

Electron-hole capture suppression and ultraviolet emission in conjugated polymers under high electric fields

En-Shi Chen, Sheng-Hsuan Yeh, and Hsin-Fei Meng*

Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China

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The probability for the Coulomb capture of an electron-hole pair to form an exciton in conjugated polymers is found to be significantly suppressed under high electric field, which is usually required for electroluminescence due to the low mobility. The Coulomb capture is a continuous descent of electronic energy through cascade emission of phonons, and the high field prevents this descent by heating up the carriers. On the other hand, ultraviolet emission through direct interband transition is found to be much less affected by the field, and becomes the dominant radiative decay channel for field beyond 10^8 V/m. Combined with impact ionization, our model provides a complete quantitative explanation of the peculiar high-field behaviors of the visible emission, ultraviolet emission, and current observed in conjugated polymer both before and after the avalanche breakdown.

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I. INTRODUCTION

The electroluminescence (EL) due to radiative recombination of injected electron-hole pairs through singlet exciton state in semiconducting conjugated polymers, especially poly(para-phenylene vinylene) (PPV) and derivatives, is now an active research topic.¹ Excitons result from the electron-hole Coulomb capture, which can be divided into two stages. In the first interchain stage, the electron and hole are on different conjugated segments and are attracted to each other through interchain hoppings in the real space by their Coulomb interactions.² Eventually, they hop into the same conjugation segment and their wave functions start to overlap. At this moment their relative kinetic energy is high and a tightly bound exciton does not form yet. In the second intrachain stage, the free electron-hole pair successively relaxes its energy to the lattice and ultimately form an exciton. However, the possibility that one of the carriers hop to other segment before exciton formation cannot be ruled out in principle. It has been assumed that such probability is small and an exciton, either singlet or triplet, is the only destination of the second stage of Coulomb capture. This assumption is plausible when there is no external electric field, because the electron is expected to be confined in the segment by the attraction of the hole and vice versa. However, due to the low mobility, a strong electric field (more than 10^7 V/m) is usually present in the active region of the conjugated polymer light-emitting-diode (LED) in order to provide sufficient electric current. This is remarkably different from the inorganic *p-n* junction LED, in which light emission mainly comes from the diffusion region with no field, instead of the depletion region with high field. The strong field is expected to keep the electron-hole pair in conjugated polymers at high relative kinetic energy and reduce their rate to capture each other to form an exciton. The possibility that the carriers escape from each other is no longer negligible and the above assumption of definite Coulomb capture breaks down. In fact, it has been observed that the ratio between the light output and the injected current decreases as the field

increases,^{1,3,4} suggesting suppressed exciton formation at high field. The first stage is found to be independent of the external field.² So it cannot account for the field suppression of EL.

In this work, we concentrate on the second stage and study the effect of the external electric field on the process of electron-hole pair Coulomb capture in an infinite conjugated polymer chain microscopically. The effect of the finite length of the conjugation segment is ignored, because the conjugation length (10–20 repeat units^{5,6}) is much larger than the exciton size (about three units^{7,8}). Agreement between exciton energy from *ab initio* calculation⁷ based on infinite perfect polymer chain and experiments provides further evidence. It is therefore plausible to ignore the boundary effect in the intrachain capture process as a good approximation. For a free electron-hole pair in the chain, the electronic energy can be decomposed as the sum of the center-of-mass and relative energy. Both of the two are initially positive referring to the bandgap. Since the relative energy of an exciton is negative (zero minus the binding energy), the relative electronic energy must be released through phonon emission (and complicated by reabsorption) in the capture process. This two-body capture process is very similar to the well-studied one-body cascade capture of an electron by a positively charged defect center,⁹ because the center-of-mass degree of freedom of the electron-hole pair can be taken as free and separated in the field due to the overall charge neutrality. It has been established for inorganic semiconductors that the capture of an electron by a positively charged defect center is not an one-step transition from the free particle state to a bound state in the potential well. Instead, the capture is a cascade process in which the energy of the electron is lost successively by the emission of many phonons.⁹ The capture rate, therefore, can not be obtained simply from the transition matrix element between the initial (free) and final (bound) states. The appropriate description is a random walk in the phase space with uneven rates for going up in energy (phonon absorption) and going down (phonon emission). The random walk can be simplified to be in an one-dimensional energy space after averaging over all degrees of freedom

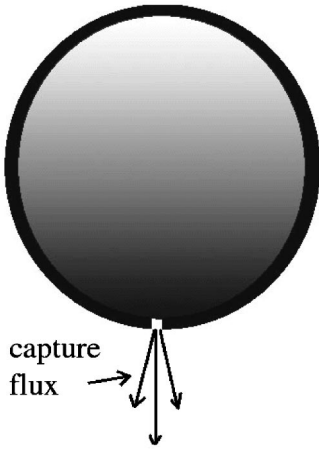


FIG. 1. The Coulomb capture flux in the energy space can be pictured as the leakage flux out of a pinhole in a balloon. The darker region has higher gas density.

except for the total energy. The capture rate is determined by the downward flux in an ensemble of pairs in the energy space. This theory can be easily adopted to describe the formation of excitons through the electron-hole capture due to the Coulomb attraction, if we concentrate on the relative degree of freedom between the electron-hole pair. While the cascade emission of phonons causes a continuous descent in the relative energy space of the pair, the existence of external electric field drives the relative motion upward in the energy space and counter-balance the downward flux. In other words, under the high field the carrier constantly gains energy from the field and becomes so hot that it becomes difficult for them to emit enough number of phonons and reach the exciton level before being heated back to the higher-energy region. One simple picture for this ensemble of electron-hole pairs is provided by its analogy with the gas in a balloon. The capture process is like the gas flux leaked out of the balloon through a pinhole corresponding to the zero level of the energy space [see Fig. (1)]. The electric field is like an external wind that not only blows the gas inside the balloon away from the pinhole, but also pushes some of the leaked gas back into the balloon. Leakage can be turned off when the leaked gas is completely compensated by the pushed back flux. The corresponding situation is that all the loosely bound pairs are dissociated by the field before any stable low-lying discrete bound state can be formed. We perform detailed calculation to confirm this picture. It is found, as expected, that the exciton formation rate is suppressed for more than one order of magnitude when the field increases from zero to about 5×10^7 V/m. In fact, the capture can be completely stopped when the field is beyond some critical value. The suppression of the exciton formation implies that the radiative decay channel for the injected carriers is reduced. Such behavior has been reported experimentally.^{1,3,4} An alternative possibility for the reduced EL yield is the enhanced non-radiative channel at high field. This is, however, not likely because the electron and hole injections become more balanced as the field increases. Moreover, it has been shown that the exciton quenching by the metal cathode is reduced at larger bias.² The field suppression of exciton

formation in EL is thus identified as the principal mechanism to limit the quantum efficiency of polymer LED under high field. This mechanism is of intrinsic nature and is present even if there are no traps and the electron-hole injection is balanced. In addition to LED, our model also be applied to the quenching of photoluminescence (PL) by the electric field, because an electron-hole pair excited by a photon in one chain with large excess kinetic energy gives a situation similar to the second (intrachain) stage of EL suppression. PL quenching in conjugated polymers is indeed observed experimentally^{10,11} and has been modeled phenomenologically.^{12,13}

Another more direct evidence for the exciton capture suppression is the ultraviolet (UV) emission observed at high field.⁴ Even though the field reduces the visible light emission as discussed above, it opens a new possibility of direct interband electron-hole recombination, which would be impossible without the field due to the fast Coulomb capture to form excitons. The free electron-hole pair continuum lies above the exciton level (2.4 eV) by the binding energy, and the corresponding photon around 3 eV is in the near-UV spectral region. The direct recombination does not require phonon and can take place at any relative energy of the pair. It is therefore much less affected by the external field, as confirmed by our calculation. In fact, it is found that the UV emission through direct interband recombination starts to dominate the visible emission through exciton decay when the field is beyond 10^8 V/m. In order to describe the peculiar voltage-current and voltage-light characteristics observed experimentally, two additional factors must be taken into account in the model. One is the impact ionization and the resulting avalanche breakdown, the other is the nonuniform effective field due to the chain orientation distribution. All the electric and optical behaviors of PPV LED under high field in our model turn out to be close to the peculiar experimental results. The overall UV emission ratio strongly depends on the chain orientation probability distribution with respect to the applied field. In order to enhance the UV, polymer chains have to be aligned mostly parallel to the field direction, instead of the perpendicular direction as in the sandwich structure.

The paper is organized as follows. In Sec. II, the Hamiltonian and phonon scattering rates are discussed. In Sec. III, we present the model for cascade capture and calculate the capture rate. In Sec. IV, the effect of the external electric field on the capture rate is studied. In Sec. V, the ratio between the visible and UV emission is calculated, impact ionization and chain distribution are included, and comparisons with the experiments are made. We discuss and conclude in Sec. VI.

II. HAMILTONIAN AND MATRIX ELEMENT

The carbon $2p_z$ atomic orbitals in PPV and other conjugated polymers form π energy bands, with direct bandgap semiconductor band structures.^{14,7} The total Hamiltonian H in the effective-mass approximation for an electron-hole pair in a perfect polymer chain coupled with the lattice can be written as

$$H = H_{ex} + H_p + H_{ex-p}, \quad (1)$$

with

$$H_{ex} = \frac{p_e^2}{2m_e} + \frac{p_h^2}{2m_h} + V(x_e - x_h), \quad H_p = \sum_{\lambda,q} \hbar \omega_q^\lambda a_{\lambda,q}^\dagger a_{\lambda,q}, \quad (2)$$

and

$$H_{ex-p} = \sum_{\lambda,q} \xi_q^\lambda (e^{iqx_e} + e^{iqx_h})(a_{\lambda,q} + a_{\lambda,-q}^\dagger). \quad (3)$$

H_{ex} is the kinetic plus the Coulomb potential energy of the electron-hole pair, whose bound states are the exciton levels. H_p is the phonon Hamiltonian. H_{ex-p} is the interaction between the electron-hole pair with the phonons. $x_{e,h}$ are the one-dimensional position operators, and $p_{e,h}$ are the momentum operators of the electron and the hole, respectively. $m_{e,h}$ are their effective masses. $V(x) = -e^2/\epsilon x$ is the effective Coulomb attraction between the two carriers. e is the electron charge. Correction on $V(x)$ for small x is usually needed in the effective-mass approximation for strongly localized bound states. However, the behavior of $V(x)$ for $x \rightarrow 0$ turns out not to be important for the capture problem, so we can leave it as the original Coulomb form. For covalent materials such as conjugated polymers, the electron-phonon coupling constant ξ_q^λ is of the deformation type, and can be expressed as $\xi_q^\lambda = \eta \alpha \alpha q \sqrt{\hbar/(2NM\omega_q^\lambda)}$. η is a dimensionless function of the phonon-mode polarization vectors, and is taken as a fitting parameter of order one.¹⁵ a is the carbon bond length, α is the change of electronic hopping integral between neighboring carbon $2p_z$ orbitals per unit bond length, q is the phonon wave number, and λ is the phonon branch index. $a_{\lambda,q}^\dagger$ and $a_{\lambda,q}$ are the phonon creation and annihilation operators, respectively. N is the number of unit cells in the chain, M is the carbon atom mass.

The Coulomb capture is a process only in the relative degrees of freedom of the electron-hole pair. When the electron and the hole are attracted to each other by their Coulomb interaction, the relative kinetic energy increases while the potential decreases to more negative values. However, the kinetic energy cannot stay high for long because it has to be in equilibrium with the surrounding lattice degrees of freedom. So the electron-hole pair keeps emitting phonons, and the total relative energy is successively lost. The center-of-mass momentum is not affected in this capture process, and is assumed to be zero initially. Its mean value will remain so for the entire process. In order to remove the center-of-mass degree of freedom, we take the well-known Lee-Low-Pines (LLP) unitary transformation.¹⁶ The resulting relative Hamiltonian is

$$H^r = \frac{p^2}{2m} + V(x) + H_{ex-p}^r + H_p, \quad (4)$$

with

$$H_{ex-p}^r = \sum_q \xi_q [\rho_q(x) a_q + \text{H.c.}], \quad \rho_q(x) = e^{is_1 qx} + e^{is_2 qx}. \quad (5)$$

Here $s_{1,2} = m_{e,h}/(m_e + m_h)$, $m = m_e m_h / (m_e + m_h)$ is the reduced mass, $x = x_e - x_h$ is the relative position, and p is the corresponding momentum operator. The phonon branch index λ is dropped because only acoustic phonons are considered below. Higher-order terms in H_p after LLP transformation is dropped, because they have no effect on the first-order perturbation. The relative motion of an electron-hole pair, as described by H^r , is equivalent to a single particle moving in a fixed frame with an attractive center at the origin. For simplicity, we refer to the effective single particle in the relative Hamiltonian as ‘‘particle’’ below. What is special to the particle is that there are now two kinds of particle-phonon scattering process, corresponding to the two terms in $\rho_q(x)$. The first one is derived from the original electron-phonon scattering, while the second one is from the hole-phonon scattering. When an electron(hole) emits a phonon of momentum $\hbar q$, the change in the relative momentum of the pair is not $\hbar q$, but $\hbar s_1(s_2)q$. This modified momentum conservation law is the reason for the appearance of the factors s_1 and s_2 in $\rho_q(x)$. H_{ex-p}^r will be considered as a perturbation below. The polaron effect is neglected, because we are concerned with the hot carriers. Indeed, it has been shown that polarons do not form for fields larger than 6×10^6 V/m.¹⁷

Let us consider the matrix element for phonon emission. The initial state is $|i\rangle = |k_i, N_q\rangle$, and the final state is $|f\rangle = |k_f, N_q + 1\rangle$, where k 's are the particle wave number, $\epsilon = \hbar^2 k^2 / 2m$ is the particle kinetic energy. N_q are the occupation number for phonon with wave number q . The matrix element $\langle f | H_{ex-p}^r | i \rangle$ is equal to $\sum_{q'} \langle N_q + 1 | a_{q'}^\dagger | N_q \rangle \times \langle k_f | \rho_{q'}^*(x) | k_i \rangle \xi_{q'} = \sqrt{N_q + 1} \langle k_f | \rho_q^*(x) | k_i \rangle \xi_q$, with $|\langle k_f | \rho_q^*(x) | k_i \rangle|^2 = (2\pi/L) [\delta(p_{1q}) + \delta(p_{2q})] \equiv M^2(k_i, k_f, q)$. $L = Na_c$ is the chain length, a_c is the repeat unit cell length. The momentum conservation laws are $p_{1q} = k_i - k_f - s_1 q$ and $p_{2q} = k_i - k_f - s_2 q$. The transition rate is

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar} \int (N_q + 1) \xi_q^2 M^2(k_i, k_f, q) \delta(\epsilon_i - \epsilon_f - \hbar \omega_q) \frac{L}{2\pi} dq \\ &= \frac{L}{\hbar^2 s} (N_q + 1) \xi_q^2 [M^2(k_i, k_f, q) + M^2(k_i, k_f, -q)] \\ &\equiv (N_q + 1) w(k_i, k_f, q), \end{aligned}$$

where $q = (\epsilon_i - \epsilon_f) / \hbar s$. $\omega_q = sq$ is acoustic phonon dispersion relation, s is the sound velocity. Optical phonons do not participate the cascade capture process in the semiclassical regime because their energy is too large. For the absorption process, the transition rate is $\Gamma^{abs} = N_q w(k_i, k_f, q)$. Note that $w(k, k', q) = w(k', k, q)$. The transition rates $\Gamma^{em,abs}$ will be used to obtain the distribution function and the flux in the energy space, from which one can derive the capture rate. These are the subjects of the next section.

III. CASCADE CAPTURE WITHOUT ELECTRIC FIELD

Consider an ensemble of n chains. Each of them contains one electron-hole pair. In the semiclassical regime, the total energy E of the pair is the sum of the relative kinetic and potential energy, i.e., $E = p^2/(2m) + V(x)$. Due to phonon emission and absorption, the energy of each pair performs random walk in the one-dimensional energy space, with uneven probability for upward step and downward step depending on the lattice temperature. If the energy of all the pairs in the ensemble are placed on the same energy space, we have a distribution function $f(E)$ defined as the occupation probability for states of energy E . Following the procedure of Abakumov, Perel, and Yassievich,⁹ we first derive the differential equation for $f(E)$, then identify the downward particle flux in the energy flux as the capture flux.

The change of the pair number in an energy interval around E with time t is equal to the scattering rate into the energy interval minus the scattering outside of the interval. So we have

$$R(E) \frac{\partial f(E,t)}{\partial t} = -R(E)f(E,t) \int_{-\infty}^{\infty} W(E,E') dE' + \int_{-\infty}^{\infty} f(E',t)R(E')W(E',E) dE', \quad (6)$$

where $W(E,E')dE'$ is the transition probability per unit time for a particle having a total energy E into an interval from E' to $E' + dE'$. $R(E)$ is the density of states in the total energy space. $f(E,t)$ is the distribution function including explicit time dependence. This equation can be written in the form of a conservation law $R(E)\partial f(E,t)/\partial t = -\partial I(E,t)/\partial E$, with

$$I(E,t) = - \int_E^{\infty} dE_1 \int_{-\infty}^E f(E_1,t)R(E_1)W(E_1,E_2) dE_2 + \int_{-\infty}^E dE_1 \int_E^{\infty} f(E_1,t)R(E_1)W(E_1,E_2) dE_2.$$

$I(E,t)$ is the flux in the total energy space. Defining a new variable $\Delta E = E_2 - E_1$, we get

$$I(E,t) = \int_{-\infty}^{\infty} d\Delta E \times \int_{E-\Delta E}^E f(E_1,t)R(E_1)W(E_1,\Delta E) dE_1. \quad (7)$$

In the quasielastic electron-acoustic phonon scattering, $W(E_1,\Delta E)$ is appreciable only for small ΔE . The distribution function changes little in such scale of ΔE . The integrand of Eq. (7) can be expand in terms of powers of $(E_1 - E)$. Keeping the first two terms we obtain an expression for the flux in a differential form,

$$I(E,t) = -B(E)f(E,t) - D(E) \frac{\partial f(E,t)}{\partial E}, \quad (8)$$

with

$$D(E) \equiv \frac{1}{2}R(E) \int_{-\infty}^{\infty} W(E,\Delta E)(\Delta E)^2 d\Delta E,$$

$$B(E) \equiv -R(E) \int_{-\infty}^{\infty} W(E,\Delta E)(\Delta E) d\Delta E + \frac{d}{dE}D(E). \quad (9)$$

If the system is in thermodynamic equilibrium, i.e., if $f(E)$ is the Boltzmann distribution, then the flux $I(E)$ should be zero. So one immediately gets the relation $D(E) = k_B T B(E)$. T is the lattice temperature and k_B is the Boltzmann constant. $I(E)$ can be written as

$$I(E) = -B(E) \left[f(E) + k_B T \frac{\partial f(E)}{\partial E} \right]. \quad (10)$$

The quantity $B(E)$ is called dynamic friction.⁹ It should be understood that both $I(E)$ and $f(E)$ have implicit time dependences so far. In the stationary condition, the distribution is time-independent, and the pair flux $I(E) = -j$ is energy-independent to avoid infinite accumulation. So $f(E)$ satisfies the ordinary differential equation

$$j = B(E) \left[f(E) + k_B T \frac{\partial f(E)}{\partial E} \right]. \quad (11)$$

A suitable boundary condition must be provided to have a definite solution for Eq. (11). Once the pairs performing random walks in the energy space reach an energy so low such that they can never return, we identify the pairs as captured and remove them from the energy space permanently. The corresponding ‘‘black-wall’’ boundary condition is $f(-E_1) = 0$, with $E_1 \gg k_B T$. The solution of Eq. (11) is then

$$f(E) = \frac{j}{k_B T} e^{-\beta E} \int_{-E_1}^E \frac{e^{\beta E'}}{B(E')} dE'. \quad (12)$$

In practice, the magnitude of E_1 is unimportant as long as it is large enough, and can be replaced by infinity.

The above considerations are for the negative energy half-space only. For the positive energy half-space, electron-hole pairs are constantly supplied by the current injection, with a fixed distribution function independent of the capture process. $f(0)$ in Eq. (12) needs to be matched at $E=0$ with the distribution function in the positive energy half-space. Assuming that the applied electric field is weak first, so the injected pairs follow the Maxwell distribution, and $f(E) = n(\hbar/L) \sqrt{2\pi\beta/m} \exp(-\beta E)$ for $E > 0$. It is related to momentum distribution function $g(k)$ by $f[\varepsilon(k)] = g(k)$, with the corresponding normalization $(L/2\pi) \int_{-\infty}^{\infty} g(k) dk = n$. $\varepsilon(k) = \hbar^2 k^2 / 2m$ is the relative kinetic energy. The capture rate R_c for one pair in a chain with length L is then

$$R_c = \frac{j}{n} = \frac{\hbar}{L} \sqrt{\frac{2\pi}{m\beta}} \left[\int_{-\infty}^0 \frac{e^{\beta E}}{B(E)} dE \right]^{-1}. \quad (13)$$

The capture lifetime τ_c can be defined as $R_c = 1/\tau_c$. The total number of pairs n in the ensemble is canceled as it should be. The L^{-1} scaling is physically desirable because of the full

extension of the electron and hole wave functions along the chain. The capture flux can be pictured as the leakage flux through a pinhole at the bottom of a balloon maintained at a fixed pressure and energy distribution as shown in Fig. 1. The calculations for the energy transition rates $W(E, \Delta E)$ and the dynamic friction $B(E)$, defined in Eq. (9), are tedious and can be found in the appendixes.

IV. CASCADE CAPTURE UNDER ELECTRIC FIELD

The electron-hole pairs in the ensemble experience no external electric field so far. In practice there is a strong external electric field \mathcal{E} in the recombination layer of the polymer LED. For $E < 0$ the relative motion of the electron-hole pair is constantly accelerated by the external electric field \mathcal{E} and the relative kinetic energy is increased due to joule heating by the external field. In other words, there is a drift flux I_d upward in the energy space in addition to the collision (random walk) flux I_c discussed in the previous section. The net capture flux results from the competition between these two opposite tendencies. As for the injected distribution function, $f(E)$ with $E > 0$ is driven out of equilibrium by \mathcal{E} , as determined by using the Boltzmann equation in principle. Instead of solving the complicated Boltzmann equation, we assume that the nonequilibrium distribution function is a shifted Maxwellian one in the momentum space, with mean momentum $\hbar \Delta k$ and electronic temperature T_e determined self-consistently by the balanced-energy condition.¹⁸

A. Drift and collision in energy space

For $E < 0$ the differential equation for the distribution function $f(E)$, modified by the external field \mathcal{E} , becomes

$$R(E) \frac{\partial f(E)}{\partial t} = - \frac{\partial}{\partial E} [I_d(E) + I_c(E)], \quad (14)$$

with

$$I_d = e v_d \mathcal{E} R(E) f(E), \quad I_c = B(E) \left[f(E) + k_B T \frac{\partial f}{\partial E} \right]. \quad (15)$$

v_d is the averaged drift velocity of the relative coordinate. $e v_d \mathcal{E}$ is the power a pair gains from the external field \mathcal{E} . As before, we are interested in steady state, in which $\partial f / \partial t = 0$, and $I_d(E) + I_c(E) = -j$ is independent of E . Defining

$$P(E) \equiv - \frac{e v_d \mathcal{E} R(E) - B(E)}{k_B T B(E)}, \quad Q(E) \equiv \frac{j}{k_B T B(E)}, \quad (16)$$

the equation for $f(E)$ becomes

$$\frac{\partial f(E)}{\partial E} + P(E) f(E) = Q(E), \quad (17)$$

with solution

$$f(E) = \left[\int \exp \left(\int P dE \right) Q dE + \text{const.} \right] \exp \left(- \int P dE \right). \quad (18)$$

Taking the black wall boundary condition $f(-E_1) = 0$ and setting $E_1 = \infty$ again, the solution becomes

$$f(E) = \exp \left[- \int_0^E P(E') dE' \right] \times \int_{-\infty}^E \exp \left[\int_0^{E'} P(E'') dE'' \right] Q(E') dE'. \quad (19)$$

The capture rate is now given by

$$R_c = \frac{j}{n} = \frac{1}{n} f(0) k_B T \left[\int_{-\infty}^0 \exp \left[\int_0^E P(E') dE' \right] \frac{1}{B(E)} dE \right]^{-1}. \quad (20)$$

The electric field \mathcal{E} enters this expression not only through $P(E')$ defined in Eq. (16), but also $f(0)$ as discussed below.

B. Injected distribution function

The relative wave numbers of the electron-hole pair is accelerated by the external field \mathcal{E} during the collision mean free time τ_{coll} . The mean value $\hbar \Delta k$ for the relative momentum is therefore $\hbar \Delta k = -e \mathcal{E} \tau_{coll}$. The corresponding drift velocity v_d is given by the group velocity $v_d = \hbar \Delta k / m$. The electronic temperature T_e is also raised by the electric field. In the steady state, the power of joule heating must be equal to the phonon energy emitted per unit time. This balanced-energy condition requires¹⁸ $T_e = T + (2/k_B) e \mathcal{E} v_d \tau_{coll}$, where T is the lattice temperature. The normalized shifted Maxwellian distribution for the relative momentum becomes

$$g(k) = n \frac{\hbar}{L} \sqrt{\frac{2\pi}{m k_B T_e}} \exp \left[- \frac{\hbar^2 (k - \Delta k)^2}{2m k_B T_e} \right]. \quad (21)$$

Because $f(0) = g(0)$, capture rate in Eq. (20) becomes

$$R_c = j = \left\{ \frac{\hbar}{L} \sqrt{\frac{2\pi}{m k_B T_e}} \exp \left[- \frac{\hbar^2 (\Delta k)^2}{2m k_B T_e} \right] \right\} \times k_B T \left[\int_{-\infty}^0 \exp \left[\int_0^E P(E') dE' \right] \frac{1}{B(E)} dE \right]^{-1}. \quad (22)$$

So far the capture rate R_c is inversely proportional to the chain size N . For convenience, we define a size-independent volume capture rate R_c^v as $R_c^v \equiv N R_c$. For an arbitrary chain with N_0 units, the capture rate for a pair in it can be expressed as R_c^v / N_0 . The volume capture rate R_c^v is shown as a function of the external field \mathcal{E} in Fig. 2 for various electron-phonon coupling parameter η . R_c^v stays at the zero-field value for \mathcal{E} smaller than 10^7 V/m, but it is dramatically suppressed when the field further increases. The main reason is that at such field $v_d \mathcal{E} R(E)$ in $P(E)$ [see Eq. (16)] cancels $B(E)$ significantly and makes $P(E)$ small. Note that R_c has an exponential dependence on $P(E)$ [Eq. (20)]. The capture rate increases with the electron-phonon coupling, because the phonon emission and energy release process becomes more efficient. R_c^v is shown in Fig. 3 for various dielectric

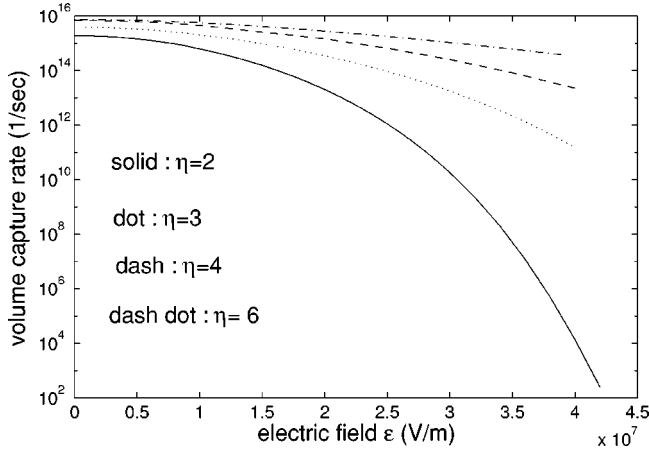


FIG. 2. The volume capture rate is shown for various dimensionless electron-phonon coupling parameter η .

constants ϵ . The capture rate is larger for smaller ϵ , because the Coulomb attraction between the electron and hole is stronger. In the calculation we use the following values for the parameters: $m_e = 0.117m_0$,¹⁹ $m_h = 0.0658m_0$ (m_0 is free-electron mass),¹⁹ $a = 1.22 \text{ \AA}$, $\alpha = 4.2 \text{ eV/\AA}$,²⁰ $\tau_{coll} = 4 \text{ fs}$,²¹ and $a_c = 6.5 \text{ \AA}$.¹⁴ η is fixed at 6 except in Fig. 2. ϵ is fixed¹⁹ at 8 except in Fig. 3. $T = 300 \text{ K}$ is used. The drift velocity is corrected at high field by the group velocity considering the band structure, with the bandwidth 2.4 eV. $s = a\sqrt{K/M}$ is used for the sound velocity, with²⁰ $K = 21 \text{ eV/\AA}^2$.

V. EXPERIMENTAL IMPLICATIONS

So far the consideration is for the capture of one electron-hole pair in a perfect chain. In order to compare with experiments and make realistic predictions, we include the UV emission, impact ionization, and orientation distribution of polymer chains in the model.

A. Direct interband UV emission

As the capture rate to form excitons is suppressed, the radiative decay of the electron-hole pair via direct interband

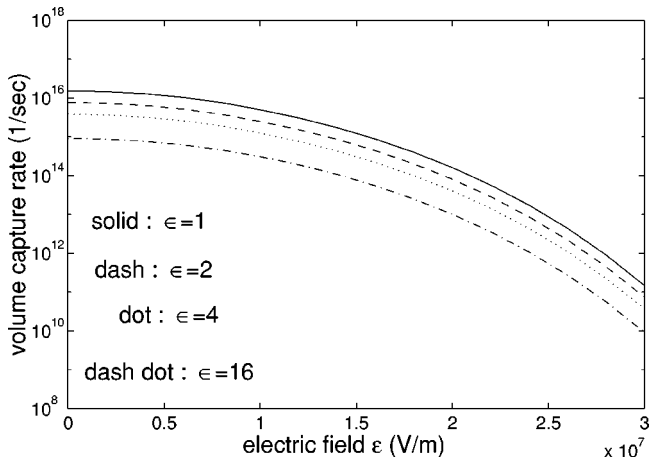


FIG. 3. The volume capture rate is shown for various strengths of electron-hole Coulomb interaction, characterized by the dielectric constant ϵ .

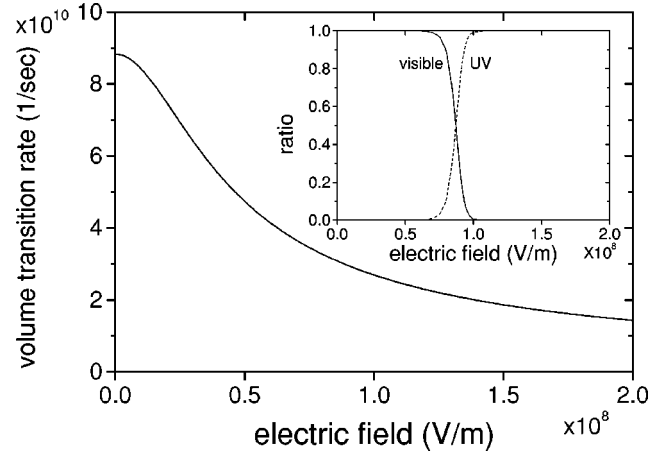


FIG. 4. The volume rate for direct interband transition R_{UV}^v is shown as a function of the external field. Its ratio to the electron-hole capture rate is also shown in the inset.

transition becomes possible. For conjugated polymers, the direct bandgap is above 3 eV, with the corresponding photon energy $\hbar\omega$ in the ultraviolet region. The radiative transition rate $1/\tau_0$ for an electron in the conduction band to decay into the vacant valence state with the same momentum is equal to²² $e^2 n_r \hbar \omega |p_{cv}|^2 / (3\pi\epsilon_0 m_o^2 c^3 \hbar^2)$, where n_r is the refractive index and p_{cv} is the momentum matrix element. For one electron-hole pair in the chain, this formula applies only when the center-of-mass momentum P of the pair is zero. In general, P is not fixed at zero, but has a distribution $f_{CM}(P)$ depending on the electronic temperature T_e . The distribution of P is assumed to be Maxwellian independent of the field \mathcal{E} , so we have

$$f_{CM}(P) = A \exp\left[-\frac{P^2}{2(m_e + m_h)k_B T_e}\right], \quad (23)$$

with normalization $(L/2\pi\hbar)\int_{-\infty}^{\infty} f_{CM}(P)dP = 1$ and $A = (\hbar/L)\sqrt{2\pi/(m_e + m_h)k_B T_e}$. The probability of finding $P = 0$ is $f(0) = A$. The UV emission rate is now

$$R_{UV} = f_{CM}(0) \frac{1}{\tau_0} = \frac{\hbar}{L} \sqrt{\frac{2\pi}{(m_e + m_h)k_B T_e}} \frac{1}{\tau_0}. \quad (24)$$

The UV emission lifetime τ_{UV} can be defined as $R_{UV} = 1/\tau_{UV}$. The L -independent volume transition rate R_{UV}^v is defined as $R_{UV}^v = NR_{UV}$. The electric field \mathcal{E} enters R_{UV} only through T_e . Unlike the exponential dependence on \mathcal{E} of R_c , R_{UV} has only a weaker power-law dependence on \mathcal{E} . R_{UV}^v is shown in Fig. 4 as a function of \mathcal{E} . The ratio between R_c and R_{UV} is also shown in the inset. It is predicted that UV emission dominates visible emission from exciton decay for field above 10^8 V/m . We adopt the formula $1/\tau_0 = \hbar\omega(eV)/0.67(1/\text{ns})$, commonly used for inorganic semiconductors.²²

B. Impact ionization and chain distribution

As discussed above, UV emission due to direct interband transition happens only at high field. In order to have a com-

plete description of the emission behaviors, another important effect at high field needs to be included. That is the impact ionization and the resulting avalanche breakdown of the electric current. UV emission in PPV LED has been observed experimentally under high field.⁴ One of the peculiar features of the reported results is that at the breakdown voltage around 300 V the UV emission jumps up by almost five orders of magnitude, while the visible emission jumps less than one order of magnitude. Such behavior can never be accounted for if only one chain is considered, because the ratio between R_{UV} and R_c is a continuous function of the electric field, no matter whether there is a current breakdown or not. With a single chain, the large breakdown current would be distributed between these two radiative decay channels with about the same ratio as immediately before the breakdown, implying that the visible and UV emission should jump by the same orders of magnitude. The discrepancy between the breakdown behaviors of the visible and UV emission suggests that the effective field for the chains is not uniform in the polymer film but divided into high-field and low-field components. The breakdown current passes through only the high-field chains where interband transition dominates, while the regular current passes through low-field chains where exciton dominates. In this case the large breakdown current contributes basically the UV emission only, and the observed discrepancy between visible and UV at the breakdown can be explained. We believe that the nonuniform effective field is due to the chain orientation distribution in the spin-cast polymer films. For a fixed applied external voltage, the effective electric field projected onto a chain depends on the angle between the chain and the applied field. In order to compare our results with the experiments, we have to consider a distribution of chain orientations and average the exciton (visible) and interband (UV) emission intensities over the distribution.

Consider the single chain current J_s first. The relation between J_s and \mathcal{E} can be modeled by a singular function as²³ $J_s(\mathcal{E}) = \sigma\mathcal{E}/[1 - c_1\mathcal{E}\exp(-c_2/\mathcal{E})]$ for $\mathcal{E} < \mathcal{E}_{bd}$. The breakdown field \mathcal{E}_{bd} is chosen to be close to the zero of the denominator. For $\mathcal{E} > \mathcal{E}_{bd}$, the breakdown current is taken as an adjustable parameter J_{bd} . c_1 and c_2 are parameters related to the band structure and scattering rates. σ is an unimportant proportional constant. We model the LED as a combination of a bulk of amorphous polymer chains and a small amount of breakdown filaments. The charge transport in the bulk is assumed to be limited by the interchain hopping, and obeys the common space-charge-limited-current (SCLC) current-voltage relations. On the other hand, the charge transport in the filaments is more like the single chain situation. The SCLC current for the bulk is

$$J_{SCLC}(\mathcal{E}) = \frac{9}{8} \epsilon \epsilon_0 \mu_{eff} \frac{V^2}{d^3}, \quad (25)$$

where ϵ is the dielectric constant of the polymer film. d is the active layer thickness. V is the applied voltage. Even though the total SCLC current is fixed, microscopically the current

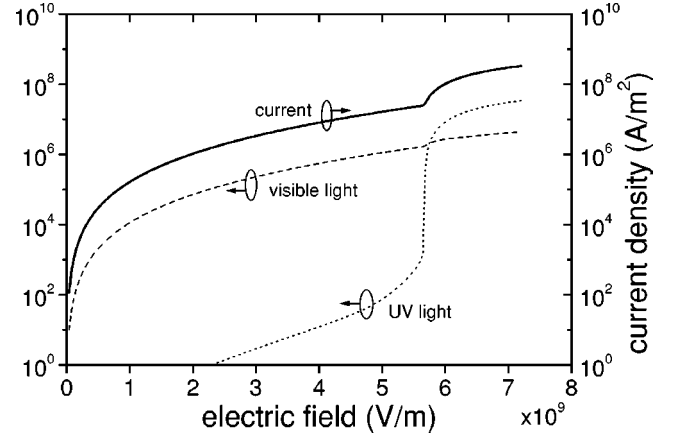


FIG. 5. The emission and current characteristics are shown for a polymer film with a Gaussian chain orientation distribution width 0.13 rad for the bulk, and uniform in $\pm [0.07-0.13]$ radian for the filaments.

in each chain depends on the local chain orientation with respect to the field. Therefore, we can decompose the bulk current as

$$J_{SCLC}(\mathcal{E}) = A(\mathcal{E}) \int J_s(\mathcal{E} \sin \theta) P_c(\theta) d\theta. \quad (26)$$

θ is the angle between chains and substrate. The external field is assumed to be applied vertically to the substrate. $P_c(\theta)$ is the probability distribution for θ , which is assumed to peak at $\theta=0$ for the spin-cast polymer film because the chains are aligned parallel to the substrate. $A(\mathcal{E})$ is an overall normalization factor that limits the current injected to each chain, and makes sure that the total integrated current in Eq. (26) is the same as the SCLC current. $A(\mathcal{E})J_s(\mathcal{E} \sin \theta)$ is therefore the current that passed through a chain with orientation angle θ . Combined with the filament current J_f , the total current J_t can be expressed as

$$J_t(\mathcal{E}) = J_{SCLC} + J_f = [A(\mathcal{E}) + r] \int J_s(\mathcal{E} \sin \theta) P_c(\theta) d\theta, \quad (27)$$

where r is a small parameter that adjusts the ratio of the filaments to bulk. The total exciton light intensity from the whole distribution can be expressed as

$$I_t^{ex}(\mathcal{E}) = I_{bulk}^{ex} + I_f^{ex} \\ = [A(\mathcal{E}) + r] \int J_s(\mathcal{E} \sin \theta) R_c(\mathcal{E} \sin \theta) P_c(\theta) d\theta. \quad (28)$$

$R_c = 1/\tau_c$ is the exciton capture rate. The total UV emission intensity $I_t^{UV}(\mathcal{E})$ can be obtained by replacing R_c in Eq. (28) by the UV emission rate $R_{UV} = 1/\tau_{UV}$. The calculated result is shown in Fig. 5, in which the current, visible light emission, and UV emission are plotted as a function of the bulk electric field. The θ distribution for the bulk is a Gaussian peaked at zero with width equal to 0.07 rad, the distribution for the filaments is uniform in the intervals $\pm [0.07-0.13]$ rad. The theoretical predictions, in particular

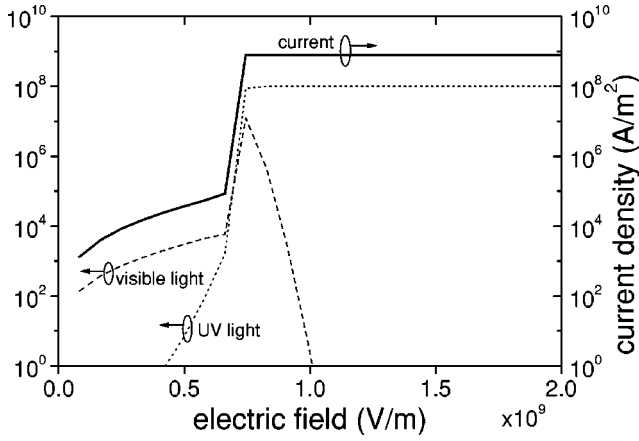


FIG. 6. The characteristics are shown for a polymer film with the orientation distribution of Fig. 5 rotated by $\pi/2$.

the features of the breakdown and UV emission, agree well with the experimental results observed by Chayet *et al.*,⁴ in which an LED of 50 nm active layer is driven up to 300 V. As expected, the ratio between the light and current decreases with the field. For the lower-field regime, the conversion efficiency (light/current) decreases by a factor of 3 as the field increases from 10^8 V/m to 10^9 V/m. Such behavior is typical of LED with active region thickness around 100 nm and driven by tens of volts. In our calculation the effective mobility μ_{eff} in Eq. (25) is approximated by $\mu_{eff} \approx \mu_h$ for $\mu_h \gg \mu_e$. The formula $\mu_h = \mu_{h,0} \exp(-\Delta/kT) \exp(\gamma\sqrt{E})$ is used for the field-dependent mobility,²⁴ with $\mu_{h,0} = 3/5 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\Delta = 0.48 \text{ eV}$, and $\gamma = 10^{-4} \text{ m}^{1/2} \text{ V}^{-1/2}$. Other parameters used are $c_1 = 5 \times 10^{-8} \text{ m/V}$, $c_2 = 1.4 \times 10^8 \text{ V/m}$, $j_{bd} = 10^{17} \text{ A/m}^2$, $d = 500 \text{ \AA}$, and $r\sigma = 10^{-11} \text{ A m/V}$.

There are three characteristic electric fields E_1 , E_2 , and E_3 in this model. E_1 is the field at which the capture starts to be suppressed. E_2 is the field at which the UV rate is equal to the visible rate. And E_3 is the breakdown field. It is crucial that they are ordered as $E_1 < E_2 < E_3$ to explain the experimental curves. Such order is fully consistent with our calculation. The behaviors of the LED depend sensitively on the chain distribution function $P_c(\theta)$. In general, a larger θ implies smaller breakdown voltage. In order to describe the case where the external field is applied parallel to the substrate, we rotate the distribution of Fig. 5 by $\pi/2$. The results are shown in Fig. 6. For the parallel device, UV dominates visible emission for a much wider range of the electric field, implying a potential-efficient UV source.

As discussed in Introduction, the high field is expected to reduce not only EL but PL as well. The experiments of PL under high field show that PL is almost completely quenched for bulk field above 3×10^8 V/m.¹¹ The corresponding microscopic field projected along the chain direction is estimated to be about 10^7 V/m because the polymer chains mainly lie on the substrate and perpendicular to the bulk field. These results agree well with our calculation that predicts significant suppression of electron-hole capture for fields beyond 10^7 V/m (Figs. 2,3). Theoretical models^{12,13} have been proposed that describe the interchain exciton mi-

gration and field quenching. In these works exciton dissociation is allowed only in a fraction α of the chains. α is then treated as a field-dependent fitting parameter, whose fitted value increases significantly for bulk field beyond 3×10^8 V/m. Our study focuses on the microscopic origin of the field quenching in one chain, and is complementary to these phenomenological works.

VI. DISCUSSION AND CONCLUSION

One interesting feature of the cascade capture process is that the capture rate is completely determined by the flux in the semiclassical region of the energy space, in which the energy levels form a quasicontinuum. The distribution function and therefore the flux in this region do not depend on the details of the boundary condition at the lower end of the energy space, as long as the boundary is far away from the zero-energy level. The simplest way is to take a black-wall condition at a negative energy $-E_1$, such that all the pairs that walk below $-E_1$ are removed from the energy space and can never walk upward back from the wall. Physically this is reasonable because lying at the bottom of the semiclassical continuum are the discrete exciton levels. The electron-hole pair can never freely absorb phonon and gain energy once they form tightly bound excitons. The final results on the capture rate is independent on the choice of $-E_1$ provided it is large enough. When an electric field is applied, the distribution function and the flux are changed by the drift of the pairs upward in energy. Almost no pairs can reach the black wall under high field and the rate is dramatically reduced. The field suppression of the exciton formation discussed here is different from the field dissociation of excitons, in which the carrier tunnel through the Coulomb barrier to the degenerate free state under the field. Because of the large binding energy of the excitons in conjugated polymers, the field dissociation is expected to be weak and not considered in this work.

The suppression of the electron-hole capture to form excitons for electric fields above 10^7 V/m has a significant consequence for potential applications that require a high exciton density, e.g., the injection laser. A large exciton density translates into a large injection current, which in turn requires a large applied field due to the low mobility. Our study shows that the exciton density cannot be raised proportionally to the field and the current, and the only way to reach high exciton density is to improve the mobility and reduce the required field. The improvement of the material quality and device structure for better mobility is therefore identified as one of the critical issues for further research on electroluminescent conjugated polymers.

The possibility for UV emission by direct interband transition is opened for conjugated polymers when the electron-hole capture is suppressed. The direct interband transition is not a cascade process and survives under the electric field. Even though the UV emission happens only at high field, the possibility that a conjugated polymer can emit not only visible but also UV light is interesting. It implies that polymers have the potential application as a semiconductor UV source, considering the ease in fabricating them compared with the

conventional III-nitride compounds. Sandwich structure is not ideal for this purpose, because the field is mostly perpendicular to the polymer chain direction. It will be much easier to achieve the high field along the chain and generate the UV output if the field is applied parallel to the chain directions. Another interesting prediction is that the UV emission can be achieved under unipolar injection, because free electron-hole pairs can be created through the injected hot carriers with impact ionization. There are therefore both types of carriers in the polymer even when only one type is directly injected through the electrodes. These carriers cannot recombine to form excitons due to the high field. So the only radiative channel for them to recombine is the UV emission through direct interband transition.

In conclusion, our theoretical study on the cascade capture process in conjugated polymers shows that the exciton formation due to electron-hole Coulomb capture is suppressed by several orders of magnitude for field in the range of 10^7 – 10^8 V/m. As the visible emission from the exciton decay is reduced, the UV emission due to direct interband transition becomes the dominant radiative channel. Combined with impact ionization, the experiments on the UV emission under high field can be explained quantitatively. Mobility improvement is identified as the critical issue for applications requiring high exciton density. A unipolar UV light source based on conjugated polymers is proposed.

ACKNOWLEDGMENT

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APPENDIX A: TRANSITION RATE $W(E, \Delta E)$ IN ENERGY SPACE

If there is no phonon present initially, the transition rate $w(\varepsilon_1, \varepsilon_2)d\varepsilon_2$ for a free pair from kinetic energy ε_1 to energy interval $(\varepsilon_2, \varepsilon_2 + d\varepsilon_2)$ via one-phonon emission process is given by [Eq. (6)]

$$w(\varepsilon_1, \varepsilon_2) = \sum_{k_i, k_f} \frac{\delta[\varepsilon_1 - \varepsilon(k_i)]}{\rho(\varepsilon_1)} w(k_i, k_f, q) \delta[\varepsilon_2 - \varepsilon(k_2)], \quad (\text{A1})$$

where $\rho(\varepsilon) = (L/\pi\hbar)\sqrt{m/2\varepsilon}$ is the kinetic energy density of states. Changing the summation \sum_k into an integral $(L/2\pi)\int dk$ and after some algebra, we obtain

$$w(\varepsilon_1, \varepsilon_2) = \frac{1}{2} \sqrt{\frac{m}{2\varepsilon_2}} \frac{L}{2\pi\hbar} \left[w\left(\frac{\sqrt{2m\varepsilon_1}}{\hbar}, \frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(-\frac{\sqrt{2m\varepsilon_1}}{\hbar}, \frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(\frac{\sqrt{2m\varepsilon_1}}{\hbar}, -\frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(-\frac{\sqrt{2m\varepsilon_1}}{\hbar}, -\frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) \right]. \quad (\text{A2})$$

$w(k, k', q)$ is defined in Sec. II. Below we replace ε_1 by ε and ε_2 by $\varepsilon - \delta\varepsilon$, then write $w(\varepsilon_1, \varepsilon_2)$ as $w(\varepsilon, \delta\varepsilon)$. $\delta\varepsilon > 0$

is the energy of the emitted acoustic phonon. Since the potential energy of the electron-hole pair does not change during phonon emission or absorption processes, the change of the total energy δE is equal to $\delta\varepsilon$. The transition rate for a pair from total energy (kinetic plus potential) E to $E - \delta E$ is related to $w(\varepsilon, \delta\varepsilon)$ by

$$w(E, \delta E) = R^{-1}(E) \int \delta[E - \varepsilon - V(x)] w(\varepsilon, \delta\varepsilon) \rho(\varepsilon) d\varepsilon dx, \quad (\text{A3})$$

where $R(E) = \int_0^\infty \rho(\varepsilon) d\varepsilon dx \delta[\varepsilon(k) + V(x) - E]$ is the density of states in total energy space. The phonon occupation number $N(\delta E) = [\exp(\delta E/k_b T) - 1]^{-1}$ has to be considered at finite temperatures. The phonon energy δE is always positive. So for $\Delta E < 0$, the energy transition rate for phonon emission can be written as⁹

$$W(E, \Delta E) = w(E, -\Delta E) [1 + N(-\Delta E)]. \quad (\text{A4})$$

For $E > 0$, the rate for phonon absorption is

$$W(E, \Delta E) = \frac{R(E + \Delta E)}{R(E)} w(E + \Delta E, \Delta E) N(\Delta E). \quad (\text{A5})$$

APPENDIX B: DYNAMIC FRICTION $B(E)$

Using Eqs. (A4), (A5), and (9), and expanding $w(E, \delta E)$ and $R(E + \delta E)$ in δE to the first order, we get

$$B(E) = R(E) \int_0^\infty w(E, \delta E) \delta E d(\delta E). \quad (\text{B1})$$

Note that $N(\delta E)$ is canceled. Inserting Eqs. (A2) and (A3) into Eq. (B1), we get

$$B(E) = \int_0^\infty \delta[E - \varepsilon - V(x)] w(\varepsilon, \delta\varepsilon) \rho(\varepsilon) \delta E d(\delta E) d\varepsilon dx \\ = \frac{1}{2} \sqrt{\frac{m}{2\varepsilon_2}} \frac{L}{2\pi\hbar} \int_0^\infty \delta[E - \varepsilon - V(x)] \\ \times \left[w\left(\frac{\sqrt{2m\varepsilon_1}}{\hbar}, \frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(-\frac{\sqrt{2m\varepsilon_1}}{\hbar}, \frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(\frac{\sqrt{2m\varepsilon_1}}{\hbar}, -\frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) + w\left(-\frac{\sqrt{2m\varepsilon_1}}{\hbar}, -\frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) \right] \\ \times \rho(\varepsilon) \delta E d(\delta E) d\varepsilon dx. \quad (\text{B2})$$

The calculation is tedious and can be separated for four terms in the square bracket as follows. According to Eq. (6), the first term in Eq. (B2) is

$$\begin{aligned}
B_1(E) &= \frac{1}{2} \sqrt{\frac{m}{2\varepsilon_2}} \frac{L}{2\pi\hbar} \int_0^\infty \delta[E - \varepsilon - V(x)] w\left(\frac{\sqrt{2m\varepsilon_1}}{\hbar}, \frac{\sqrt{2m\varepsilon_2}}{\hbar}, q\right) \rho(\varepsilon) \delta E d(\delta E) d\varepsilon dx \\
&= \frac{1}{2} \sqrt{\frac{m}{2\varepsilon_2}} \frac{L}{2\pi\hbar} \int_0^\infty \delta[E - \varepsilon - V(x)] \frac{L}{\hbar^2 s} \xi_q^2 \left[\frac{2\pi}{L} [\delta(p_{1q}) + \delta(p_{2q})] + \frac{2\pi}{L} [\delta(p_{1-q}) + \delta(p_{2-q})] \right] \rho(\varepsilon) \delta E d(\delta E) d\varepsilon dx \\
&= \frac{1}{2} \sqrt{\frac{m}{2\varepsilon_2}} \frac{L}{2\pi\hbar} \int_0^\infty \delta[E - \varepsilon - V(x)] \frac{L}{\hbar^2 s} \xi_q^2 \left[\frac{2\pi}{L} [\delta(k_i - k_f - s_1 q) + \delta(k_i - k_f - s_2 q)] \right. \\
&\quad \left. + \frac{2\pi}{L} [\delta(k_i - k_f + s_1 q) + \delta(k_i - k_f + s_2 q)] \right] \rho(\varepsilon) \delta E d(\delta E) d\varepsilon dx. \tag{B3}
\end{aligned}$$

All other terms can be expanded in the same way. Their integrands contain integral of the form $\int_0^\varepsilon g(\delta\varepsilon) \delta\varepsilon \delta[p(\delta\varepsilon)] d\delta\varepsilon$, where $g(\delta\varepsilon)$ is a certain function, and $p(\delta\varepsilon)$ having the form $p(\delta\varepsilon) = \pm k_i \pm k_f \pm s_{1,2} q$. $q = \delta\varepsilon/\hbar s$ and we restrict k and q to be positive. Note that ε is the initial particle kinetic energy and $\delta\varepsilon$ is the emitted phonon energy. $p(\delta\varepsilon)$ implies energy and momentum conservation laws. There are four δ functions in the last expression for $B_1(E)$ in Eq. (B3). Only the first two conditions can be satisfied. For example

$$\begin{aligned}
&\int_0^\varepsilon \delta\varepsilon g(\delta\varepsilon) \delta(k_i - k_f - s_{1,2} q) d\delta\varepsilon \\
&= \int_0^\varepsilon \delta\varepsilon g(\delta\varepsilon) \\
&\quad \times \delta\left[\frac{\sqrt{2m\varepsilon}}{\hbar} - \left(\frac{\sqrt{2m(\varepsilon - \delta\varepsilon)}}{\hbar} + \frac{s_{1,2}}{\hbar s} \delta\varepsilon\right)\right] d\delta\varepsilon. \tag{B4}
\end{aligned}$$

Defining

$$\begin{aligned}
f &\equiv \frac{\sqrt{2m(\varepsilon - \delta\varepsilon)}}{\hbar} + \frac{s_{1,2}}{\hbar s} \delta\varepsilon, \\
f' &= \frac{df}{d\delta\varepsilon} = -\frac{\sqrt{2m}}{2\hbar} \frac{1}{\sqrt{\varepsilon - \delta\varepsilon}} + \frac{s_{1,2}}{\hbar s}, \tag{B5}
\end{aligned}$$

then Eq. (B4) becomes

$$\int \delta\varepsilon(f) g(f) \delta\left(\frac{\sqrt{2m\varepsilon}}{\hbar} - f\right) \frac{1}{f'} df. \tag{B6}$$

The result is nonzero only when $(s\sqrt{2m}/2s_{1,2})^2 < \varepsilon \leq (s\sqrt{2m}/s_{1,2})^2$. The same procedure can be repeated for $p(\delta\varepsilon) = -k_i + k_f + s_{1,2} q$. Collecting all contributions derived from the same conservation law from the four terms in the square bracket of Eq. (9) in $B_a(E)$, we have

$$\begin{aligned}
B_a(E) &= 2 \int_{(s\sqrt{2m}/2s_1)^2}^{(s\sqrt{2m}/s_1)^2} \delta[E - V(x) - \varepsilon] h(\delta\varepsilon_1) \frac{2\pi}{L} \rho(\varepsilon) \delta\varepsilon_1 \left(\frac{\sqrt{2m}}{2\hbar\sqrt{\varepsilon - \delta\varepsilon_1}} - \frac{s_1}{\hbar s}\right)^{-1} d\varepsilon dx \\
&\quad + 2 \int_{(s\sqrt{2m}/2s_2)^2}^{(s\sqrt{2m}/s_2)^2} \delta[E - V(x) - \varepsilon] h(\delta\varepsilon_2) \frac{2\pi}{L} \rho(\varepsilon) \delta\varepsilon_2 \left(\frac{\sqrt{2m}}{2\hbar\sqrt{\varepsilon - \delta\varepsilon_2}} - \frac{s_2}{\hbar s}\right)^{-1} d\varepsilon dx, \tag{B7}
\end{aligned}$$

where

$$h(\delta\varepsilon) = \frac{1}{2} \sqrt{\frac{m}{2(\varepsilon - \delta\varepsilon)}} \frac{L^3}{2\pi\hbar^3 s} \eta^2 a^2 \alpha^2 \frac{\hbar}{2NM s} \frac{\delta\varepsilon}{\hbar s},$$

$$\delta\varepsilon_{1,2} = \frac{2s\sqrt{2m\varepsilon}}{s_{1,2}} - \frac{2ms^2}{s_{1,2}^2}.$$

The other set of the conservation conditions that can be satisfied is $\delta(k_i + k_f - s_{1,2} q)$. All such terms are collected in $B_b(E)$ as

$$\begin{aligned}
B_b(E) = & 2 \int_{(s\sqrt{2m}/s_1)^2}^{\infty} \delta(E - V(x) - \varepsilon) h(\delta\varepsilon_1) \frac{2\pi}{L} \rho(\varepsilon) \delta\varepsilon_1 \left(\frac{\sqrt{2m}}{2\hbar\sqrt{\varepsilon - \delta\varepsilon_1}} + \frac{s_1}{\hbar s} \right)^{-1} d\varepsilon dx \\
& + 2 \int_{(s\sqrt{2m}/s_2)^2}^{\infty} \delta(E - V(x) - \varepsilon) h(\delta\varepsilon_2) \frac{2\pi}{L} \rho(\varepsilon) \delta\varepsilon_2 \left(\frac{\sqrt{2m}}{2\hbar\sqrt{\varepsilon - \delta\varepsilon_2}} + \frac{s_2}{\hbar s} \right)^{-1} d\varepsilon dx. \quad (\text{B8})
\end{aligned}$$

Finally we have $B(E) = B_a(E) + B_b(E)$.

*Corresponding author. Electronic address: meng@cc.nctu.edu.tw

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