (or electronic structure/quantum picture) and diffusion is extrinsically dominant (such as electron–hole doping, applied bias, and temperature), which is naturally incorporated in the chemical potential. In general, in any degenerate crystalline solids, the existence of degenerate levels will be more when there is a small enough applied chemical potential, which leads to mobility-dominant transport. If the required energy is more to activate the carrier to hop across the barrier in the disordered solids (nondegenerate cases), then we anticipate diffusion dominant transport rather than mobility. Therefore, the one-to-one variation between the energy flux (chemical potential) along the consequent hopping sites and the degeneracy weightage (or differential entropy, $h_0$) are fundamentally important for understanding the cutting-edge organic semiconductors, which is indeed ideal for next-generation semiconductor technology. Our theoretical findings require the development of a more detailed understanding of the dynamic behavior of single-particle transport in organic molecular solids.
results confirm the accuracy of our analytic expressions derived here, mainly correlating both the linear and nonlinear transport phenomena. In this study, we also have confirmed earlier descriptions in appropriate limits, such as Troisi’s localization transport limitation by dynamic disorder, Tessler’s charge energy transport in degenerate organic semiconductors, and Gregg’s entropy-dependent charge separation process, and Beljonne’s crossover transport mechanism.

4. CONCLUSIONS
The transition from nonsteady- to steady-state charge dynamics (and vice versa) is numerically analyzed in the layered triphenylamine-based molecular systems, which suggests the possibility of drift-coupled diffusion transport. The potential redistribution analysis in octupolar molecules further confirms the nonsteady charge and energy transport even at zero applied electric field conditions. Here, the amplitude of site energy fluctuation is the deterministic factor even at zero applied electric field conditions. Here, the molecule has a high rate of traversing potential of around 5.28 × 10^{13} V/s for electron transport, which facilitates the fast charge redistribution nature of this molecule, and hence, it is suitable for designing organic electronic devices. Using our differential entropy (h_{r})-driven diffusion, charge density, and energy rate expressions (see eqs 1–4), we have illustrated the nonsteady carrier energy flux principle. From our investigation, it is observed that the diffusion process is directly synergized with the nonsteady energy flux. The crossover between hopping and band transport is characterized through the frictional coefficient, which is the consequence of static-to-dynamic disorder transition or vice versa. The fast structural fluctuation (dynamic disorder) relies on a low frictional coefficient, which facilitates band-like transport from the hopping mechanism, which is observed in octupolar 1c molecules. In this low frictional domain of dynamical disorder limit, the diffusion coefficient value for the octupolar 1c molecular solid is 418 cm^{2}/s (for electron transport), and hence, the estimated conductivity is also large. To elucidate the crossover transport (i.e., hopping to band/band to hopping) in molecular devices, we have generalized the hopping and band transport via the charge transfer rate (K_{CT})−relaxation time (\tau_{rel}) relation. Here, we interestingly noted that the ratio between carrier relaxation time and the effective mass of electron/hole relates to the diffusion coefficient over thermal energy. Using our nonsteady energy flux principle (comprising eqs 1–4), we can categorize the transport either as linear or nonlinear, which depends on the magnitude of typical disorder (static or dynamic) and potential drift on the carrier by site energy fluctuations. In our model, the energetic disorder is incorporated with the effective entropy and is verified for electron transport in dialkyl-substituted thienothiophene-capped benzobisthiazole (BDHTT-BBT) molecules. For different sets of the electric field-assisted rate of traversing carrier energy in BDHTT-BBT molecular solids, the calculated diffusion coefficient and current density follow the nonlinear transport regime. The nonlinearity of drift-diffusion transport reveals the limitations of Einstein’s relation in certain physical domains, which is explicitly explained by the nonsteady energy flux principle. Using our entropy-ruled transport method, the accurate electron mobility and conductivity for the BDHTT-BBT molecule are calculated at different electric field-assisted site energy differences of 0, 20, 40, 60, and 80 meV. The analysis suggests that for electron transport in the BDHTT-BBT molecule, the enhancement in conductivity is large enough, even though the mobility is low. Here, the effect of entropy and \pi-electron density is mainly responsible for good conductivity. At zero applied electric field, the obtained electron mobility and conductivity in this BDHTT-BBT molecule are 0.068 cm^{2}/V s and 1.07 S/cm, respectively. Here, the calculated thermally populated electronic states (DOS) have a significant value of around 1.205 × 10^{18} eV^{-1} cm^{-3}, which allows a more delocalized \pi-electron density of 1.64 × 10^{20} cm^{-3}. The Navamani’s entropy-ruled method on the diffusion−mobility relation clearly emphasizes that the diffusion coefficient depends on chemical potential (or charge density flux), and the mobility is related to the existence of degeneracy strength, which is quantified by differential entropy. This study further clarifies that mobility is intrinsically dominant (or electronic structure/quantum picture) and diffusion is extrinsically dominant (such as electron-hole doping, applied bias, temperature, etc., via chemical potential). Thus, in this work, we have found that differential entropy is the better descriptor for field response transport properties via degeneracy strength on electronic transport (especially for mobility), which is indeed ideal for next-generation molecular semiconductors.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01118.

Chemical structures of triazine-based octupolar molecules (1b, 1c, and 2); alkyl-substituted triphenylamine (TPA)-based molecules (X1, X2, and X3); and BDHTT-BBT molecules are given in Figures S1, S2, and S3, respectively (PDF)

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Author Contributions
K.N. planned, designed, and performed the research; also he (K.N.) developed analytical methods and performed the theoretical study. K.N. and K.R. analyzed data and wrote the paper. All authors contributed to the critical review and final version of the manuscript. All authors have given approval to the final version of the manuscript.

Notes
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DEDICATION

The authors dedicated this work to Dr. V. Devanathan, Formerly Professor and Head, Department of Nuclear Physics (also the founder of this Department), University of Madras, Guindy Campus, Chennai 600 025, India, on the occasion of his 90th Birthday.

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