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Saturation of Charge Carrier Velocity with Increasing Electric Fields: Theoretical Investigations for Pure Organic Crystals

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Saturation of charge carrier velocity with increasing electric fields: Theoretical investigations for pure organic crystals

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Should one expect injected charge carrier velocities to saturate as the applied electric field is increased simply because of the nonparabolicity of bands? Does the apparent saturation observed in recent experiments in hydrocarbon crystals signify, as supposed in some current interpretations of the data, that the carrier motion is coherent or bandlike and that the disappearance of the saturation at higher temperatures is indicative of a crossover from coherent to incoherent motion? These questions are addressed with the help of general theoretical investigations involving Drude-like considerations, quantum kinetic equations, and a Fokker-Planck analysis.

I. INTRODUCTION: NEED FOR CLARIFICATION

Recent transport experiments on injected charges in ultra-pure organic solids have revealed high mobilities with temperature dependences more typically associated with inorganic crystalline semiconductors.[1] Two striking features of these observations are worthy of note. The first has to do with the temperature behavior of the mobility, and bears close kinship to the so-called band-hopping transition problem which arose a couple of decades ago as the result of the experiments[2,3] on pure crystals of naphthalene.[4] The second has to do with the observed saturation of carrier velocities with increased applied fields which occurs at low temperatures. The focus of the present paper is this second feature. This observed velocity saturation was recently interpreted[1] as demonstrating coherent, bandlike motion of the carrier when it is present, and incoherent hopping when it is absent—an interpretation recently used by its proponents for the quantitative extraction of bandwidths. Because the latter are an essential input into studies of the nature of charge carriers, the character of their motion, and related fundamental issues that have been the target of investigations into coherence in excitation and carrier transport in organic materials for decades,[5–7] a theoretical investigation into the phenomenon of velocity saturation at this time is of particular importance.

An examination of the field dependence of carrier velocity in pentacene, as reported in Fig. 2 of Ref. 1, shows saturation at a lower temperature but no saturation as temperature is increased. The qualitative appearance of those observed curves is identical to that displayed in Fig. 6 in Sec. V of the present paper. We begin our discussion with such plots, and ask whether it is true that such data inevitably lead to the conclusion, currently popular in some circles, that the different behavior displayed by the two curves is indicative of a crossover from coherent to incoherent motion. Three separate mechanisms were discussed in the experimental literature as possible sources for the nonlinear dependence of the drift velocity with field. The first is based on Shockley's hot electron theory;[8] the second on a heuristic argument involving the emission of optical phonons, also due to Shockley;[8] and the third on a related argument apparently due to Warta and Karl,[3] whose focus was the nonparabolicity of bands, i.e., the wave-vector dependence of the effective mass.

The first mechanism[1] appears to do a reasonable job of explaining the nonlinear increase of the velocity at fields below about 10^5 V/cm, but predicts velocities that asymptotically continue to grow as the square root of the field,[8,9] in contrast to the saturation which appears in the low-temperature data for pentacene[1] as well as in early observations for naphthalene.[3] In the second mechanism, the carrier repeatedly gains momentum as the result of the field and loses it through the emission of an optical phonon of energy $\hbar\Omega$, returning the carrier to the initial state at $k=0$. For a parabolic band this leads to a saturation velocity $v=\hbar\Omega/2m^*$, where m^* is the carrier effective mass. However, the velocity calculated from it leads, according to Refs. 3 and 1, to unreasonably large bandwidths.

It is the third mechanism, based on the nonparabolic shape of bands, which is deserving of close inspection, since it was invoked by the authors of Refs. 3 and 1 to explain saturation, and used by them to interpret data and extract bandwidths. Bandwidths in organic crystals being generally smaller than their counterparts in inorganic materials, it is important to consider the nonparabolic nature of bands in the polyacenes. The argument invoked in Refs. 3 and 1 is based on a physical picture in which, starting with the initial value $k=0$, the wave vector of the carrier grows linearly for a fixed collision time τ, before a scattering event returns it to the initial value. An average of the particle velocity is taken over the time interval between collisions to yield, for a tight-binding band, the drift velocity

$$v = \frac{Wa}{2\hbar}\left[\frac{1-\cos(qEa\tau/\hbar)}{qEa\tau/\hbar}\right], \tag{1}$$

where W is the bandwidth, E the electric field, q the carrier charge, and a the lattice constant. It was asserted in Ref. 3,
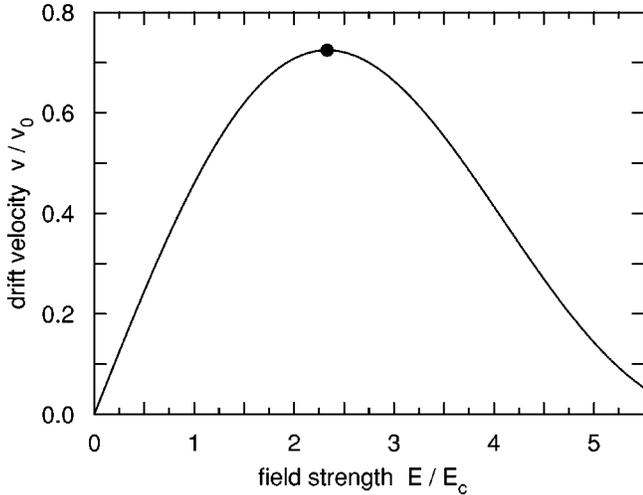
FIG. 1. Explicit demonstration that the expression frequently used for interpreting velocity saturation [Eq. (1)], exhibits no saturation. Plotted is the drift velocity scaled to $v_0 = Wa/2\hbar$ as a function of the field $E_c = \hbar/q\tau a$. The circular symbol identifies the peak value of the velocity, incorrectly taken in Ref. 3 to be the saturation value.

and repeated in Ref. 1, that this leads to a saturation velocity approximately given by

$$v \approx (0.724)\frac{Wa}{2\hbar}. \qquad (2)$$

This relation between the saturation velocity and the bandwidth is then used by Schön *et al.* and Warta and Karl for a quantitative interpretation of data taken for a large number of polyacenes.[1,3]

One of the motivations for the present paper arises from the easily verified fact that Eq. (2) *cannot* arise from Eq. (1) because the latter does *not* predict any saturation of the velocity. It does predict an Ohmic velocity at low fields ($qEa < \hbar/\tau$) and a peak when $qEa \approx 2.3\hbar/\tau$. Rather than a saturation, Eq. (1) actually predicts a decrease in the velocity for high fields. The velocity indicated in Eq. (2) refers to no saturation, but only to the peak value in expression (1). This should be clear from Fig. 1, where we have plotted Eq. (1) in terms of the maximum velocity $v_0 = 2Va/\hbar$ that the carrier can have in the band, and the characteristic electric field $E_c = \hbar/q\tau a$. No mechanism considered so far seems, thus, to predict the velocity saturation clearly observed in the low-temperature data.

We therefore ask under what conditions simple models based on the obvious dependence of the effective mass on velocity (i.e., on the nonparabolic nature of the bands) could show such a velocity saturation at high fields. In Sec. II, we treat a simple quasi-Newtonian model which captures the essential features of the nonparabolic dispersion, and find that it also predicts no saturation, but an Ohmic rise, followed by a peak, and an eventual decrease of velocity with increasing field. We also find a sharp transition, with a striking cusp separating the low-field Ohmic from the high-field non-Ohmic regime. In order to go beyond the simplified single-particle ideas characteristic of this model, in Sec. III

we consider a simple quantum kinetic equation treatment based on the stochastic Liouville equation obeyed by the carrier density matrix, or equivalently on the Boltzmann equation. That approach is also found to predict an Ohmic increase followed by a decrease, but no saturation. We then present, in Sec. IV, a treatment based on a Fokker-Planck description of the dynamics, which not only interpolates cleanly between the extreme temperature limits, but provides a clear and quantitative bridge from the quasi-Newtonian to the kinetic equation approach. Once again, however, no saturation is observed. In our final remarks in Sec. V, we comment in passing on two other possible sources of saturation which are different from coherence considerations, and conclude that observed saturation may have little to do with coherence, in contrast to current interpretations.

Most of our considerations apply for general band shapes, but in the interest of specificity in many cases we will use formulas applicable to the one-dimensional tight-binding situation in which the band energy ε_k is given by $2V(1-\cos ka)$, where $\hbar k$ is the quasimomentum, V is the nearest-neighbor overlap integral and, as noted earlier, a is the lattice constant. These formulas include the velocity and effective-mass expressions

$$v_k = \frac{1}{\hbar}\frac{d\varepsilon_k}{dk} = \frac{2Va}{\hbar}\sin ka = v_0 \sin ka, \qquad (3)$$

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\varepsilon_k}{dk^2} = \frac{v_0 a}{\hbar}\cos ka = \frac{a}{\hbar}\sqrt{v_0^2 - v^2}. \qquad (4)$$

II. EVOLUTION OF THE CRYSTAL MOMENTUM AND A ZERO-TEMPERATURE TRANSITION

Effective-mass theory[10] states that, provided its necessary conditions such as the slow spatial and temporal variation of external fields are satisfied, forces exerted on the carrier by agencies other than the periodic potential in the crystal can be represented as additive terms in the evolution equation for the carrier crystal momentum $\hbar k$. The appropriate starting point to develop a quasi-Newtonian approach to our problem is therefore the crystal momentum evolution equation augmented by the addition of a damping force proportional to the velocity in the band,

$$\hbar\frac{dk}{dt} + \gamma v_k = qE \qquad (5)$$

through a constant of proportionality γ, which we take to be independent of k for the sake of simplicity, and with v_k given by Eq. (3) in a tight-binding situation. To quadratures, the evolution of the crystal momentum (in the tight-binding case) obeys

$$\left(\frac{qE}{\hbar}\right)t + \text{const} = \int \frac{dk}{1 - \left(\dfrac{E_c}{E}\right)\sin ka}. \qquad (6)$$

Different kinds of behavior result according to whether the applied field E is greater or smaller than the critical value

$E_c = \gamma v_0 / q$. For small fields, the denominator in the integral in Eq. (6) can diverge, but not for fields exceeding the critical value. What this means is that, for small fields ($E < E_c$), k and the corresponding velocity v_k approach a constant value, but not for large fields ($E > E_c$). In the latter case, the carrier exits the Brillouin zone at one end to reenter it at the other and asymmetric Bloch oscillations occur.[11] This is the well-known phenomenon of an ac current being produced by a dc field. Because of the damping term, however, the average velocity is not zero—the carrier actually spends more time in the half of the Brillouin zone along the direction parallel to the field. This difference in the time spent in each half ultimately decreases with increasing field, with the consequence that the average velocity ultimately decreases with increasing field. Thus the prediction of our quasi-Newtonian model straightforwardly leads, for large fields, to the widely known phenomenon of negative differential mobility.

The above qualitative statements can be verified explicitly from an analytical evaluation of the integral in Eq. (6). Identifying, for notational convenience, the quantity $\gamma v_0 a / \hbar$ by $1/\tau$ where τ is a "relaxation time," and introducing the ratio $\zeta = E / E_c$, the solution for $k(t)$ is

$$\tan \frac{ak(t)}{2} = \left(\frac{1}{\zeta} \right) \left[1 - \sqrt{1 - \zeta^2} \tanh \left(\frac{t}{\tau} \frac{\sqrt{1 - \zeta^2}}{2\zeta} + \text{const} \right) \right], \tag{7}$$

which can also be written as

$$\tan \frac{ak(t)}{2} = \left(\frac{1}{\zeta} \right) \left[1 + \sqrt{\zeta^2 - 1} \tan \left(\frac{t}{\tau} \frac{\sqrt{\zeta^2 - 1}}{2\zeta} + \text{const} \right) \right]. \tag{8}$$

These two results are useful for small fields ($E < E_c$) and large fields ($E > E_c$), respectively. For all field values smaller than or equal to E_c, the hyperbolic tangent saturates to 1 for large times and the crystal momentum approaches the constant value

$$\hbar k_\infty = \frac{2\hbar}{a} \arctan \left(\frac{1 - \sqrt{1 - \zeta^2}}{\zeta} \right), \tag{9}$$

which lies between 0 and $\pi/2$. For this case $E < E_c$, the velocity of the carrier approaches the constant value v_∞. Substitution of the value of k_∞ in the expression $v_\infty = v_0 \sin k_\infty a$ shows that the steady-state velocity v_∞ is always proportional to the electric field:

$$v_\infty = v_0 \zeta. \tag{10}$$

That the behavior is *perfectly* Ohmic for *all fields below* E_c is also directly clear from Eq. (5), which shows that, if dk/dt vanishes at long times (this happens for $E < E_c$ but not if $E > E_c$), v_k is equal to qE/α which is $v_0 \zeta$.

If the field is larger than the critical value, i.e., $E > E_c$, the dynamics differs sharply. The carrier exits the Brillouin zone at one end, reenters from the other, and periodically passes through the zone in a time period

$$T_0 = \int_0^{2\pi/a} \frac{dk}{\zeta - \sin ka} = \frac{\hbar}{\gamma v_0} \frac{2\pi}{\sqrt{\zeta^2 - 1}}, \tag{11}$$

obtained by integrating Eq. (6) over appropriate limits. Thus, if the field is sufficiently large, there is no approach of k or of the velocity v_k to a constant value. The oscillations are clear from the fact that Eq. (8), which governs the carrier motion for large field, has the trigonometric tangent on its right-hand side. This is in contrast to Eq. (7) appropriate to the small field case, which contains the hyperbolic tangent, and thus reaches a constant value for large times. While there is thus no constant v_∞ for large fields, there is a nonzero average

$$v_{av} = \frac{1}{T_0} \int_0^{T_0} v_k(t) dt$$

$$= \frac{1}{T_0} \int_0^{2\pi/a} \frac{v_k(t)}{(dk/dt)} dk$$

$$= \frac{\hbar}{\gamma T_0} \int_0^{2\pi/a} \frac{\sin ka \, dk}{\zeta - \sin ka}$$

$$= v_0 (\zeta - \sqrt{\zeta^2 - 1}) \tag{12}$$

of the oscillating velocity over the period of time T_0.

The time dependence of the velocity as predicted by Eqs. (7) and (8) is displayed in Fig. 2(a) for $E < E_c$ and in Fig. 2(b) for $E > E_c$. The steady-state velocity that a dc detector would measure is v_∞ in the low-field case and v_{av} in the high-field case. We call this observable velocity v_{obs}, and plot its ratio

$$v_{obs}/v_0 = \zeta \quad \text{for} \quad \zeta \leq 1,$$

$$v_{obs}/v_0 = \zeta - \sqrt{\zeta^2 - 1} \quad \text{for} \quad \zeta \geq 1 \tag{13}$$

to the maximum band velocity v_0 in Fig. 3(a) as a function of the dimensionless electric field $\zeta = E/E_c$. The transition at $E = E_c$ from linear (Ohmic) behavior to nonlinear behavior displaying a negative differential mobility is worthy of note. Beyond the critical field, the slope of the velocity with respect to the field is negative and infinite at the transition, and decreases in value as the field increases. The velocity tends to vanish as the field is increased without limit. No saturation is visible. The existence of the cusp at $E = E_c$ where the differential mobility (slope) is negative infinite, and the transition from a constant slope on the low side to one with decreasing magnitude on the high side of the transition are remarkable, but entirely physical, consequences of this simple analytical model.

III. QUANTUM KINETIC EQUATION ANALYSIS

How do the predictions of a quasi-Newtonian (Drude-like) model such as the one treated above differ from those of one based on quantum kinetic equations normally used in transport theory? We address this question in the present section. The so-called stochastic Liouville equation (SLE) for the density matrix ρ of the carrier, employed extensively in exciton transport in molecular crystals,[7] may be written in
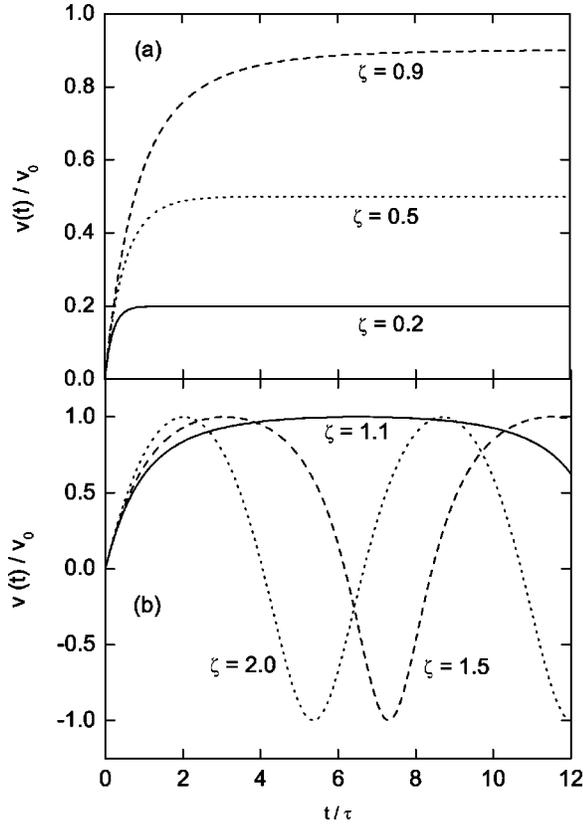
FIG. 2. Instantaneous velocity as a function of time for a particle starting with $k=0$, at various field strengths $\zeta=E/E_c$ as indicated, for (a) $\zeta<1$ and (b) $\zeta>1$, as predicted by the quasi-Newtonian theory of Sec. II.

real space (representation of Wannier states m, n, etc.) as

$$i\hbar\frac{d\rho_{m,n}}{dt}=[V,\rho]_{m,n}+(qEa)(m-n)\rho_{m,n}-i\hbar\,\alpha_0(1-\delta_{m,n})$$

$$\times[\rho_{m,n}-\rho_{m,n}^e], \qquad (14)$$

where the scattering is represented by the single relaxation rate α_0 at which the off-diagonal elements of the density matrix relax to their equilibrium values $\rho_{m,n}^e$ in the absence of the field. By Fourier transforming the SLE to k space, the distribution function

$$f(k)=\langle k|\rho|k\rangle=\frac{a}{2\pi}\sum_{m,n}\rho_{m,n}e^{ika(m-n)}, \qquad (15)$$

obtained from the diagonal part of ρ in reciprocal space, can be shown to obey

$$\frac{\partial f(k,t)}{\partial t}=-\left(\frac{qE}{\hbar}\right)\frac{\partial f(k,t)}{\partial k}-\alpha_0[f(k,t)-f^{th}(k)], \qquad (16)$$

where $f^{th}(k)$ is the thermal distribution.

A well-known shortcoming of Eq. (16) lies in its assumption of a *single* relaxation time $1/\alpha_0$. A more accurate description is provided by the Boltzmann equation with arbitrarily k-dependent relaxation times $1/\alpha_k$:
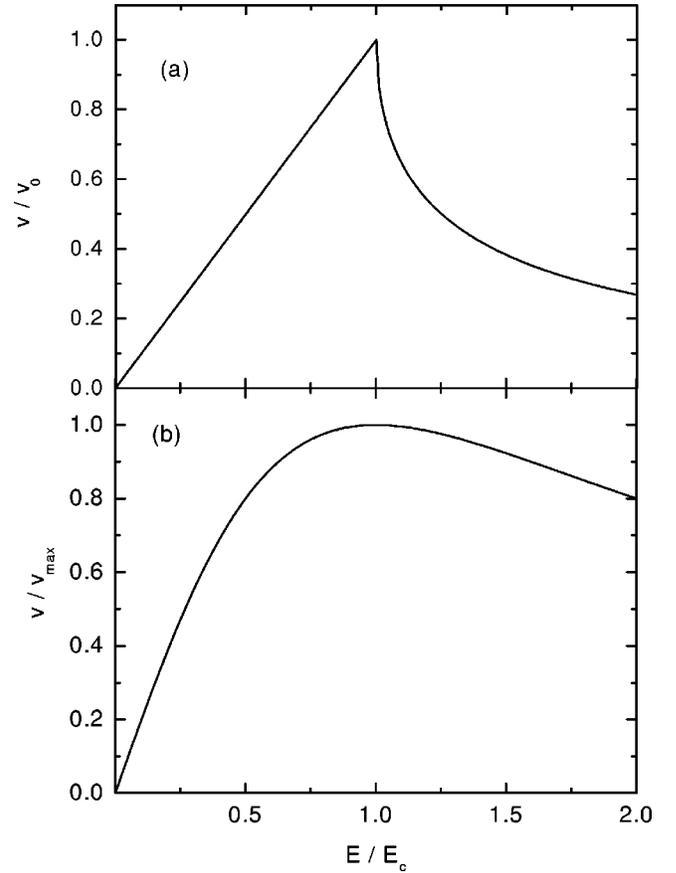

FIG. 3. Steady-state velocity v_{obs}/v_0 as a function of the electric-field strength E/E_c, as predicted by (a) the quasi-Newtonian theory of Sec. II and (b) the single relaxation time Boltzmann equation from Sec. III.

$$\frac{\partial f(k,t)}{\partial t}+\mathcal{E}\frac{\partial f(k,t)}{\partial k}+\alpha(k)[f(k,t)-f^{th}(k)]=0. \qquad (17)$$

Here $\mathcal{E}=qE/\hbar$. Whereas textbook procedures[10] for solving an equation such as Eq. (17) replace the second term by $-\mathcal{E}\partial f^{th}(k)/\partial k$ under the linear approximation, we will keep the full nonlinearity in the field and develop a method of solving Eq. (17) without approximation.

Casting Eq. (17) in terms of the linear operator $L=\alpha+\mathcal{E}\partial/\partial k$, the solution is written down at once,

$$f(k,t)=G(k,t)f(k,0)+\int_0^t ds\,G(k,s)\alpha(k)f^{th}(k), \qquad (18)$$

where the Green function is given by the exponential operator

$$G(k,t)=e^{-Lt}=e^{-[\alpha t+\mathcal{E}t(\partial/\partial k)]}. \qquad (19)$$

In order to understand the action of the Green function, we consider the identity

$$e^{c(A+B)}=e^{cA}e^{\int_0^c dx\,e^{-xA}Be^{xA}}, \qquad (20)$$

where c (or x) is a c number and A and B are generally noncommuting operators. Such an identity is easily proved[12]

by noting that the derivative of the left-hand side with respect to c is equal to that of the right-hand side for all c, and that the identity holds for one specific value of c, viz., $c = 0$. If $c = 1$, and the operators B and A are respectively, multiplication by the scalar (k-dependent) function $-\alpha t$ and the differentiation operation $-\mathcal{E}t\partial/\partial k$, application of Eq. (20) gives

$$e^{-t(\alpha+\mathcal{E}\partial/\partial k)} = e^{-\mathcal{E}t(\partial/\partial k)}e^{-\int_0^1 dx e^{x\mathcal{E}t(\partial/\partial k)}\alpha t e^{-x\mathcal{E}t(\partial/\partial k)}}. \quad (21)$$

Expansion of the integrand, and the recognition that $[\partial/\partial k, \alpha] = \partial\alpha/\partial k$, lead to

$$e^{x\mathcal{E}t(\partial/\partial k)}\alpha e^{-x\mathcal{E}t(\partial/\partial k)} = \alpha(k+x\mathcal{E}t) \quad (22)$$

which may also be understood immediately[13] from Eq. (21). We now see that, for any function $\Omega(k)$,

$$e^{-\int_0^1 dx e^{x\mathcal{E}t\frac{\partial}{\partial k}}\alpha t e^{-x\mathcal{E}t\frac{\partial}{\partial k}}}\Omega(k) = e^{-t\int_0^1 dx \alpha(k+x\mathcal{E}t)}\Omega(k). \quad (23)$$

Explicit evaluation of the Green function operation is now possible,

$$G(k,t)\Omega(k) = e^{-Lt}\Omega(k) = e^{-(\alpha t + \mathcal{E}t\frac{\partial}{\partial k})}\Omega(k)$$
$$= e^{-\bar{\alpha}(k-\mathcal{E}t,t)t}\Omega(k-\mathcal{E}t) \quad (24)$$

for any function $\Omega(k)$, where

$$\bar{\alpha}(k,t) = \frac{1}{\mathcal{E}t}\int_k^{k+\mathcal{E}t}\alpha(y)dy \quad (25)$$

is the average of the reciprocal relaxation time $\alpha(k)$ over a region in k space of extent $\mathcal{E}t$ centered around $k+\mathcal{E}t/2$.

The general solution of the Boltzmann equation (17) is thus obtained as

$$f(k,t) = e^{-\bar{\alpha}(k-\mathcal{E}t,t)t}f(k-\mathcal{E}t,0) + \int_0^t ds\, e^{-\bar{\alpha}(k-\mathcal{E}s,s)s}$$
$$\times \alpha(k-\mathcal{E}s)f^{th}(k-\mathcal{E}s). \quad (26)$$

It leads to the average time-dependent velocity

$$\langle v \rangle = \int_{-\pi/a}^{\pi/a} dk\, e^{-\bar{\alpha}(k,t)t}v(k+\mathcal{E}t)f(k,0)$$
$$+ \int_0^t ds \int_{-\pi/a}^{\pi/a} dk\, e^{-\bar{\alpha}(k,s)s}\alpha(k)f^{th}(k)v(k+\mathcal{E}s). \quad (27)$$

This exact evolution equation can be used for several different purposes. One is to develop a general response formalism for all times.[14] Our present interest being in the steady state only, we neglect the first term which decays at long times. For the steady-state velocity, we obtain

$$v_{obs} = \int_0^\infty ds \int_{-\pi/a}^{\pi/a} dk\, e^{-\bar{\alpha}(k,s)s}\alpha(k)f^{th}(k)v(k+\mathcal{E}s). \quad (28)$$

Equation (28) is an exact consequence of the Boltzmann equation in the relaxation time form for arbitrarily k-dependent relaxation times. It can be used to explore the nonlinear dependence of velocity on the field in complex systems. The constant relaxation time case $\alpha(k) = \alpha_0 = \bar{\alpha}$ gives

$$v_{obs} = \int_0^\infty ds \int_{-\pi/a}^{\pi/a} dk\, e^{-\alpha_0 s}\alpha_0 f^{th}(k)v(k+\mathcal{E}s). \quad (29)$$

Explicit evaluation is trivial in the tight-binding limit where $v(k)$ is taken as $v_0 \sin ka$, and

$$f^{th}(k) = a[2\pi I_0(2V/k_BT)]^{-1}\exp(2V\cos ka/k_BT) \quad (30)$$

where k_B is Boltzmann's constant, T the temperature, I_0 the modified Bessel function, and V the nearest-neighbor transfer integral which is proportional to the bandwidth. One evaluates the factor $\int_0^\infty ds\, e^{-\alpha_0 s}\sin\mathcal{E}s$ as the Laplace transform of the sine function, uses the symmetry of $f^{th}(k)$ and the antisymmetry of $\sin ka$ in the band, and obtains

$$v_{obs} = v_0 \frac{\mathcal{E}\alpha_0}{\mathcal{E}^2 + \alpha_0^2}\frac{I_1(2V/k_BT)}{I_0(2V/k_BT)}, \quad (31)$$

in agreement with a result given by Dunlap and Kenkre[15] in their treatment of dynamic localization. We plot this result in Fig. 3(b). Unlike in Fig. 3(a), no sharp transition is visible, but we see a similar Ohmic rise for low fields and negative differential mobility for high fields.

General result (28) may be used along with specific realizations of $\alpha(k)$ through an evaluation of the double quadrature. We also provide an approximation procedure which is useful for practical calculations. It interpolates between limits in which the average $\bar{\alpha}$ in Eq. (25) may be replaced by the value of α at k, on the one hand, and by the average of α over the band on the other hand. The motivation for the approximation can be understood by considering a particular form of the relaxation rate, e.g.,

$$\alpha(k) = \alpha_0 - \alpha_1 \cos ka, \quad (32)$$

which leads from Eq. (25) to

$$\bar{\alpha}(k,s) = \frac{1}{\mathcal{E}s}\int_k^{k+\mathcal{E}s}\alpha(y)dy$$
$$= \alpha_0 - \alpha_1 \cos(ka + \mathcal{E}as/2)\left[\frac{\sin(\mathcal{E}as/2)}{\mathcal{E}as/2}\right]. \quad (33)$$

Figure 4 shows this exact time dependence of $\bar{\alpha}(k,s)$. We see, both from Fig. 4 and from Eq. (33), that, on the one hand, for small $(qEa/\hbar)s$, when the sinc function is equal to 1, the approximation $\bar{\alpha}(k,s) = \alpha(k)$ holds, and that, on the other hand, for large $(qEa/\hbar)s$, when the sinc function is equal to 0, the approximation $\bar{\alpha}(k,s) = \alpha_0$ holds. The crossover occurs in a time of the order of $1/\mathcal{E}a$. This suggests that, for arbitrary k dependence of $\alpha(k)$, the time integration in Eq. (28) be performed by replacing $\bar{\alpha}(k,s)$ by the time-
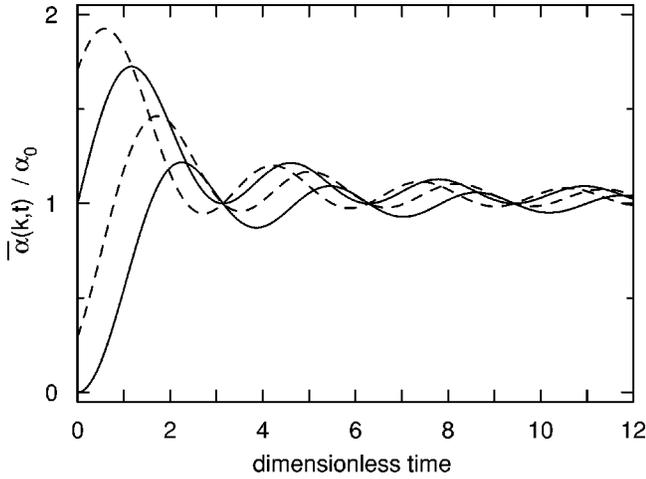
FIG. 4. Decay of $\alpha(k,t)$ as a function of the dimensionless time $T = \mathcal{E}at/2$, as given by Eq. (33), with $\alpha_1 = \alpha_0$. The different curves shown correspond, from bottom to top, to values of the wave vector $k = 0, \pi/4, \pi/2, 3\pi/4,$ and π, respectively. The plot justifies the approximation discussed in the text whereby the quantity plotted is replaced by the initial value $\alpha(k)$ at short times and by the band average α_0 at long times.

independent value $\alpha(k)$ from 0 to a constant times $1/\mathcal{E}a$, and by the time-independent value α_0 from that value to infinity. This leads, in the tight-binding case, to

$$v_{obs} = v_0 \frac{\mathcal{E}a}{2\pi I_0(2V/k_BT)} \int_{-\pi/a}^{\pi/a} dk\, \alpha(k) \mathcal{A}(k) e^{(2V/k_BT)\cos ka}.$$
(34)

If we take the demarcation time to be the reasonable and convenient value $2\pi/\mathcal{E}a$, the quantity $\mathcal{A}(k)$ is given by

$$\mathcal{A}(k) = \frac{1 - e^{-2\pi\alpha(k)/\mathcal{E}}}{\mathcal{E}^2 + \alpha^2(k)} + \frac{e^{-2\pi\alpha_0/\mathcal{E}}}{\mathcal{E}^2 + \alpha_0^2},$$
(35)

and reduces for small fields to $[\mathcal{E}^2 + \alpha^2(k)]^{-1}$ and for large fields to $[\mathcal{E}^2 + \alpha_0^2]^{-1}$, respectively. These limits correspond to $\bar{\alpha}(k,s) \approx \alpha(k)$ and $\bar{\alpha}(k,s) \approx \alpha_0$ respectively.

We have explored a variety of assumed relaxation times (equivalently scattering mechanisms) on the basis of Eq. (34). In all the simple cases considered, we find an Ohmic tendency at small fields and an eventual negative differential mobility at large fields, the essential behavior being given by the simple constant relaxation time case of our result displayed in Fig. 3(b), and rewritten here as

$$v_{obs} = v_0 \left(\frac{EE_c}{E^2 + E_c^2} \right) \left(\frac{I_1(2V/k_BT)}{I_0(2V/k_BT)} \right).$$
(36)

The characteristic field value which marks the turnover of the two field regimes is equal to $\hbar/q\tau a$, and is denoted by the symbol E_c as in the quasi-Newtonian treatment of Sec. II.[16] By τ here we mean the relaxation time $1/\alpha_0$.

The steady-state velocity predicted by this simplified (constant relaxation time) SLE/Boltzmann treatment emerges as the product of three factors: the peak band velocity v_0

$= 2Va/\hbar$, a factor describing the nonlinear field dependence which rises or falls with the field according to the value of the field relative to E_c, and a factor describing the temperature dependence of the velocity which is decided by the ratio of the bandwidth to the thermal energy. The last factor shows that while temperature effects appear in the quantum kinetic equation analysis, they are treated there in a rather simplistic manner: unless τ is taken to have a prescribed temperature dependence,[17] the field dependence and the temperature dependence appear in separate multiplicative factors in this simplified treatment.[18] For high temperatures ($k_BT \gg 2V$), I_0 tends to 1 while I_1 tends to V/k_BT, and the maximum velocity becomes inversely proportional to the temperature. If we introduce a thermal velocity $v_{th} = ak_BT/\hbar$ obtained by dividing the lattice constant by the thermal time $\hbar/k_BT$, the high-temperature limit can be written as

$$v_{obs} = \frac{v_0^2}{2v_{th}} \frac{EE_c}{E^2 + E_c^2}.$$
(37)

At low temperatures ($k_BT \ll 2V$), we have

$$v_{obs} = v_0 \frac{EE_c}{E^2 + E_c^2}$$
(38)

which should be compared to the quasi-Newtonian result [Eq. (13)].

IV. FOKKER-PLANCK ANALYSIS AND A UNIFICATION OF THE QUASI-NEWTONIAN AND KINETIC EQUATION RESULTS

In order to bridge the quasi-Newtonian approach of Sec. II, which clearly corresponds to zero temperature, with the quantum kinetic equation approach of Sec. III, we now present a Fokker-Planck analysis. Finite-temperature environment effects on the quasi-Newtonian evolution of Sec. II are included in the spirit of the Langevin approach by adding to Eq. (5) a Brownian motion term involving a white noise random force,

$$\frac{dk}{dt} + \left(\frac{\gamma}{\hbar^2} \right) \left(\frac{d\varepsilon_k}{dk} \right) = \frac{qE}{\hbar} + R(t),$$
(39)

where $\langle R(t)R(t') \rangle$ is proportional to $\delta(t-t')$, and v_k is expressed explicitly as $(1/\hbar)(d\varepsilon_k/dk)$.

Since Eq. (39) is a *nonlinear* Langevin equation, a convenient calculational procedure is to convert it to a Fokker-Planck (or Smoluchowski) equation through standard prescriptions,[19]

$$\frac{\partial f(k,t)}{\partial t} = \frac{\gamma}{\hbar^2} \frac{\partial}{\partial k} \left[\left(\frac{d\varepsilon_k}{dk} - \frac{\hbar qE}{\gamma} \right) f(k,t) + k_BT \frac{\partial f(k,t)}{\partial k} \right],$$
(40)

and to solve the latter in the steady state. A formally identical evolution equation was analyzed by Kuś and Kenkre[20] in their investigation of a classical problem of microwave heating in ceramic materials.[21] This formal similarity was ex-

ploited recently by Parris, Kuś, and Kenkre[22] to show that the steady-state solution of Eq. (40) is

$$f(k) \equiv \lim_{t \to \infty} f(k,t) = B^{-1} \int_k^{k+2\pi/a} dp e^{\beta(\varepsilon_p - \varepsilon_k) - \beta\hbar qE(p-k)/\gamma},$$

(41)

where $\beta = 1/k_B T$, from which the steady-state velocity is obtained as

$$v_{obs} = \int_{-\pi}^{\pi} dk f(k) \frac{1}{\hbar} \frac{d\varepsilon_k}{dk} = \frac{qE}{\gamma} - \frac{2\pi(1 - e^{-2\pi\hbar\beta qE/\gamma a})}{\beta a \hbar B}.$$

(42)

The crucial quantity in Eqs. (41) and (42) is

$$B = \int_0^{2\pi/a} dk e^{-\hbar k\beta qE/\gamma} \int_0^{2\pi/a} dp e^{\beta(\varepsilon_{p+k} - \varepsilon_p)}.$$

(43)

For the sinusoidal band of the tight-binding system, it can be reexpressed as a single integral,

$$B = \frac{2\pi}{a} \int_0^{2\pi/a} dk e^{-\hbar k\beta qE/\gamma} I_0(4\beta V \sin ka/2),$$

(44)

of the modified Bessel function $I_0(z)$ and can also be rewritten using Bessel identities.[23] The latter reduces Eq. (42) to the following compact form[22]:

$$v_{obs} = \frac{qE}{\gamma} - \frac{1}{\pi} \frac{a \sinh(\pi\hbar\beta qE/\gamma a)}{\beta\hbar I_{-i\hbar\beta qE/\gamma a}(2\beta V) I_{i\hbar\beta qE/\gamma a}(2\beta V)}.$$

(45)

Here the orders $\nu = \pm i\hbar\beta qE/\gamma a$ of the modified Bessel function $I_\nu(z)$ are strictly imaginary, proportional to the field E, and inversely proportional to the temperature and the scattering strength γ. Recalling the definitions of v_∞, the drift velocity attained in our zero-temperature quasi-Newtonian model for small fields, and v_{th}, the thermal velocity introduced in Sec. III, appearing, respectively, in Eqs. (10) and (37), we see that the orders of the Bessel functions can also be written in the simple form $\nu = \pm i(v_\infty/v_{th})$. The argument of the Bessel functions, i.e., the ratio $z = 2V/k_B T$ of the bandwidth to the thermal energy, is simply related to the order of the Bessel functions through the expression

$$z \equiv \frac{2V}{k_B T} = \left(\frac{v_0}{v_{th}}\right) = \left(\frac{v_\infty}{v_{th}}\right)\zeta.$$

(46)

Figure 5 shows a plot of the field-dependent velocity for several values of the temperature including extreme temperature limits. The surprising similarity of the low-temperature limit of the Fokker-Planck analysis to the Drude-like prediction of Sec. II [see Fig. 3(a)], including the cuspy transition, and the similarity of the high temperature limit to the predictions of the SLE treatment [see Fig. 3(b)], motivate an asymptotic analysis of the Fokker-Planck result [Eq. (45)]. As we show below, the exact Fokker-Planck solution [Eq. (45)] indeed reduces in the high-temperature limit to the functional form [Eq. (36)] found in the SLE treatment, with a suitable redefinition of E_0. Furthermore, the zero-
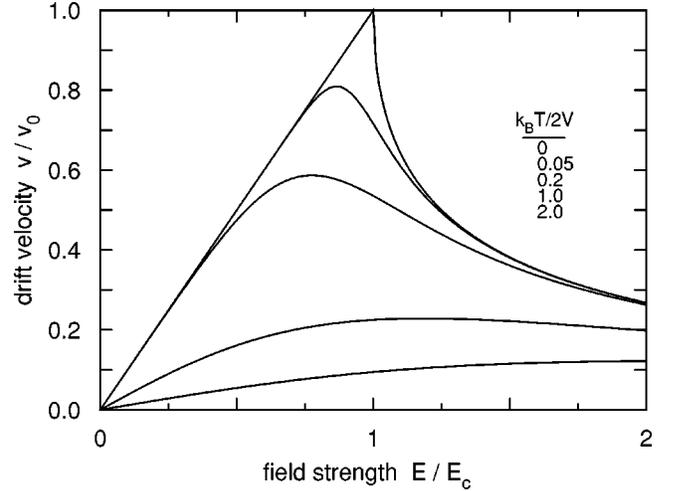

FIG. 5. Steady-state velocity as a function of field strength, as predicted by the Fokker-Planck treatment of Sec. IV for different temperatures as indicated. Comparison with Fig. 3 shows that the top curve reproduces the quasi-Newtonian result exactly. Bottom curves tend identically to the shape of the quantum kinetic equation result for infinite temperature.

temperature limit of Eq. (45) reduces to the quasi-Newtonian expression [Eq. (13)], the sharp transition with the discontinuous slope characteristic of the latter result being thus an exact consequence of the Fokker-Planck expression [Eq. (45)].

We first focus on the high-temperature case. Because $z = v_0/v_{th} \to 0$, integral (44) becomes

$$B = \frac{2\pi}{a} \int_0^{2\pi/a} dk e^{-z\zeta ka} I_0(2z \sin ka/2),$$

(47)

and can be evaluated by expanding the Bessel function in powers of its argument:

$$B \sim \frac{2\pi}{a} \int_0^{2\pi/a} e^{-z\zeta ka}(1 + z^2 \sin^2 ka/2) dk$$

$$\sim \frac{2\pi(1 - e^{-2\pi z\zeta})}{z\zeta a^2}\left(1 + \frac{1}{2}\frac{z^2}{z^2\zeta^2 + 1}\right).$$

(48)

In this small-z limit, from (42) we thus obtain for the sinusoidal band,

$$v_{obs} = \frac{v_0}{2}\frac{\zeta}{\zeta^2 + v_{th}^2/v_0^2} = \frac{v_0^2}{2v_{th}}\frac{EE_0}{E^2 + E_0^2},$$

(49)

where we introduce a temperature-dependent characteristic field

$$E_0 = E_c v_{th}/v_0.$$

(50)

With this definition, we note that the high-temperature limit [Eq. (49)] of the Fokker-Planck expression [Eq. (45)] is formally identical to the SLE result [Eq. (37)]. However, the location of the peak in the v-E curve displays a dependence

on temperature which is different in the Fokker-Planck analysis since E_0, the characteristic field in this case, increases with temperature.

To understand the low temperature behavior of Eq. (45) requires more care, since the result has a discontinuous derivative at $E = E_c$ (see Fig. 5). We therefore separately treat the high-field $\zeta > 1$ and low-field $\zeta < 1$ cases. In both cases, the ratio $z = v_0/v_{th}$ diverges. For low fields ($\zeta < 1$), and z large, the integrand in Eq. (47) is sharply peaked at a value of k in the interior of the integration region. In the neighborhood of this peak, as $z \to \infty$, the value and argument of the Bessel function become large. Use of the asymptotic expansion $I_0(x) \sim e^x/\sqrt{2\pi x}$ gives

$$B \sim \frac{1}{2\pi a} \int_0^{2\pi/a} dk \, \frac{\exp(-kaz\zeta + 2z \sin ka/2)}{\sqrt{4\pi z \sin ka/2}}. \quad (51)$$

The peak of the integrand occurs at the value $k = k_0 = 2a^{-1} \cos^{-1} \zeta$, provided $\zeta < 1$. A saddle-point integration performed about this peak value leads to the asymptotic results valid for $z \gg 1$:

$$B \sim \frac{1}{2\pi z a^2} \frac{\exp[2z(\sqrt{1-\zeta^2} - \cos^{-1}\zeta)]}{\sqrt{1-\zeta^2}}. \quad (52)$$

Substitution of this result into Eq. (42) then leads to

$$v_{obs} \sim v_0 \zeta - \frac{2\pi a z}{\beta \hbar} (1 - e^{-2\pi z \zeta}) \sqrt{1-\zeta^2}$$
$$\times \exp\{-2z[\sqrt{(1-\zeta^2)} - \cos^{-1}\zeta]\}, \quad (53)$$

whose limit for $\zeta < 1$ as $z \to \infty$ is indeed just the first term $v_0 \zeta$ as in the first part of Eq. (38).

We now obtain the limiting behavior of Eq. (45) at low temperatures and large fields ($\zeta > 1$). From the previous analysis, as ζ approaches 1 from below, the peak of the integrand in Eq. (51) moves to the left, since $k_{peak} = 2a^{-1} \cos^{-1} \zeta$. It is easy to verify that for all $\zeta > 1$, the peak of the integrand is no longer in the interior of the integration region, but at $k = 0$. Thus, for $\zeta > 1$ and z large, we return to Eq. (47), expand $\sin ka/2$ about $k = 0$, and approximate $I_0(2z \sin ka/2) \sim I_0(zka)$. For large z, the exponential factor in Eq. (47) kills off any contributions from large k. On extending the upper limit of the integration to infinity, we find

$$B \sim \frac{1}{2\pi a^2} \int_0^{\infty} e^{-z\zeta k} I_0(zk) = \frac{1}{2\pi z a^2 \sqrt{\zeta^2 - 1}}, \quad (54)$$

which yields, for $z \to \infty$ and $\zeta > 1$,

$$v_{obs} = v_0(\zeta - \sqrt{\zeta^2 - 1}), \quad (55)$$

which is identical to the large field part of the quasi-Newtonian result [Eq. (13)].

Unlike the kinetic equation approach, the Fokker-Planck approach treats the effect of temperature in a nontrivial manner. In addition, it cleanly connects the cuspy transition of the quasi-Newtonian analysis with the smooth field depen-

dence of the SLE/Boltzmann result, and shows that the characteristic field values in extreme temperature limits are given, respectively, by

$$E_c = \frac{\gamma v_0}{q}, \quad E_0 = E_c \left(\frac{k_B T}{2V} \right). \quad (56)$$

A careful analysis of the low-temperature limit shows that the location of the peak of the $v - E$ curve on the field axis first decreases as the temperature is increased, and then increases. Eventually, the peak location is linear in the temperature as is clear in the definition of E_0. This means that, at sufficiently large temperatures, the extent of the Ohmic regime keeps increasing as the temperature is increased, according to the Fokker-Planck description. In the simple SLE description with a single relaxation time, the extent is independent of temperature. The general kinetic equation description, given for instance by Eq. (34), predicts a temperature variation of the extent of the Ohmic regime but only between values proportional to the band average of the relaxation rate $\alpha(k)$, and its thermal average.

V. CONCLUDING REMARKS AND ALTERNATE SOURCES OF SATURATION

The main results presented in this paper, in addition to its primary focus discussed below, are the sharp (cuspy) transition in the field dependence of the velocity in the quasi-Newtonian model in Sec. II, the method of solution of the Boltzmann equation without making the linear approximation in the field given in Sec. III, and the asymptotic analysis from the Fokker-Planck equation provided in Sec. IV.

The primary focus of the paper is the investigation of the effects of finite bandwidths and nonparabolicity on field dependence of the velocity. The interpretation of the data was based on the belief that the nonparabolicity of bands is responsible for the low-temperature behavior. We showed in Sec. I that formula (1), which formed the basis of this interpretation, is quite inappropriate since it does not correspond to any saturation.[24]

Although formula (1) as a basis for saturation is incorrect, the idea of investigating the effects of nonparabolicity of bands in organic crystals, suggested by the authors of Ref. 1, and others, is indeed significant. In order to test whether nonlinearity effects arising from the nonparabolic nature of bands include saturation, in this paper we have carried out a number of investigations: on the basis of quasi-Newtonian considerations, of quantum kinetic equations, and of the Fokker-Planck equation. We have shown that each of these physically reasonable approaches fails to predict any saturation, *on the sole basis* of the nonparabolicity of bands. Furthermore, all approaches considered agree in their prediction of Ohmic behavior followed by a peak and a decrease in the velocity with increasing field as do other earlier reported investigations.[15,25] We have restricted our analysis to band-based theories, and not touched upon saturation in hopping transport or any polaronic issues in the present paper. We emphasize that we have not given a proof that saturation cannot occur from simple theoretical considerations. Indeed, we will show below how certain features other than band

nonparabolicity, in combination with that feature or otherwise, could be responsible for field saturation of the velocity. Our purpose here has been to point out that the observed saturation requires further investigation, that no analysis so far lends support to the saturation providing a test of coherence (bandlike behavior), and that values of bandwidths, so crucially important to the understanding of other transport features in the polyacenes, should not be deduced from these saturation values of the velocity until the origin of saturation is understood.

The primary characteristic field value that appears in the various expressions we have provided is E_c, which is given by $\gamma v_0/q$, or equivalently by $\hbar/q\tau a$. The first of these expressions shows that the field value at which nonlinear effects of the type investigated in this paper can arise is proportional to the carrier bandwidth. The Ohmic regime clearly extends to much larger fields in inorganic materials in which the bandwidths are of the order of eV's. In typical organic materials the bandwidths are relatively smaller,[26] making it possible that the non-Ohmic regime is observable before fields achieve breakdown values. Using a typical value $\tau = 10^{-14}$ s in the second expression given above, we see that E_c can be less than 10^6 V/cm if a is of the order of 5 Å characteristic of organic materials. In inorganic materials, where the lattice constant is much smaller, it is less likely that this non-Ohmic regime is observed before a breakdown of the material occurs.

We now suggest two other possible sources of saturation, and comment on them at a heuristic level. One is based on the assumption that the scattering rate γ in Eq. (5) is *field dependent*, and the other that it is *k dependent*. The Drude-like considerations of Sec. II can be shown to give saturation if γ is field dependent, the dependence being given by

$$\gamma = \gamma_0 \sqrt{1 + (E/E_1)^2} \qquad (57)$$

which means that the scattering rate increases with, and is proportional to, the field for large fields.[27] In the context of our quasi-Newtonian analysis, this means that a critical field signaling the crossover from the Ohmic regime to the negative-differential-mobility regime need not be ever reached. The field ratio $\zeta = E/E_c$ appearing in Eq. (13) is now given by

$$\zeta = \frac{E/E_s}{\sqrt{1 + (E/E_1)^2}} \qquad (58)$$

where E_1 appears in the definition of $\gamma(E)$ above and $E_s = \gamma_0 v_0/q$. In the absence of field-dependent scattering, ζ would grow without limit with the field. Given the dependence described by Eq. (57) it saturates, instead, to the value $\zeta_s = E_1/E_s = qE_1/\gamma_0 v_0$. The relative magnitudes of the two quantities E_1 and E_s which arise from the specific scattering mechanism in the system will determine whether the negative-differential-mobility regime is *ever* reached. If $E_1 < E_s$, that regime will never be reached, and saturation will persist for all field magnitudes as the field continues to increase. Otherwise, one will see a gradual flattening of the velocity of the field followed by an eventual decrease with
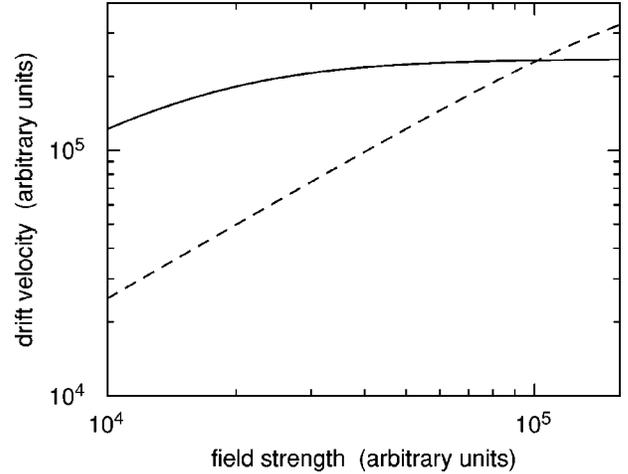

FIG. 6. Apparent saturation of velocity with increasing field. Plotted is the single relaxation rate version of the kinetic equation result in Sec. III, i.e., Eq. (37), with a *field-dependent* scattering rate for two different sets of parameter values in the two respective curves. Solid and dashed lines correspond to the low- and high-temperature cases respectively. See the text for details.

increasing field. Note that, in the former case, our solutions involving the hyperbolic tangent will always prevail, there being no crossover to the trigonometric tangents. For the simple kinetic equation results we have obtained, this idea means that the velocity would be given by Eq. (36) with the characteristic field value, $E_0 = \sqrt{D_1^2 + (D_2 E)^2}$, determined by the constants D_1 and D_2. Figure 6 shows a plot of our SLE expression [Eq. (36)]. Field and velocity values are in arbitrary units. Under the heuristic assumption that, in the arbitrary units employed, the quantities D_1, and D_2 have values of 7 and 4 for the (solid) saturating curve (lower temperature), and 40 and 1 for the (dashed) nonsaturating curve (higher temperature), it is possible to produce a striking resemblance to the observations reported in Fig. 2 of Schön et al.[1]

Saturation can be obtained in an even more interesting manner if the scattering rate is assumed to be k dependent. The k dependence must be such that, as the carrier moves in the zone from $k = 0$ under the action of the field as in Eq. (5), the scattering increases so strongly that the carrier cannot traverse the zone beyond a certain point, no matter what the field strength. Such a singular scattering mechanism could arise from a resonance of the carrier with another part of the system such as a molecular vibration. To motivate these considerations, note that Eq. (5), which describes the crystal momentum evolution, can also be written as an evolution equation for the velocity. Dividing Eq. (5) by the effective mass $m^* = (1/\hbar)(dv_k/dk)$ given in Eq. (4), and putting $\gamma = 0$, we see that, in the absence of scattering, the time derivative of the velocity is simply qE/m^*. If the scattering is now taken to contribute a term $-v/\tau$ to the evolution of v, we obtain the plausible velocity equation

$$\frac{dv}{dt} + \frac{v}{\tau} = \frac{qE}{m^*} = \frac{qEa}{\hbar}\sqrt{v_0^2 - v^2}, \qquad (59)$$

with a nonlinear driving term, the specific nonlinear expression in the extreme right-hand side arising from the tight-binding relation. It is immediately clear that this equation predicts saturation. The steady-state velocity obeys

$$v_\infty = \frac{qE\tau}{m^*} = \frac{qE\tau a}{\hbar}\sqrt{v_0^2 - v_\infty^2} = v_0 \frac{E}{\sqrt{E_c^2 + E^2}}, \quad (60)$$

where $E_c = \hbar/q\tau a$. The behavior is Ohmic at small fields ($E \ll E_c$) with mobility $\mu_0 = v_0/E_c = 2Vq\tau(a/\hbar)^2$. The velocity saturates for large fields ($E \gg E_c$) to the maximum value $v_0 = 2Va/\hbar$ that the carrier velocity can have in the band. A simple way of understanding this result is that the product m^*v, which is proportional to $\tan ka$, increases with field without limit while the velocity v, which is proportional to $\sin ka$, saturates at $ka = \pi/2$ in the middle of the Brillouin zone, where the effective mass becomes infinite. Not only do these considerations predict saturation, but the apparent loss of saturation observed at higher temperatures in pentacene could correspond to the temperature dependence of τ, more scattering occurring at higher temperatures, or of v_0 through Huang-Rhys (polaronic) reduction of bandwidth.

It might appear that nonparabolic nature of bands is the sole ingredient responsible for this saturation mechanism that we have provided. This is not true. In light of effective-mass theory,[10] Eq. (5) is known to be a legitimate starting point to introduce forces on the carrier as additive inputs. A damping force proportional to a constant scattering rate γ introduced in this manner [see Eq. (5)] *does not* lead to saturation, as the analysis in Sec. II has already shown. The velocity evolution equation (59), which shows saturation, has been obtained by first turning off scattering in Eq. (5), then transforming it into a velocity equation, and then reintroducing scattering through a constant τ. If we had directly attempted to transform Eq. (5) with its constant γ, the resulting velocity equation would not show saturation as the dissipative term would also develop nonlinearity which would exactly cancel the driving term nonlinearity.

What scattering term in Eq. (5) corresponds to Eq. (59), which guarantees saturation? It is easy to show, by back transforming, that the $\gamma(k)$ required is proportional to $\sec ka$, which means an infinite scattering rate at $k = \pi/2a$. We thus see that to obtain the saturation predicted by Eq. (59), the scattering rate γ in Eq. (5) must become singular in the band. Actually it is enough for γ to become extremely large at some point k_1 in the zone (not necessarily at $\pi/2a$) for this effect to occur. We are in the process of investigating specific mechanisms that could be responsible for such singular behavior.

Whether such ideas hold water in the light of quantitative requirements, as well as what precise physical ingredients could give rise to the mechanisms we have suggested heuristically above are issues that are beyond the scope of the present investigation. Figure 6, or the arguments based on singular scattering rates given above, is by no means presented here as an explanation of the observations, but only to strike a cautionary note against drawing hasty conclusions about coherence from observed saturation. The present authors feel confident that the beautifully clear experiments of Ref. 1 leave no doubt that the velocity saturates at low temperatures in pentacene and that the saturation is destroyed at higher temperatures. They feel equally confident that the current explanation of the saturation in terms of coherence (bandlike behavior) based on Eq. (1) is totally unjustified; and that the reason for the observed saturation remains largely a puzzle. It is hoped that it will be soon possible to convert the suggestions we have made here on the basis of field-dependent or k-dependent scattering rates into a comprehensive explanation of the saturation phenomena.

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[3] W. Warta and N. Karl, Phys. Rev. B **32**, 1172 (1985).

[4] After many unsuccessful attempts, that problem in naphthalene was considered solved in the mid-1980s through the application of polaron concepts. See V. M. Kenkre, J. D. Andersen, D. H. Dunlap, and C. B. Duke, Phys. Rev. Lett. **62**, 1165 (1989) for the theory which provides the explanation; the monograph by Martin Pope and Charles E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York 1999), p. 968, for a brief sketch of the theory; and M. W. Wu and E. M. Conwell, Chem. Phys. Lett. **266**, 363 (1997); M. Pope and C. E. Swenberg, *ibid.* **287**, 535 (1998), and V. M. Kenkre and D. H. Dunlap, Philos. Mag. **65**, 831 (1992) for comments on the theory. The naphthalene analysis, while not applicable directly to pentacene, contains a number of elements useful to the pentacene problem, as will be shown in a series of ensuing publications.

[5] Martin Pope and Charles E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York, 1999), p. 110.

[6] R. J. Silbey, Annu. Rev. Phys. Chem. **27**, 203 (1976); D. Burland and A. Zewail, Adv. Chem. Phys. **50**, 385 (1980); C. B. Harris and D. Zwemer, Annu. Rev. Phys. Chem. **29**, 473 (1978).

[7] V. M. Kenkre and P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates* (Springer-Verlag, New York, 1982).

[8] W. Schockley, Bell Syst. Tech. J. **30**, 990 (1951).

[9] E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967).

[10] See, e.g., N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).

[11] P. W. Anderson, *Concepts in Solids* (Benjamin/Cummings, New York, 1963).

[12] While such identities can probably be found in almost any mod-

ern advanced quantum mechanics textbook, a source known to us is Appendix C of V. M. Kenkre, Ph.D. thesis, Stony Brook, 1971.

[13] Whatever k function the operator is acting on, it is first displaced by $-x\varepsilon t$ and then multiplied by α; then the product displaced by $+x\varepsilon t$ so that the result is simply the product of α displaced by $+x\varepsilon t$ and the given function undisplaced.

[14] Comments on a general nonlinear theory of response in this context and the connection to a solution of the infinite time differential equation $\varepsilon\partial f(k)/\partial k + \alpha(k)[f(k)-f^{th}(k)]=0$ will be reported elsewhere: L. Giuggioli and V. M. Kenkre (unpublished).

[15] D. H. Dunlap and V. M. Kenkre, Phys. Rev. B **37**, 6622 (1988).

[16] The formal relationship of the constants τ and γ appearing in the two different theories of Sec. II and III, obtained by identifying the critical field E_c in the two cases is $\tau=\hbar/\gamma a v_0$.

[17] For instance, $1/\tau$ might be taken to be proportional to $k_B T$ if the scattering arises from phonons or to the Bose-Einstein factor for greater accuracy at low temperatures.

[18] Although temperature and field effects do appear in combination in results deduced from the exact expression [Eq. (28)] or the practical prescription [Eq. (34)], neither of which incorporates the constant relaxation-time approximation, the kinetic equation treatment is oversimplified in this regard. This will be seen by comparison to the subsequent results from the Fokker-Planck equation.

[19] See, e.g., L. E. Reichl, *A Modern Course in Statistical Physics,* 2nd ed. (Wiley, New York 1998); K. Lindenberg and B. J. West, *The Nonequilibrium Statistical Mechanics of Open and Closed Systems* (Wiley, New York, 1990).

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[22] P. E. Parris, M. Kuś, and V. M. Kenkre, Phys. Lett. A **289/4-5**, 188 (2001).

[23] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic Press, Boston, 1980). See, e.g., p. 756.

[24] Since Eq. (1) formed the basis of important data interpretation, it is interesting to ask how the equation might have arisen. If in a model such as that of Sec. II one puts $\gamma=0$ in Eq. (5), solves for $k(t)$, writes an expression for $v_k(t)=v_0 \sin k(t)$, and averages it from $t=0$ to $t=\tau$ (where τ is a collision time); one obtains Eq. (1). It is thus an approximation lacking self-consistency, and its validity is limited to the unimportant case when collisions are negligible. More to the point is, however, that it shows no saturation.

[25] See, e.g., D. Emin and C. F. Hart, Phys. Rev. B **32**, 6503 (1985); **36**, 2530 (1987).

[26] Carrier bandwidths in most inorganic materials of interest are typically of the order of eV. They are not known with precision in organic materials, but are believed to be orders of magnitude smaller, the corresponding values of the effective masses thus being orders of magnitude larger in organics. For instance, the value of the injected carrier bandwidth in naphthalene extracted from mobility measurements (see Ref. 4) is of the order of 10 meV.

[27] Such rates appeared earlier in Ref. 15. However, because they appear as effective rates rather than microscopically given rates, that treatment cannot be used in the present context as useful input.