


Conductivity of an electron coupled to anharmonic phonons: Quantum-classical simulations and comparison of approximations

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We study the impact of phonon anharmonicity on the electronic dynamics of soft materials using a non-perturbative 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. With *ab initio* simulations in mind, 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.

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I. INTRODUCTION

Designing 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, recent 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 regard to spectral quantities, such as vibrational spectroscopies, anharmonicity most commonly manifests as two well-known 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 titanate [17]. Soft modes in strontium titanate 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 temperature-dependent effective phonons.

From a theoretical and computational point of view, the treatment of coupling between electrons and anharmonic phonons is difficult. The most affordable route, taken, for example, in Ref. [18], is to combine a mean-field treatment of phonon anharmonicity with a perturbative treatment of electron-phonon coupling. However, many soft materials have strong electron-phonon coupling and/or phonon anharmonicity, which may preclude the use of such methods. Specifically, the effect of phonon anharmonicity on electronic transport in this regime of strong electron-phonon coupling is not systematically understood.

In this paper, we use a quantum-classical approach to study the dynamics of a model system of charge carriers coupled to phonons with anharmonicity. Our employed method is approximate but nonperturbative with respect to both the electron-phonon coupling and the phonon anharmonicity, and it is expected to be very accurate in the parameter regime appropriate for many soft materials. Similar quantum-classical approaches, historically applied with only harmonic phonons, are responsible for the dynamic disorder and transient localization pictures [1,2] and predict a power-law temperature dependence of the mobility $\mu(T) \sim T^{-2}$ that is in good

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agreement with experiment [2–4,19] and is not captured by perturbative approaches [2,20]. The failure of perturbative approaches and the accuracy of nonperturbative, quantum-classical approaches are also well documented in the study of excitation energy transfer of molecular aggregates [21–23].

With this quantum-classical approach in hand, our work has two purposes. First, we aim to identify the qualitative effects that phonon anharmonicity has on electronic dynamics when the electron-phonon coupling and/or degree of anharmonicity is large. Such a limit is hard to study using other techniques. However, our quantum-classical technique is too expensive for routine application to materials with *ab initio* Hamiltonians, i.e., with many electronic bands and phonon branches. Therefore, our second purpose is to benchmark the accuracy of more affordable techniques that can be used with *ab initio* Hamiltonians.

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_n . For the model considered here, the electronic bands and phonons are trivially defined by symmetry. The Hamiltonian is $H = H_{\text{el}} + H_{\text{ph}} + H_{\text{el-ph}}$, with

$$H_{\text{el}} = -\tau \sum_n c_n^\dagger c_{n+1} + \text{H.c.} = \sum_k \varepsilon_k c_k^\dagger c_k, \quad (1a)$$

$$H_{\text{ph}} = \sum_n \frac{p_n^2}{2m} + \mathcal{V}(u_1, \dots, u_N) \\ = \sum_q \left[\frac{p_q^2}{2} + \frac{1}{2} \omega_q^2 u_q^2 \right] + \mathcal{V}^{\text{an}}(u_{q_1}, \dots, u_{q_N}), \quad (1b)$$

$$H_{\text{el-ph}} = G \sum_n (c_n^\dagger c_{n+1} + \text{H.c.})(u_{n+1} - u_n) \\ = \sum_{kq} G_{kq} c_k^\dagger c_{k-q} u_q, \quad (1c)$$

where ε_k are electronic band energies, ω_q are phonon frequencies, \mathcal{V}^{an} is the anharmonic part of the potential energy surface, and we have assumed a linear Peierls form of the electron-phonon coupling

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

We will study one model of optical phonons and one model of acoustic phonons according to the potentials

$$\mathcal{V}_{\text{op}}(u_1, \dots, u_N) = \sum_n V(u_n), \quad (3a)$$

$$\mathcal{V}_{\text{ac}}(u_1, \dots, u_N) = \sum_n V(u_{n+1} - u_n), \quad (3b)$$

$$V(u) = \frac{1}{2}Ku^2 + c_3u^3 + c_4u^4. \quad (3c)$$

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.

Although real molecular crystals also have local Holstein-type electron-phonon coupling (mostly to high-frequency intramolecular vibrations), it is excluded from the current study for several reasons. First, in our previous work [4] we showed that even when the Holstein coupling is large, Peierls coupling to low-frequency vibrations dominates the carrier mobility. Second, these high-frequency intramolecular vibrations are significantly more harmonic and can thus be treated by standard techniques, such as the Lang-Firsov transformation leading to a static, temperature-dependent renormalization of hopping parameters [4].

B. Nonperturbative and anharmonic simulation

To accurately simulate the coupled electron-nuclear dynamics without assuming weak electron-phonon coupling or weak anharmonicity, we appeal to the quantum-classical Ehrenfest approach [1,24]. Specifically, we let the nuclear degrees of freedom evolve according to Newtonian dynamics on the anharmonic potential energy surface, $m\ddot{u}_n = -\partial\mathcal{V}/\partial u_n$. From the nuclear trajectories $u_n(t)$, we define a time-dependent electronic Hamiltonian

$$h_{\text{el}}(t) = -\sum_n \tau_n(t) (c_n^\dagger c_{n+1} + \text{H.c.}) \\ = \sum_{kq} [\varepsilon_k \delta_{k,k-q} + G_{kq} u_q(t)] c_k^\dagger c_{k-q}, \quad (4)$$

where $\tau_n(t) = \tau - G[u_{n+1}(t) - u_n(t)]$. Note that we neglect the feedback of the electronic degrees of freedom on the nuclei, which ignores the contribution of electron-phonon scattering to the phonon lifetime. Although this can be straightforwardly included at the mean-field level, this approximation has been shown to be accurate for the low-frequency nuclear dynamics and relatively high-mobility parameter regime we study here [24].

Following our previous work [4], the time-dependent Hamiltonian (4) is used in a mixed quantum-classical evaluation of the electronic current autocorrelation function,

$$C_{jj}(t) = \int d\mathbf{p} \int d\mathbf{u} \mathcal{P}(\mathbf{p}, \mathbf{u}) \langle U_{\text{el}}(0, t) j(t) U_{\text{el}}(t, 0) j \rangle_{\text{el}}. \quad (5)$$

Here, $\mathcal{P}(\mathbf{p}, \mathbf{u}) \sim e^{-H_{\text{ph}}(\mathbf{p}, \mathbf{u})/k_{\text{B}}T}$ is the phase-space distribution of the classical nuclear degrees of freedom,

$$U_{\text{el}}(t, 0) = T \exp \left[-\frac{i}{\hbar} \int_0^t dt' h_{\text{el}}(t') \right] \quad (6)$$

is the time-ordered evolution operator,

$$j(t) = ia \sum_n \tau_n(t) (c_n^\dagger c_{n+1} - \text{H.c.}) \quad (7)$$

is the current operator for the Hamiltonian (1), $\langle O \rangle_{\text{el}} = \text{Tr}_{\text{el}} \{ O e^{-h_{\text{el}}(t=0)/k_{\text{B}}T} \} / Z_{\text{el}}$ is a thermal average over electronic degrees of freedom, and $Z_{\text{el}} = \text{Tr}_{\text{el}} \{ e^{-h_{\text{el}}(t=0)/k_{\text{B}}T} \}$ is the

electronic partition function. From this, the AC conductivity is readily obtained via the Kubo formula

$$\text{Re}\sigma(\omega) = \frac{1 - e^{-\hbar\omega/k_B T}}{2N\omega} \int_{-\infty}^{+\infty} dt e^{i\omega t} C_{jj}(t), \quad (8)$$

with the DC component obtained by taking the zero-frequency limit, $\sigma_{\text{DC}} \equiv \sigma(\omega \rightarrow 0)$. The mobility is $\mu = (Na/e)\sigma_{\text{DC}}$, where e 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 [20,25–27] such that Eq. (8) reduces to

$$\text{Re}\sigma(\omega) = \frac{1 - e^{-\hbar\omega/k_B T}}{2N\omega} \int du \mathcal{P}(\mathbf{u}) \times Z_{\text{el}}^{-1} \sum_{\alpha\beta} |\langle \alpha | j | \beta \rangle|^2 \delta[\omega - (\varepsilon_\beta - \varepsilon_\alpha)/\hbar], \quad (9)$$

where α and β are \mathbf{u} -dependent eigenstates of the disordered electronic Hamiltonian and $\mathcal{P}(\mathbf{u}) \sim e^{-\mathcal{V}(\mathbf{u})/k_B T}$. We will refer to this as the ‘‘static Kubo’’ approach. One drawback is that the δ function must be given an artificial linewidth η , which is analogous to imposing an artificial decay to the current autocorrelation function (also called the ‘‘relaxation time approximation’’ in the transient localization literature [2,28]). The choice of η has been shown to substantially affect the temperature dependence of the mobility [25]; 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 [1,2,4,24]. Because of its non-perturbative nature, this method can be applied to materials that simultaneously have a large electronic transfer integral τ and large electron-phonon coupling G , a combination which precludes treatment with a perturbative small polaron or Boltzmann transport theory [29,30]. 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 affordable extension to high-frequency, anharmonic phonons is a greater methodological challenge. For the parameter range we are interested in here, the accuracy of quantum-classical methods was previously verified via comparison with accurate quantum Monte Carlo with analytic continuation [2,31] and multilayer multiconfigurational time-dependent Hartree calculations [32]. An advantage of using the Kubo formula to evaluate the conductivity, compared to the more common slope of the mean square displacement, is that the current autocorrelation function decays to zero at long times and is therefore less impacted by the well-documented equilibration failures of quantum-classical methods [33], especially those that neglect the feedback.

In an *ab initio* context, calculations of electronic mobility require all electronic band energies, phonon frequencies, and electron-phonon coupling constants. The dynamical Kubo approach further requires an atomistic molecular dynamics simulation to generate the nuclear trajectories and associated

time-dependent electronic Hamiltonian; such a simulation could be performed using a classical force-field or *ab initio* electronic structure theory, such as density functional theory, leading to a relatively high computational cost. The static Kubo approach requires sampling of atomic configurations from the same potential energy surface. If the time-dependent one-electron Hamiltonian matrix elements are approximated to be spatially uncorrelated, then the distribution of the individual matrix elements over nuclear samples is sufficient for a static Kubo calculation. Although computationally tractable, the relatively high cost of these methods and their dependence on explicit molecular dynamics or sampling motivates the testing of more approximate methods based on perturbation theory, as described in the next section.

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 [34–38]; see Ref. [39] 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

$$\Gamma_{k,k+q}(T) = \frac{\pi}{\hbar\omega_q} |G_{kq}|^2 \{ [n_q + 1] \delta(\varepsilon_k - \varepsilon_{k+q} - \omega_q) + n_q \delta(\varepsilon_k - \varepsilon_{k+q} + \omega_q) \} \quad (10)$$

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 ω_q , which holds for the materials of interest here, the quasielastic approximation can be made [27,30], giving

$$\Gamma_{k,k+q}(T) = \frac{\pi\omega_0 k_B T}{\hbar\omega_q} |G_{kq}|^2 \delta(\varepsilon_k - \varepsilon_{k+q}) \{ 1 - \cos(\theta_{k,k+q}) \}, \quad (11)$$

where ω_0 was defined below Eq. (3), $\theta_{k,k+q}$ is the angle between the initial and scattered states, 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 [35,40] to calculate the conductivity,

$$\sigma_{\text{DC}} = \frac{e^2}{Nak_B T} Z_{\text{el}}^{-1} \sum_k v_k^2 \Gamma_k^{-1} e^{-\varepsilon_k/k_B T}, \quad (12)$$

where $v_k = \hbar^{-1} \partial \varepsilon_k / \partial k$ is the band velocity. The quasielastic BTE provides a useful comparison for the limit of electronic band transport with weak scattering due to phonons. Because it is based on 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 overestimate 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,

$$\mathcal{V}(u_{q_1}, \dots, u_{q_n}) \approx \frac{1}{2} \sum_q \tilde{\omega}_q^2(T) u_q^2, \quad (13)$$

where the effective phonon frequencies $\tilde{\omega}_q(T)$ can be determined by a number of mean-field type methods [41–45]. Specifically, we highlight Ref. [18], which treats the dynamics of electrons coupled to soft modes in SrTiO₃ 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

$$\tilde{V}(u) = \frac{1}{2} \tilde{K} u^2 = \frac{1}{2} m \tilde{\omega}_0^2 u^2, \quad (14)$$

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 $\tau_n(t)$. 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, $\langle \tau_n \rangle = \tau$, even with anharmonicity. We thus choose the effective harmonic frequency to reproduce the variance of the transfer integral calculated with the anharmonic potential, $\langle (\tau_n - \tau)^2 \rangle_{\text{ha}} = \langle (\tau_n - \tau)^2 \rangle_{\text{an}}$, which is equivalent to matching the variance in the nearest-neighbor separations, $\langle (u_{n+1} - u_n)^2 \rangle_{\text{ha}} = \langle (u_{n+1} - u_n)^2 \rangle_{\text{an}}$. This requirement leads to

$$\tilde{\omega}_0^2 = C \frac{2G^2 k_B T}{\langle (\tau_n - \tau)^2 \rangle_{\text{an}}} = C \frac{2k_B T}{\langle (u_{n+1} - u_n)^2 \rangle_{\text{an}}}, \quad (15)$$

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 [2,46]. 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. [47] for the b axis of single-crystal rubrene, which have been used in numerous studies [2,4,25]. The parameters are $\tau = 143$ meV, $G = 493.5$ meV/Å, $m = 532$ amu, $a = 7.2$ Å, and $K = m\omega_0^2 = 4.89$ eV/Å² (corresponding to $\hbar\omega_0 = 6.2$ meV = 50 cm⁻¹). As already mentioned, we do not allow thermal expansion, which guarantees $\langle \tau_n \rangle = \tau$. We used periodic lattices with 100–200 sites

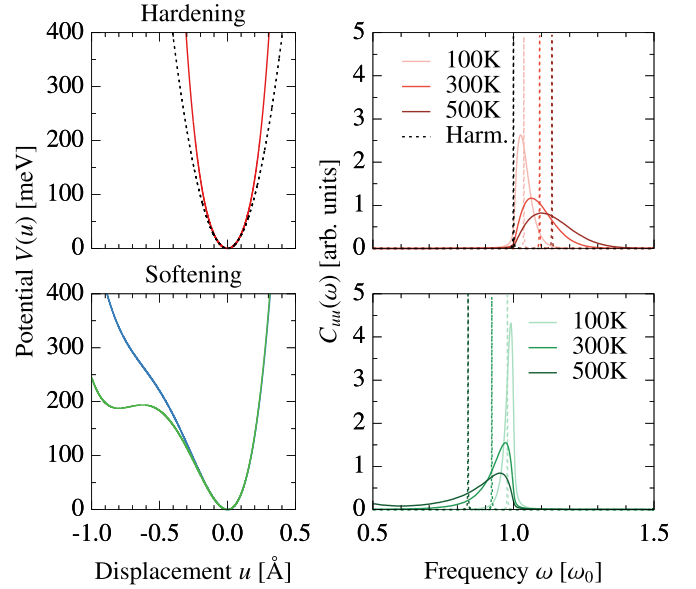


FIG. 1. Potential $V(u)$ (left) and spectral function $C_{uu}(\omega)$ (right) for optical phonons. The phonon potential is of the form in Eq. (3a) with hardening (top left, red) corresponding to $c_3 = 0$ and $c_4 = 19.56$ eV/Å⁴. The phonon softening potentials (bottom left) both use $c_4 = 2.45$ eV/Å⁴ with $c_3 = -4.40$ and -4.65 eV/Å³ for the single and double wells, respectively. The dashed black curve is the harmonic potential with $c_3 = c_4 = 0$ (top left). The spectral function $C_{uu}(\omega)$ is shown at different temperatures using the hardening parameters (top right) and the double-well softening parameters (bottom right). The dashed lines correspond to the effective harmonic frequencies $\tilde{\omega}_0(T)$ obtained using Eq. (15).

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 , and c_4 for the optical and acoustic phonons. For each phonon model, we consider two types of anharmonicity. For the first type, which we call “phonon hardening,” we use $c_3 = 0$ and $c_4 = 19.56$ eV/Å⁴; 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 $c_4 = 2.45$ eV/Å⁴ and two possible values for c_3 . The first value, $c_3 = -4.40$ eV/Å³, yields an asymmetric single-well potential; the second value, $c_3 = -4.65$ eV/Å³, yields an asymmetric double-well potential.

In Fig. 1, we plot these three potentials (left column) and the temperature-dependent spectral function $C_{uu}(\omega) \sim \text{Re} \int dt e^{i\omega t} \langle u(t)u(0) \rangle_{\text{an}}$ (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 potentials. 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

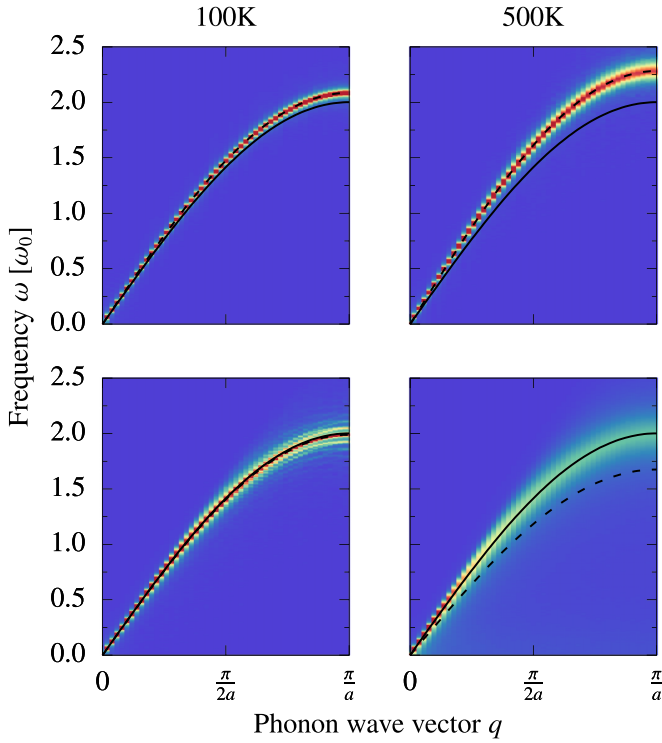


FIG. 2. Momentum-resolved phonon spectral function $C_{uu}(q, \omega)$ for acoustic phonons. The color map data show the spectra for the hard mode potential (top) and double-well soft mode potential (bottom) at two different temperatures. The solid black line shows the harmonic dispersion $2\omega_0|\sin(qa/2)|$, while the dashed black line shows the effective harmonic dispersion $2\tilde{\omega}_0(T)|\sin(qa/2)|$.

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 $C_{uu}(q, \omega) \sim \text{Re} \int dt e^{i\omega t} \langle u_q(t) u_{-q}(0) \rangle$ 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 $\tilde{\omega}_q = 2\tilde{\omega}_0|\sin(qa/2)|$, 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 color scale 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

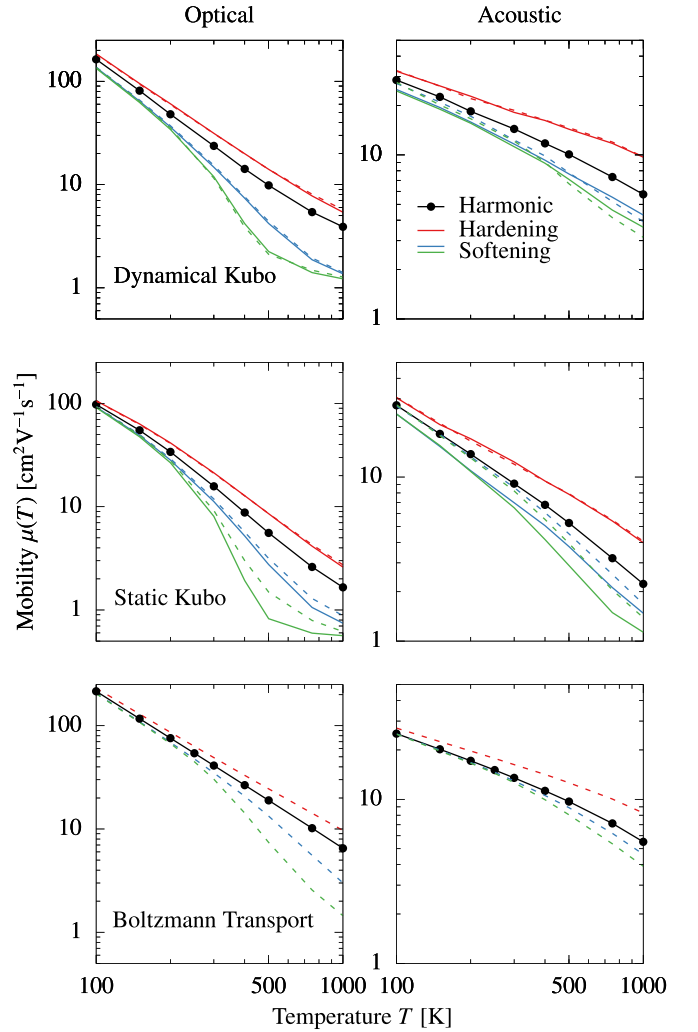


FIG. 3. Log-log plot of temperature-dependent mobility $\mu(T)$ for a carrier coupled to optical phonons (left) or acoustic phonons (right). Mobility is calculated with the dynamical Kubo formula (top), the static Kubo formula with $\eta = \omega_0/2$ (middle), and the Boltzmann transport equation (bottom). In addition to the mobility with harmonic phonons (black dotted lines), we show mobility with anharmonic phonons that lead to hardening (solid red lines) and softening (blue and green lines). Results are shown with full anharmonicity (solid lines) and with temperature-dependent harmonic phonons (dashed lines) according to Eq. (15).

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 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 $\mu \propto T^{-1.8}$, consistent with other Kubo formula calculations

[2,25–27] and Ehrenfest-style mixed quantum-classical diffusion models [1,47–49]. We see that the “bandlike” 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 [20,50]. 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 η^{-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 [20,26,27]; 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 2 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 3 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 [20]. 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

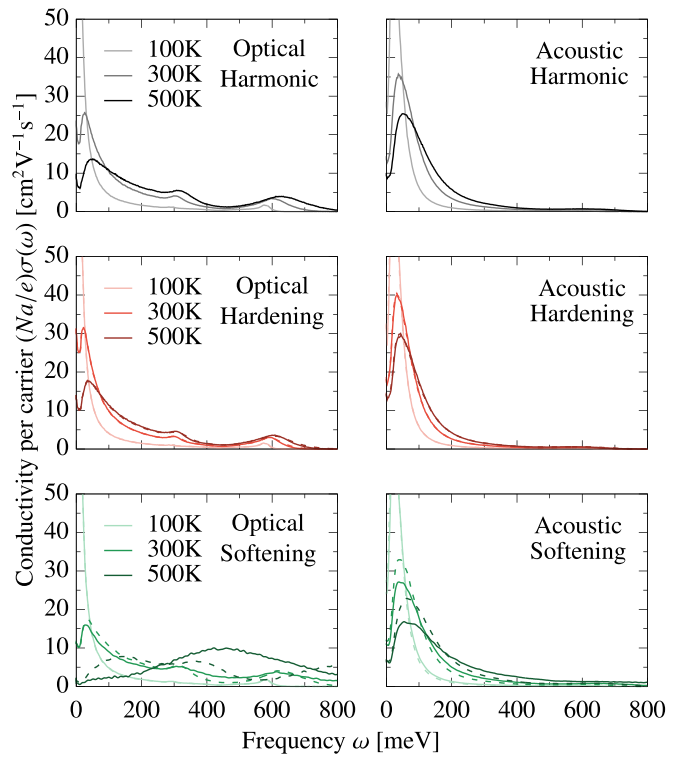


FIG. 4. AC conductivity per carrier $(Na/e)\sigma(\omega)$ with coupling to optical (left) and acoustic phonons (right). Conductivities are calculated using the dynamical Kubo formula (solid lines) and are shown at different temperatures for harmonic phonons (top), anharmonic phonons that harden with temperature (middle), and double-well anharmonic phonons that soften with temperature (bottom). Dashed lines use an effective harmonic potential with $\tilde{\omega}_0$ from Eq. (15).

challenge. Another contributor to the static Kubo mobility is the electronic lifetime η^{-1} . We used a constant $\eta = \omega_0/2$ regardless of the effective frequency $\tilde{\omega}_0(T)$ for the static Kubo results; using $\eta = \tilde{\omega}_0(T)/2$ 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, 300, and 500 K. In the harmonic limit, we see the characteristic features of asymmetric electron-phonon coupling to optical phonons [25,26,51]. Peaks appear at low frequency (below 50 meV) and at

multiples of the half bandwidth 2τ (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 [27,52]. 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 [27]. 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 η . In agreement with the dynamical Kubo results, the BTE predicts $\mu \propto T^{-1/2}$ at low temperature and $\mu \propto T^{-2}$ 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 remarkably similar to the dynamical Kubo mobility and semiquantitatively captures the effects of all types of anharmonicity.

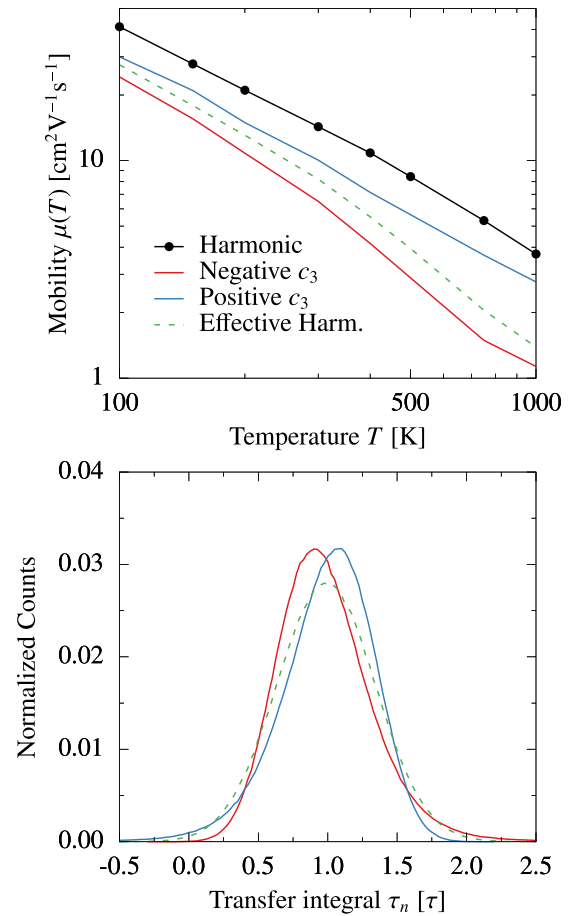


FIG. 5. Static Kubo formula mobility with $\eta = \omega_0/2$ (top) and example distributions of transfer integral τ_n at 500 K (bottom) for an electron coupled to a soft acoustic mode. All distributions in the bottom panel share the same average transfer integral $\langle \tau_n \rangle = \tau$ and 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 $c_3 = \pm 4.65 \text{ eV}/\text{\AA}^3$. Both potentials lead to the same effective harmonic distribution of τ_n and mobility (green dashed lines).

The frequency-resolved AC conductivity calculated by the dynamical Kubo approach with harmonic and anharmonic acoustic phonons is shown on the right-hand side of Fig. 4. With coupling to acoustic phonons, the AC conductivity is significantly different from that 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 for 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 versions of the asymmetric double-well pair potential, leading to acoustic phonon softening: one with $c_3 = -4.65 \text{ eV}/\text{\AA}^3$ (the same one considered so far) and one with $c_3 = +4.65 \text{ eV}/\text{\AA}^3$. 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 τ_n is not present in (strictly dispersionless) optical phonons. This is because u_{n+1} and u_n are uncorrelated, which yields a symmetric distribution for τ_n even for asymmetric potentials. Correlated nearest-neighbor displacements, like those in acoustic phonons, produce an asymmetric distribution of τ_n and thus create the ambiguity demonstrated here.

IV. CONCLUSIONS

We have demonstrated the impact of low-frequency 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 [53,54]. 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], and thermoelectric materials [55,56], perhaps in an *ab initio* framework. Although we do not expect the quantum-classical approaches employed here to work well for high-frequency anharmonicities, their effects are not expected to be significant except at very high temperatures. We are also interested in applying these methods to study nonequilibrium electronic dynamics [57,58], for which we expect the impact of nonperturbative electron-phonon interactions and phonon anharmonicity to be larger.

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