Conductivity of an electron coupled to anharmonic phonons

Jonathan H. Fetherolf,1,† Petra Shih,1 and Timothy C. Berkelbach1,2, †
1Department of Chemistry, Columbia University, New York, New York 10027, USA
2Center for Computational Quantum Physics, Flatiron Institute, New York, New York 10010, USA

We study the impact of phonon anharmonicity on the electronic dynamics of soft materials using a nonperturbative quantum-classical approach. The method is applied to a one-dimensional model of doped organic semiconductors with low-frequency intermolecular lattice phonons. We find that anharmonicity that leads to phonon hardening increases the mobility and anharmonicity that leads to phonon softening decreases the mobility. We also test various approximations, including the use of adiabatic phonon disorder, an effective harmonic model with temperature-dependent frequencies, and the Boltzmann transport equation with second-order perturbation theory scattering rates. Overall, we find surprisingly good agreement between all methods but that accounting for phonon anharmonicity is important for accurate prediction of electronic transport including both quantitative mobility values and their qualitative temperature dependence. For the model studied, phonon lifetime effects have relatively little impact on carrier transport, but the effective frequency shift due to anharmonicity is essential. In cases with highly asymmetric, non-Gaussian disorder, an effective harmonic model cannot quantitatively reproduce mobilities or finite-frequency conductivity, and this is especially true for acoustic phonons.

I. INTRODUCTION

Design of efficient functional materials requires a detailed microscopic understanding of the charge transport mechanism. In recent years, low-frequency dynamic disorder has been shown to have a dominant role in the carrier dynamics of soft semiconductors such as organic molecular crystals and lead halide perovskites [1–4]. Like most theories of electron-phonon interactions, the microscopic theory of dynamic disorder commonly assumes linear coupling of carriers to harmonic phonons; however, experimental and theoretical work suggests that the low-frequency phonon modes in many materials—especially organic molecular crystals—exhibit significant anharmonicity [5–11].

In solids, anharmonic effects are responsible for thermal expansion, thermal transport and structural phase transitions among other important nuclear effects [12, 13]. With regards to spectral quantities, such as vibrational spectroscopies, anharmonicity most commonly manifests as two well-known and temperature-dependent effects: A frequency shift away from the harmonic value (softening or hardening) and a finite vibrational lifetime that introduces a spectral linewidth. Unlike that of harmonic phonons, the temperature dependence of anharmonic phonons may influence the temperature dependence of coupled degrees of freedom, such as electrons or excitons. For example, a structural phase transition associated with anharmonic mode-coupling has been shown to induce an insulator-metal transition in cuprates [14, 15]. Anharmonic modes are implicated in the band-gap renormalization of several materials such as organic molecular crystals [11], halide perovskites [3, 16] and strontium titanite [17]. Soft modes in strontium titanite were also shown to be responsible for the specific temperature dependence of the carrier mobility [18], in a study that made use of the perturbative Boltzmann transport equation with a temperature-dependent effective phonons. However, many soft materials have strong electron-phonon coupling, which may preclude the use of perturbative methods. The effect of vibrational anharmonicity on electronic transport in this context is not systematically known. Previous theoretical studies on organic molecular crystals have demonstrated that the details of harmonic phonons, such as dispersion and symmetry, will lead to qualitative differences in the carrier dynamics, particularly for temperature-dependent mobilities [19–21]. In this paper, we use a nonperturbative quantum-classical approach to study the motion of charge carriers coupled to phonons with anharmonicity.

II. THEORY

A. Model Hamiltonian

We study a single electron interacting with anharmonic phonons on a one-dimensional lattice with fixed lattice constant $a$, $N$ sites, and periodic boundary conditions. Each lattice site $n$ has a single electronic orbital with creation operator $c_{n}^\dagger$ and a single nuclear degree of freedom with momentum $p_n$ and displacement $u_q$. For the model considered here, the electronic bands and phonons are trivially defined by symmetry. The Hamiltonian is $H = H_{el} + H_{ph} + H_{el-ph}$ with

$$H_{el} = -\tau \sum_{k} \frac{\hbar^2 c_{n+1,k}^\dagger c_{n,k}}{m} + \hbar c_c = \sum_{k} \epsilon_k c_{n,k}^\dagger c_{n,k}, \quad (1a)$$

$$H_{ph} = \sum_{n} \frac{p_n^2}{2m} + V(u_1, \ldots, u_N)$$

$$= \sum_{q} \left[ \frac{p_q^2}{2} + \frac{1}{2} \omega_q^2 u_q^2 \right] + \Omega^m(u_1, \ldots, u_N), \quad (1b)$$

$$H_{el-ph} = G \sum_{n} \left( c_{n,k}^\dagger c_{n,k+1} + \hbar c_c \right) (u_{n+1} - u_{n})$$

$$= \sum_{k,q} G_{k,q} c_{k+q}^\dagger c_{k+q} u_{q}, \quad (1c)$$

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* Present address: Department of Chemistry, Yale University, New Haven, Connecticut 06520, USA
† tim.berkelbach@gmail.com
where $\epsilon_k$ are electronic band energies, $\omega_q$ are phonon frequencies, $V_{\text{arm}}$ is the anharmonic part of the potential energy surface, and we have assumed a linear Peierls form of the electron-phonon coupling

$$G_{kq} = \frac{2G}{N^{1/2}} \left[ \sin(ka) - \sin[(k - q)a] \right].$$

(2)

We will study one model of optical phonons and one model of acoustic phonons according to the potentials $V_{\text{op}}(u_1, \ldots, u_N) = \sum_n V(u_n)$, $V_{\text{ac}}(u_1, \ldots, u_N) = \sum_n V(u_{n+1} - u_n)$, $V(u) = \frac{1}{2}Ku^2 + c_3u^3 + c_4u^4$.

(3a)

(3b)

(3c)

Note that for simplicity we use the same function $V(u)$ in both cases. In the strictly harmonic limit, the above potentials yield optical phonons that are dispersionless with $\omega_q = \omega_0$ and acoustic phonons with dispersion $\omega_q = 2\omega_0|\sin(qa/2)|$, where $\omega_0 = \sqrt{K/m}$. Numerical values of the parameters used in our simulations are given in Sec. III.

B. Nonperturbative and anharmonic simulation

To accurately simulate the coupled electron-nuclear dynamics, we appeal to the quantum-classical Ehrenfest approach [1, 22]. Specifically, we let the nuclear degrees of freedom evolve according to Newtonian dynamics on the anharmonic potential energy surface, $m\ddot{u}_n = -\partial V/\partial u_n$. From the nuclear trajectories $u_n(t)$, we define a time-dependent electronic Hamiltonian

$$h_{el}(t) = -\sum_n \tau_n(t) \left( c_n^\dagger c_n + 1 + \text{H.c.} \right) + \sum_{kq} [\epsilon_k \delta_{k+q,k} + G_{kq}u_{-q}(t)] c_{k+q}^\dagger c_k$$

(4)

where $\tau_n(t) = \tau - G[u_{n+1}(t) - u_n(t)]$. Following our previous work [4], this time-dependent Hamiltonian is used in a mixed quantum-classical evaluation of the electronic current autocorrelation function,

$$C_{jj}(t) = \int dp \int du \mathcal{P}(p, u)(U_{el}(0, t)j(t)U_{el}(t, 0)f)_{el}.$$  

(5)

Here, $\mathcal{P}(p, u) \sim e^{-\hbar h_{el}(p, u)/\hbar}$ is the phase-space distribution of the classical nuclear degrees of freedom,

$$U_{el}(t, 0) = T \exp \left[ -\frac{i}{\hbar} \int_0^t dt' h_{el}(t') \right]$$

(6)

is the time-ordered evolution operator,

$$j(t) = i\hbar \sum_n \tau_n(t) \left( c_n^\dagger c_{n+1} - \text{H.c.} \right)$$

(7)

is the current operator for the Hamiltonian (1), $\langle O \rangle_d = \text{Tr}_e(Oe^{-\hbar h_{el}(t=0)/\hbar}\hat{T})/Z_d$ is a thermal average over electronic degrees of freedom, and $Z_d = \text{Tr}_e(e^{-\hbar h_{el}(t=0)/\hbar})$ is the electronic partition function. From this, the AC conductivity is readily obtained via the Kubo formula

$$\text{Re} \sigma(\omega) = \frac{1 - e^{-\hbar \omega/k_B T}}{2N\omega} \int_0^{+\infty} dt e^{i\omega t} C_{jj}(t),$$

(8)

with the DC component obtained by taking the zero-frequency limit, $\sigma_{\text{DC}} \equiv \sigma(\omega \to 0)$. The mobility is $\mu = (N\delta/\omega)\sigma_{\text{DC}}$, where $N$ is the electron charge. The nonperturbative and anharmonic approach described here will be referred to as the “dynamical Kubo” approach in later sections.

Previous studies of conductivity performed via the Kubo formula have generally been done in the adiabatic limit [19, 20, 23, 24] such that Eq. (8) reduces to

$$\text{Re} \sigma(\omega) = \frac{1 - e^{-\hbar \omega/k_B T}}{2N\omega} \int d\mathbf{p} \mathcal{P}(\mathbf{p})$$

(9)

$$\times Z_{el}^{-1} \sum_{\alpha \beta} |\langle \alpha | \beta \rangle|^2 \delta(\omega - (\epsilon_\beta - \epsilon_\alpha)/\hbar),$$

where $\alpha, \beta$ are $u$-dependent eigenstates of the disordered electronic Hamiltonian and $\mathcal{P}(\mathbf{p}) \sim e^{-\mathcal{V}(\mathbf{p})/k_B T}$. We will refer to this as the “static Kubo” approach. One drawback is that the delta function must be given an artificial linewidth $\eta$, which is analogous to imposing an artificial decay to the current autocorrelation function (also called the “relaxation time approximation” in the transient localization literature [2, 25]). The choice of $\eta$ has been shown to substantially affect the temperature dependence of the mobility [24]; this ambiguity is avoided in the dynamical Kubo approach, where the current autocorrelation function decays naturally due to dynamic disorder (for both harmonic and anharmonic phonons).

The quantum-classical Ehrenfest approach has been one of the preferred methods for calculating carrier dynamics in models of soft materials [1, 2, 4, 22]. Because of its nonperturbative nature, this method can be applied to materials with simultaneously large electronic transfer integral $t$ and large electron-phonon coupling $G$, a combination which precludes treatment with perturbative small polaron or Boltzmann transport theory [26, 27]. The classical treatment of the phonon degrees of freedom is approximate, but highly accurate when $\hbar \omega_0/k_B T$ is small, as is the case for many soft semiconductors, including those we study here. The accuracy of quantum-classical methods was previously verified via comparison with accurate quantum Monte Carlo results with analytic continuation [2, 28]. In addition to the classical approximation for nuclear dynamics, we also neglect the feedback of the electronic degrees of freedom on the nuclei; this approximation has been shown to be accurate for the low-frequency nuclear dynamics and relatively high-mobility parameter regime we study here [22].

C. Perturbation theory with harmonic phonons

In fully ab initio studies, it is most common to calculate electronic dynamics by neglecting anharmonicity and treating
the electron-phonon interaction by perturbation theory [29–33]; see Ref. 34 for application to naphthalene, an organic molecular crystal similar to the model that we study in this work. This approach yields the intraband scattering rates

\[ \Gamma_{k,k+q}(T) = \frac{\pi}{\hbar \omega_q} |G_{kj}|^2 \left[ (n_q + 1) \delta(\epsilon_k - \epsilon_{k+q} - \omega_q) + n_q \delta(\epsilon_k - \epsilon_{k+q} + \omega_q) \right] \]

and inverse lifetimes \( \Gamma_k(T) = \sum_q \Gamma_{k,k+q}(T) \); here, \( n_q \) is the Bose-Einstein distribution function at temperature \( T \). In the limit of low \( \omega_q \), which holds for the materials of interest here, the quasielastic approximation can be made \([20, 27]\) giving

\[ \Gamma_{k,k+q}(T) = \frac{\pi \omega_q k_B T}{\hbar \omega_q} |G_{kj}|^2 \left[ \delta(\epsilon_k - \epsilon_{k+q}) \right] \left( 1 - \cos(\theta_{k,k+q}) \right), \]

where \( \omega_0 \) was defined below Eq. (3), \( \theta_{k,k+q} \) is the angle between the initial and the scattered state, and \( 1 - \cos(\theta_{k,k+q}) = 1 - (k + q)/k \) in one dimension. These lifetimes can be used within a linearized Boltzmann transport equation (BTE) framework \([30, 35]\) to calculate the conductivity,

\[ \sigma_{DC} = \frac{e^2}{N \alpha k_B T} Z_{el}^{-1} \sum_k v_k^2 \Gamma_k^{-1} e^{-\epsilon_k/\hbar k_B T} \]

where \( v_k = \hbar^{-1} \partial \epsilon_k / \partial k \) is the band velocity. The quasielastic BTE provides a useful comparison for the limit of electronic band transport with weak scattering due to phonons. As lowest-order perturbation theory, the BTE ignores multiphonon processes that mediate relaxation when the electronic energy difference and the phonon energies are mismatched. Thus we expect the BTE to overestimate electronic lifetimes and therefore underestimate the conductivity. These multiphonon processes are captured in the nonperturbative quantum-classical theory.

D. Effective harmonic theory

The phonon anharmonicity may be treated approximately by using an effective, temperature-dependent harmonic model,

\[ V(u_1, \ldots, u_n) \approx \frac{1}{2} \sum_q \tilde{\omega}_q(T) u_q^2 \]

where the effective phonon frequencies \( \tilde{\omega}_q(T) \) can be determined by a number of mean-field type methods \([36–40]\). Specifically, we highlight Ref. 18, which treats the dynamics of electrons coupled to soft modes in SrTiO\(_3\) in this manner. Here we propose an alternative but closely related approach motivated by the application to electronic dynamics.

For the anharmonic potentials considered here, we will consider effective harmonic potentials of the same form as in Eqs. (3) but with

\[ \tilde{V}(u) = \frac{1}{2} \tilde{K} u^2 = \frac{1}{2} m \tilde{\omega}_0^2 u^2, \]

and we will employ the same form of electron-phonon coupling as in Eq. (1c). The temperature-dependent effective frequency \( \tilde{\omega}_0 \) is chosen to reproduce the statistics of the dynamically disordered transfer integrals \( \tau_{\alpha}(t) \). Our later simulations will be performed at fixed volume (i.e., in the absence of thermal expansion), which guarantees that the average transfer integral is always given by the bare transfer integral, \( \langle \tau_{\alpha} \rangle = \tau \), even with anharmonicity. We thus choose the effective harmonic frequency to reproduce the variance of the transfer integral calculated with the anharmonic potential, \( \langle (\tau_{\alpha} - \tau)^2 \rangle_{an} = \langle (\tau_{\alpha} - \tau)^2 \rangle_{an} \), which is equivalent to matching the variance in the nearest-neighbor separations, \( \langle (u_{n+1} - u_n)^2 \rangle_{an} = \langle (u_{n+1} - u_n)^2 \rangle_{an} \). This requirement leads to

\[ \tilde{\omega}_0^2 = C \frac{2 G^2 k_B T}{\langle (\tau_{\alpha} - \tau)^2 \rangle_{an}} = C \frac{2 k_B T}{\langle (u_{n+1} - u_n)^2 \rangle_{an}}, \]

where \( C = 2 \) for optical phonons and \( C = 1 \) for acoustic phonons. We emphasize that the anharmonic variance is a statistical quantity that can be calculated with Monte Carlo sampling and does not require any information about the dynamics of the phonons. This formalism is closely related to other mean-field theories of phonon anharmonicity.

This approach approximately captures the instantaneous electronic disorder in the Hamiltonian, which is the primary ingredient of the transient localization/dynamic disorder picture \([2, 41]\). In the next section, simulations using this effective harmonic model of phonons (with the dynamical Kubo, static Kubo, and Boltzmann transport theories described above) will be compared to fully anharmonic simulations. In this way, we can isolate the effects of anharmonicity (treated approximately or exactly) and nonperturbative electron-phonon coupling.

III. RESULTS AND DISCUSSION

A. Simulation details and phonon anharmonicity

As a harmonic limit for our transport model, we use the parameters from Ref. 42 for the b-axis of single-crystal rubrene, which have been used in numerous studies \([2, 4, 24]\). The parameters are \( \tau = 143 \text{ meV}, G = 493.5 \text{ meV/Å}, m = 532 \text{ amu} \) and \( a = 7.2 \text{ Å} \). As already mentioned, we do not allow thermal expansion, which guarantees \( \langle \tau_{\alpha} \rangle = \tau \). We used periodic lattices with 100-200 sites and sampled up to 50 000 trajectories for each calculation to converge all results.

For simplicity, we consider the same set of potential parameters \( K, c_3, c_4 \) for the optical and acoustic phonons. The harmonic force constant is always \( K = m \tilde{\omega}_0^2 = 4.89 \text{ eV/Å}^2 \), corresponding to \( \hbar \omega_0 = 6.2 \text{ meV} \). For each phonon model, we consider two type of anharmonicity. For the first type, which we call "phonon hardening", we use \( c_3 = 0 \) and \( c_4 = 19.56 \text{ eV/Å}^4 \); this type of purely quartic anharmonicity will result in an increase in the phonon frequency with temperature. For the second type, which we call "phonon softening", we use \( c_4 = 2.45 \text{ eV/Å}^4 \) and two possible values for \( c_3 \). The first value, \( c_3 = -4.40 \text{ eV/Å}^4 \), yields an asymmetric single-
well potential; the second value, $c_3 = -4.65 \text{ eV/Å}^3$, yields an asymmetric double-well potential.

In Fig. 1, we plot these three potentials (left column) and the temperature-dependent spectral function $C_{uu}(\omega) \sim \text{Re} \int dt e^{i\omega t} \langle u(t) u(0) \rangle_{\text{cm}}$ (right column) for a single anharmonic oscillator calculated with classical dynamics. Unlike for a harmonic potential, the anharmonic potentials lead to spectral functions whose peaks shift to higher frequencies (phonon hardening) or lower frequencies (phonon softening) with increasing temperature, along with a decrease in the phonon lifetimes. We also plot the temperature-dependent effective frequencies (vertical dashed lines) determined by matching the variance $\langle u^2 \rangle$ between the anharmonic and effective harmonic potential. The variance is related to the spectral function by $\langle u^2 \rangle = \int d\omega C_{uu}(\omega)$ and therefore the effective harmonic frequency is determined by $\tilde{\omega}_0^2 = k_B T/\int d\omega C_{uu}(\omega)$. We note that while the effective frequency roughly matches the maximum of the spectral function in the model with phonon hardening, it deviates more strongly from the maximum in the model with phonon softening. This is due to the more asymmetric distribution of the latter, whose maximum does not shift significantly with temperature despite the development of a large tail extending to lower frequencies.

When these potentials are used as the pair potential for our model of acoustic phonons, they yield the momentum resolved phonon spectral function $C_{uu}(q, \omega) \sim \text{Re} \int dt e^{iqt} \langle u_q(t) u_{-q}(0) \rangle$ shown in Fig. 2; results are shown at two temperatures. With quartic anharmonicity, we see clear phonon hardening of the entire phonon branch, with a peak position that is well-matched by the effective harmonic dispersion $\omega_q = 2\tilde{\omega}_0 |\sin(qa/2)|$, and a decreased phonon lifetime. For the phonon softening case, there is a clear decrease in the phonon lifetime. The effective phonon frequency shows the expected signature of phonon softening, although the spectral structure of the anharmonic result is hard to see with the employed colorscale due to the large linewidth. Like in Fig. 1, the maximum of the spectral function does not shift significantly but a large tail develops that extends to low frequency, which is captured in an average sense by the effective harmonic model.

The phonon model parameters were chosen to represent physically realistic amounts of anharmonicity. In particular, the frequency shifts and broadenings observed in Figs. 1 and 2 are comparable to those observed in low-frequency Raman measurements and ab initio simulations of organic crystals [5, 6].

B. Optical phonons

Having constructed a model for phonon anharmonicity in solids, we now shift our attention to the impact on electronic transport. On the left hand side of Fig. 3 we present the mobility of a carrier coupled to optical phonons, using the three levels of theory described in Sec. II: the dynamical Kubo approach, the static Kubo approach, and the Boltzmann trans-
FIG. 3. Log-log plot of temperature-dependent mobility \( \mu(T) \) for a carrier coupled to optical phonons (left) or acoustic phonons (right). Mobility is calculated with the dynamical Kubo formula (top), the static Kubo formula (bottom), and the Boltzmann transport equation (BTE). We first consider the harmonic limit with \( c_3 = c_4 = 0 \) (black circles). The dynamical Kubo approach yields a power law of roughly \( \mu \propto T^{-1.5} \), consistent with other Kubo formula calculations [2, 19, 20, 24] and Ehrenfest-style mixed quantum-classical diffusion models [1, 42–44]. We see that the “band-like” power law behavior extends to low temperatures, but the mobility begins to saturate above 500 K. This high-temperature mobility saturation is a well-known result of the nonperturbative quantum-classical models, equivalent to resistivity saturation in metals [23, 45]. The static Kubo approach with \( \eta = \omega_0/2 \) produces similar features but exhibits different low-temperature behavior and a different power law exponent. Both of these differences between static and dynamical Kubo formula are due to the artificial lifetime \( \eta^{-1} \) in the static Kubo formula. The dynamical Kubo formula results in a natural lifetime that changes with temperature, most notably at low temperature. Finally, the quasielastic BTE predicts a power law of \( T^{-1.5} \) at low-temperature and \( T^{-2} \) at high-temperature [19, 20, 23]; only the former is visually apparent for the current model parameters within the temperature range shown. Despite the differences in their detailed behaviors, all methods yield absolute mobilities that are within a factor of two of the “exact” dynamical Kubo approach at all temperatures.

We now consider the impact of phonon anharmonicity. Qualitatively, we expect phonon hardening to increase the mobility and phonon softening to decrease the mobility, because electrons near the bottom of the band are more effectively scattered by low-frequency phonons. Indeed, in our simulations, we see that purely quartic anharmonicity leading to phonon hardening (red lines) increases the overall mobility (by no more than 50%) and slightly decreases the power law coefficient. Both types of anharmonicity leading to phonon softening, an asymmetric single well (blue lines) and a double well (green lines), reduce the mobility—by up to a factor of three in the high temperature limit of the dynamical Kubo results. Moreover, phonon softening lowers the onset of “high-temperature” behavior; all methods show a crossover to \( \mu \sim T^{-2} \) power law behavior but only the nonperturbative Kubo results (dynamical or static) show the later onset of mobility saturation [23]. For the double-well potential, the anharmonic frequency shift is larger and thus the reduction in the mobility is larger. Compared to the exact dynamical Kubo method, the static Kubo method overestimates the reduction in the mobility.

Replacing the anharmonic phonons by effective harmonic phonons (dashed lines) is seen to be an excellent approximation. For the dynamical Kubo approach, the agreement is almost perfect, suggesting that the phonon lifetime has no appreciable effect on the mobility. This is not surprising given the separation of timescales for the parameters used here: the electronic lifetimes are hundreds of femtoseconds and the phonon lifetimes are thousands of femtoseconds, even at high temperature. Within the static Kubo framework, discrepancies between mobilities with the effective harmonic and with fully anharmonic potential are due to the shape of the disorder distribution. While both cases have the same electronic disorder variance \( \langle (\tau_n - \tau)^2 \rangle \), the fully anharmonic potential produces a highly non-Gaussian distribution, which modifies the electronic dynamics. The agreement is best for purely quartic (hardening) anharmonicity because the distribution is symmetric and thus can be accurately modeled by an appropriate Gaussian distribution; the asymmetric distributions associated with phonon softening present a greater challenge. Another contributor to the static Kubo mobility is the electronic lifetime \( \eta^{-1} \). We used a constant \( \eta = \omega_0/2 \) regardless of the effective frequency \( \tilde{\omega}_n(T) \) for the static Kubo results; using \( \eta = \tilde{\omega}_n(T)/2 \) was found to produce an even larger discrepancy with the dynamical Kubo results and a large overestimate of the effect of phonon softening on carrier mobility.
The BTE framework qualitatively captures the effect of phonon hardening; in fact, the mobility is just scaled by a factor of $\tilde{\omega}_0(T) / \omega_0$. Phonon softening accentuates the disagreement between BTE and the nonperturbative Kubo results, since it reduces the onset temperature of mobility saturation, which cannot be captured by the BTE. In summary, the DC mobility of an electron coupled to anharmonic optical phonons is accurately reproduced by effective harmonic phonons within the full dynamical Kubo formula; this approximation becomes less accurate for the static Kubo approach. This effective harmonic approximation is the only way to apply BTE, which becomes increasingly inaccurate at high temperature, especially in the presence of phonon softening.

In Fig. 4, we show the frequency-resolved AC conductivity of the same systems calculated with the dynamical Kubo formula at three temperatures: 100 K, 300 K, and 500 K. In the harmonic limit, we see the characteristic features of asymmetric electron-phonon coupling to optical phonons [19, 24, 46]. Peaks appear at low frequency (below 50 meV) and at multiples of the half bandwidth $2\tau$ (around 300 and 600 meV). With increasing temperature, the spectral weight shifts to higher energies and the DC mobility is reduced. In the presence of pure quartic anharmonicity (phonon hardening), we see very similar results, although the anharmonicity induces a slight shift of spectral weight to lower energies, consistent with the increased mobility. The effective harmonic model produces nearly exact results at all frequencies, extending the agreement seen in the mobility. When the anharmonicity is of the double-well form (phonon softening), we find a low-temperature conductivity similar to the harmonic or quartic anharmonic cases, but quite different high-temperature conductivities with significantly less structure. While the effective harmonic model can reproduce the DC conductivity of the anharmonic model reasonably well, it is less successful for the full AC conductivity, especially at higher temperatures. Results obtained with the static Kubo formula (not shown) confirm that this discrepancy is not a phonon lifetime effect, but rather is due to the harmonic approximation’s inability to capture the non-Gaussian distribution of electronic disorder.

**C. Acoustic phonons**

We now study an electron coupled to anharmonic acoustic phonons, recalling that it has been previously demonstrated that, within the harmonic approximation, acoustic phonons and optical phonons lead to qualitatively different transport behavior [20, 21]. The right-hand side of Fig. 3 shows the temperature dependent mobility. For harmonic acoustic phonons, the dynamical Kubo formula predicts a power law of roughly $\mu \propto T^{-1/2}$ below 500 K. In the regime where saturation occurs for optical phonons, the mobility has the opposite behavior for acoustic phonons, showing an increased power law coefficient; mobility saturation will occur at very high temperature but is not evident for harmonic acoustic phonons at the temperatures shown [20]. Static Kubo and BTE calculations show similar behavior, although the power law exponent of the static Kubo mobility is overestimated. Surprisingly, the BTE mobility is more accurate than the static Kubo mobility, presumably due to the latter’s use of a constant $\eta$. In agreement with the dynamical Kubo results, the BTE predicts $\mu \propto T^{-1/2}$ at low temperature at $\mu \propto T^{-2}$ at high temperature.

Turning to the impact of anharmonicity, we see that acoustic phonon hardening produces the expected behavior based on our previous analysis: it increases the mobility and reduces the power-law coefficient, effects that are qualitatively captured by all three methods. Acoustic phonon softening decreases the mobility and introduces mobility saturation at lower temperatures. Unlike for optical phonon anharmonicity, phonon hardening generally modifies the mobility more than phonon softening.

Again we find that phonon hardening effects are well reproduced by an effective harmonic model. However, phonon softening is even harder to capture with a harmonic model than it was for optical phonons; the mobility is overestimated at all temperatures and disagreement is most severe for the static Kubo approach. The BTE mobility is a remarkably good approximation to the dynamical Kubo results and semiquantitatively captures the effects of all types of anharmonicity.

The frequency-resolved AC conductivity calculated by the dynamical Kubo approach with harmonic and anharmonic acoustic phonons is shown in the right hand side of Fig. 4. With coupling to acoustic phonons, the AC conductivity is
FIG. 5. Static Kubo formula mobility with $\eta = \omega_B/2$ (top panel) and example distributions of transfer integral $\tau_n$ at 500 K (bottom panel) for an electron coupled to a soft acoustic mode. All distributions in the bottom panel share the same average transfer integral $\langle \tau_n \rangle = \tau$ and variance $\langle (\tau_n - \tau)^2 \rangle = 0.123\tau^2$, with the red and blue curves differing only in the sign of the cubic coefficient $c_3 = \pm 4.65$ eV/Å$^3$. Both potentials lead to the same effective harmonic distribution of $\tau_n$ and mobility (green dashed lines).

significantly different than with coupling to optical phonons. Specifically, there is absolutely no structure at high frequencies; only a DC conductivity and a simple maximum at low frequency. For this reason, the effective harmonic approximation is more successful than it was with optical phonons. The agreement is worst with phonon softening, where the effective harmonic approximation slightly underestimates the linewidth.

Before concluding, we give an example of the challenge associated with effective harmonic approximations. We consider two version of the asymmetric double well pair potential, leading to acoustic phonon softening: one with $c_3 = -4.65$ eV/Å$^3$ (the same one considered so far) and one with $c_3 = +4.65$ eV/Å$^3$. In the bottom panel of Fig. 5, we show the distribution of nearest-neighbor transfer integrals $P(\tau_n)$. Both anharmonic potentials have the same mean $\langle \tau_n \rangle$ and variance $\langle (\tau_n - \tau)^2 \rangle$; therefore, the effective harmonic potential constructed according to our prescription (15) is identical. The top panel of Fig. 5 shows the static Kubo mobility for each of these three potentials. We see that the magnitude and temperature dependence of the mobility differs depending on the sign of $c_3$, an effect that cannot be captured by an effective harmonic model. While asymmetric potentials are difficult to capture using a harmonic model for optical modes, the issue of asymmetric distributions of $\tau_n$ is not present in (strictly dispersionless) optical phonons. This is because $\mu_{n+1}$ and $\mu_n$ are uncorrelated, which yields a symmetric distribution for $\tau_n$ even for asymmetric potentials. Correlated nearest-neighbor displacements, like those in acoustic phonons, produce an asymmetric distribution of $\tau_n$ and thus create the ambiguity demonstrated here.

IV. CONCLUSIONS

We have demonstrated the impact of phonon anharmonicity on the equilibrium electronic dynamics of soft materials and assessed the accuracy of various approximations. For all methods, we see a change in the magnitude and temperature dependence of the mobility based on the strength and form of the anharmonicity. Within the dynamical Kubo formula, changes to the mobility are well-characterized by an effective harmonic model of phonons, especially for optical phonons. The effective harmonic model is less accurate when the static Kubo formula is employed. This discrepancy is especially apparent for acoustic phonons, where the correlated phonon motion can lead to asymmetric disorder profiles that cannot be unambiguously modeled by a harmonic potential.

Future work could include lattice expansion or lattice strain, studies of which have been mostly limited to harmonic models [47, 48]. The approaches described are quite general and could be applied to other soft materials such as metal-oxide perovskites [17], lead-halide perovskites [3, 16], or thermoelectric materials [49, 50], perhaps in an ab initio framework. We are also interested in applying these methods to study nonequilibrium electronic dynamics [51, 52] where we expect the impact of nonperturbative electron-phonon interactions and phonon anharmonicity to be larger.

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