Anharmonic coupling between electrons and TO phonons in the vicinity of ferroelectric quantum critical point.

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We explore a novel coupling mechanism of electrons with the transverse optical (TO) phonon branch in a regime when the TO mode becomes highly anharmonic and drives the ferroelectric phase transition. We show that this anharmonicity, which leads to a collective motion of ions, is able to couple electronic and lattice displacement fields. An effective correlated electron-ion dynamics method is required to capture the effect of the onset of the local electric polarization due to this collective behavior close to the quantum critical point. We identify an intermediate temperature range where an emergent phonon drag may contribute substantially to thermoelectric conductivity in this regime. We find that, under optimal conditions, this extra contribution may be larger than values achieved so far in the benchmark material, PbTe. In the last part we make a case for the importance of our results in the generic problem of anharmonic electron-lattice dynamics.

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Motivated by the search for new efficient renewable sources of energy, a huge experimental effort has been made towards identifying materials with better thermoelectric properties in the recent years. So far, this intense search has been based mostly on a single particle theoretical description of electrons and standard electron-phonon coupling due to displacement potential, supported by numerical ab-initio simulations[1][2]. While this research program has had some notable successes[3] it should be noted that the progress has been slow and so novel pathways are needed. At the same time it has been observed that in several cases good thermoelectrics (TE) are weakly doped semiconductors, such as PbTe[4], SnTe or SrTiO$_3$, that are in the vicinity of a ferroelectric quantum critical phase transition (FE-QCP). It is then natural to ask if it is just a pure coincidence, or whether an yet undiscovered mechanism enhances the Seebeck coefficient.

As the system approaches the FE-QCP, a crucial role is played by the transverse optical (TO) phonons. In the Landau macroscopic framework the TO mode spectral weight is coupled to the material’s electric polarization[5] (the order parameter), so as the FE transition takes place, the TO softening at $q = 0$ indicates the emergence of a uniform displacement and the polar order. The electrons should be susceptible to this dipole ordering and usually the appearance of the FE is accompanied by a disappearance of the electron pockets. Otherwise the remaining free electrons would screen the FE order. A massive softening at the $\Gamma$ point implies that the TO branch emerges as a new family of phonons with a very substantial velocity, often comparable to the one of the longitudinal acoustic (LA) branch[6], and so they certainly contribute to the transport properties of the system.

The assertion about coupling between electrons and the TO phonons is experimentally confirmed in an incipient FE, PbTe, by observation[7] that i) photoexcited electrons do change the TO phonons frequency and ii) in return these TO phonons do modify the electrons’ spectral gap. However, within the Fermi liquid framework it is assumed that the TO phonons are only very weakly coupled with electrons. This is based on the fact that the vector of polarization of the Fermi-liquid and the displacement vector associated with the TO mode are perpendicular to each other[8], which diminishes their coupling, see Fig[1]. Even the most recent ab-initio studies dedicated to PbTe[9][10] conventionally claimed that the TO phonons have the weakest coupling with electrons[11]. This has led to the contradictory conclusion that electron coupling with the TO phonons will play a very minor role close to the FE-QCP. Clearly, the TO coupling must emerge at a collective level, which is not captured in a single particle picture, and there is an obvious demand for theory to uncover the microscopic mechanism. An emergent model of correlated electron-lattice dynamics in a non-adiabatic regime is needed to make an unbiased proof of the energy transfer. This is the key result of this work.

The mechanism of electron-phonon coupling, present close to the FE-QCP, can be illustrated by a phenomenological argument (see Fig[1]). An underlying reason of the TO phonon softening are long-range interactions between lattice vibrations. Such interactions change the character of the ion potential from quadratic to quartic[2] along the line of FE distortion. In second quantization language $\hat{x}_i^\dagger$ translates into phonon-phonon interactions. The TO phonon is not an eigen-state of the lattice oscillations any more, in its motion it is accompanied by a cloud of other low energy phonons[12]. Physically this cloud of co-excited phonons (i.e. their displacements $\Xi_q$) is re-summed into a collective variable, a vector field $\vec{\zeta}(x,t)$ that describes the ordering of the system in the vicinity of the QCP[5][24]. In the FE-QCP case the ordering is equivalent to an electric polarization of the system.
FIG. 1. In the conventional model for coupling between electron and lattice displacements an electron-hole excitation in a Fermi pocket with momentum $k_{el}$ (blue) creates an electric field $\vec{E}_{el}$ while the matching TO mode with momentum $q_{ph}$ (green), $q_{ph} = k_{el}$, moves lattice atoms in a way that induces an electric field $\vec{E}_{ph}$ such that $\vec{E}_{ph} \perp \vec{E}_{el-k} = \vec{E}_{el} = 0$ i.e. negligible coupling. The novel electron-TO phonon-coupling mechanism is possible in the presence of an accompanying lattice distortion described by a generalized collective variable $\xi(x, t)$ (with its direction indicated by an orange dashed line). Inset: A slice of Fermi pocket showing a dispersion $\epsilon(k)$ in the vicinity of the heavy pockets, phonon dispersion($b_{q}$ operators), electron-electron interactions $V_{ee}(k, q)$ and phonon-phonon interactions $U_{ph}(q, q')$. The linear dispersion of fermions with velocity $V_F$ is justified in a narrow energy window (order of a few THz) close to $E_F$. We expect the Fermi surface (FS) to be highly anisotropic, since the FS’s with a high complexity factor is common in TE, with a large effective mass in at least one direction and we study the dynamics along the $x$ direction with the lowest value of $V_F$. The most prominent feature of our system is its proximity to FE-QCP (although on the quantum paraelectric side) and the parameters of the model must reflect this. A sole assumption of a long range nature of $U_{ah}$, needed for FE, suffices to strongly renormalize downwards $\omega_{TO}(q \to 0)$ and induce a large self-energy experimentally detected as broadening – the waterfall effect. For larger $q$ the TO phonons become strongly dispersive and contribute substantially to transport. This is anomalous for this phonon branch and puts it beyond the adiabatic regime. A microscopic theory of pre-formed FE order parameter is derived by re-summing locally the $q \to 0$ vibrations to obtain a vector field of displacement $\vec{\xi}(x, t)$ which is proportional to an emergent polarization. Upon averaging out the low energy $\vec{\xi}_{q \to 0}$, see details, the effective hamiltonian for $T > \omega_{TO}(\Gamma = \tilde{\omega}_0)$ regime reads:

$$H = \sum_k V_F k_c c_k^\dagger + \sum_q \tilde{\omega}_r(q) b_q^\dagger b_q + \sum_{k, q, q'} V_{ee}(k, q) c_k^\dagger c_{k-q}^\dagger c_{q} + \sum_{k, q, q'} F_{el-ph}[k, q; \xi_c(t)][c_k^\dagger c_{q} + b_q^\dagger b_{q'}]$$

where we take linear dispersion for the remaining rapid phonons $\tilde{\omega}_r(q) = c_{ph} q$ and the last two terms, with $g_2 = U_{ah}|_{q \to 0}$ and $F_{el-ph} \sim \xi_c$, are emergent due to the spontaneous symmetry breaking described by $\vec{\xi}(x, t)$. Terms with such an operator content have been derived using a different formalism in Ref. [11]. Here we take $\vec{\xi}(x, t) = \xi_c(t) \varphi(x) \otimes \vec{\xi}$ with a spatial profile $\varphi(x)$ known from QCP decay. The time dependence of the amplitude $\xi_c(t)$ is determined from an anharmonic equation of motion:

$$\dot{\xi}_c(t) + \tilde{\omega}_0 \xi_c(t) + g(\xi_c(t))^3 = 0$$

Here $\tilde{\omega}_0 = \sqrt{K/M} = \min(\tilde{\omega}_r(q))$ and $g = U_{ah}|_{q \to 0}$. The pseudo-spin variable $\tilde{\xi}(t)$, which captures the two possible directions of FE distortion, obeys the Ising-Kondo hamiltonian:

$$H_{\tilde{\xi}} = \sum_q \tilde{g}_2 \tilde{\xi}_z (b_q + b_{q'}^\dagger)$$

(1)

Both Eq’s define analytically solvable theories. In the following, the parameters that enter into Eq (2) are
taken from Refs. 6 and 13 to make a link with a real material, PbTe. The mutual motion of electrons and ions induces energy transfer between the two sub-systems, a central quantity of this study. To capture it we need to go beyond the adiabatic approximation. We then take a non-adiabatic case \( V_F = \epsilon_{ph} \), which supports a maximal drag through vertical electron scatterings, i.e. electrons exchange energy with phonons and still remain available for further scattering events along the “heaviest” axis of the Fermi surface instead of spreading evenly over the entire Fermi surface. The ability to exchange energy with phonons many times maximizes the distortion of occupancies along \( \hat{x} \) (see Fig. 1 inset).

The effective model given by Eq.’s 23 reduces our problem to electrons and phonons interacting with a classical variable whose equation of motion is known. To solve the electron-phonon problem we use a variant of correlated electron-ion dynamics, where the analytic equations of motions for electron and phonon densities are integrated. The set includes the momentums’ correlation, \( \lambda(q,t) \) in 19, which is forced to be decoupled in the adiabatic approximation\[17\], while in our time evolution it follows an unbiased trajectory caused by \( F_{el-ph} \). The simpler, real-space variant of the method, called ECEID\[20\], was proven to be able to capture non-adiabatic case beyond the adiabatic approximation. We then take a central quantity of this study. To capture it we need to take \( \lambda(q,t) \) from Ref.\[6\] and \[13\] to make a link with a real material, PbTe. The mutual motion of electrons and ions induces energy transfer between the two sub-systems, a central quantity of this study. To capture it we need to go beyond the adiabatic approximation. We then take a non-adiabatic case \( V_F = \epsilon_{ph} \), which supports a maximal drag through vertical electron scatterings, i.e. electrons exchange energy with phonons and still remain available for further scattering events along the “heaviest” axis of the Fermi surface instead of spreading evenly over the entire Fermi surface. The ability to exchange energy with phonons many times maximizes the distortion of occupancies along \( \hat{x} \) (see Fig. 1 inset).

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**Electron-TO phonon coupling** The initial state is the thermal equilibrium state \( |\Psi\rangle_T \) with one phonon added (in a given q-mode)\[22\]: \( |\Psi\rangle_i = b_0^\dagger(t = t_0)|\Psi\rangle_T \). We study the expectation values of equal-time fermionic occupations \( \langle c(t,k)c(t,k) \rangle \) and by monitoring their time dependence, as the extra phonon is propagating through the system, we are able to obtain the transferred energy \( \delta E_k = \langle |\Psi\rangle_i | \lambda_k | |\Psi\rangle_i \rangle \sim \delta n_k \) which is equal to the electron-phonon coupling strength.

The results of the calculation are shown in Fig. 2. Our simulations clearly show the presence of electron-phonon coupling — there is an energy transfer due to an extra phonon into the fermionic system. The electronic densities \( \rho_e \) are not constant, their time evolution is defined by high and low frequency oscillations. We are modelling a closed quantum system, so we monitor how the energy is transferred between the available discrete levels. In order to analyse the oscillations we take a Fourier transform of the time dependence. Since the transient state, when phonons are trying to accommodate the extra excitation, is observed only for phonon densities, the spectrum of quasi-stationary \( \rho_e \) reveals the clear separation of energy scales. The high frequencies can now be associated with the difference of discrete energy levels of the harmonic model (with quantized values of momenta) and are broadened by anharmonicity. At low frequencies we observe the most pronounced peak whose energy scale falls close to \( F_{el-ph} \). We interpret this feature as being present due to Rabi oscillations that develop in our closed quantum system that was initially set out of equilibrium.

To explore the quantitative effect of the FE-QCP proximity, we need to find how the parameters in Eq. 3 are changing as the system is moved on the \( T - \delta \) plane (here \( \delta \) is a control parameter e.g. strain). The renormalization group flow of scalar \( \phi^4 \) theory\[23\] is known to give a correct description of the FE-QCP\[24\]\[25\], then we know universal flow of the Gruneisen parameter\[26\] and its relation with the anharmonicity\[27\].

**Transport coefficients** We focus on the Seebeck coefficient which can be expressed in terms of Kubo current-current susceptibilities \( L_{ij}^\sigma \); \( S = L^\sigma/\langle T \rangle \) where \( L^\sigma \) will contain both electronic liquid dissipative part \( L_{el}^\sigma \) and new phonon-drag part \( L_d^\sigma \). As the system approaches the FE-QCP it is known that the electronic resistivity \( (\sim 1/L_{el}^\sigma) \) increases but at the same time the Fermi pockets shrink so the entropy associated with these carriers \( (\sim L_{el}^\sigma) \) also decreases. We then aim to compute the drag component \( L_d^\sigma \) to check if it is able to profit from QCP fluctuations of \( \xi_c \).

From the time evolution of the densities \( \Delta \rho_e(\epsilon_i,t) \) one can extract expectation values of electron and phonon currents and compute cross-correlation functions of currents’ variations. Extra care needs to be taken, since the output of our simulation is a superposition of Floquet states. However, one may argue that the drag effect itself takes place in the presence of unequilibrated state of the phonon distribution \( N_{B}^{(0)} + \Delta N_{B} \). Hence our description captures the experimental situation rather well. We then apply Kubo formalism adapted, by Lehmann representation of currents cross-correlation functions \( \langle j^\ell_{i,j} \rangle \), for the Floquet states\[29\]:
FIG. 2. Response of the fermionic system upon applying a bosonic creation operator in a $q_1 = 1q_0$ mode with energy $1\omega_0$. The calculation is done for discrete bosonic/fermionic modes with energies $E_n = n\omega_0$ (for fermions $\epsilon = E_F \pm E_n$) where $\omega_0$ is the lowest energy of the linear part of TO spectrum (hence around 20% above $\omega_0$), $n \in [1, 5]$. In the top panel the temporal evolution of expectation values of fermions occupancies are shown for each bosonic mode, this is a solution of our EOM. In the bottom panel we show its Fourier transform (on a natural logarithmic scale), hence an effective electron-TO phonon coupling as a function of energy and (fermion’s) momentum.

The result of this procedure is shown in Fig.3. The temporal fluctuations of both densities can produce a net correlation between respective currents, hence the drag effect. The effect becomes more pronounced as the system approaches the FE-QCP, where the QCPs vicinity is parameterized as a function of strain and temperature. The natural unit of thermoelectric conductance is $he/k_B$, natural length-scale is $2\pi/q_0$ and energy unit throughout the calculation is $\omega_0$. By taking $\omega_0^{\text{ph}}|_{\delta=-0.3\%} = 1THz$ it allows us to estimate the amplitude of the effect on a vertical scale. The inset shows the region in the parameter space (grey) where our reasoning applies. PbTe would be located on the right side of the grey zone.

thermoelectric conductance $L_{T,\sigma}^{\text{ph}}$ as the system approaches the FE-QCP, where the QCPs vicinity is parameterized as a function of strain and temperature. The natural unit of thermoelectric conductance is $he/k_B$, natural length-scale is $2\pi/q_0$ and energy unit throughout the calculation is $\omega_0$. By taking $\omega_0^{\text{ph}}|_{\delta=-0.3\%} = 1THz$ it allows us to estimate the amplitude of the effect on a vertical scale. The inset shows the region in the parameter space (grey) where our reasoning applies. PbTe would be located on the right side of the grey zone.

FIG. 3. Thermoelectric conductance $L_{T,\sigma}^{\text{ph}}$ as the system approaches the FE-QCP, where the QCPs vicinity is parameterized as a function of strain and temperature. The natural unit of thermoelectric conductance is $he/k_B$, natural length-scale is $2\pi/q_0$ and energy unit throughout the calculation is $\omega_0$. By taking $\omega_0^{\text{ph}}|_{\delta=-0.3\%} = 1THz$ it allows us to estimate the amplitude of the effect on a vertical scale. The inset shows the region in the parameter space (grey) where our reasoning applies. PbTe would be located on the right side of the grey zone.

The broad importance of this work stems from our method that goes beyond adiabatic approximation – a paradigm, since Born-Oppenheimer work almost a century ago, that has turned out to be insufficient with the advent of theoretical and experimental quantum non-adiabatic and non-equilibrium dynamics. Formally, the adiabatic ansatz means that the Fock spaces for many body bosonic and fermionic states are decoupled into a simple product, which implies that their entropies are additive. In practice, applying the phonon creation operator (in the adiabatic basis) does not alter the many body state of fermions. Our formalism then clearly allows to go beyond this approximation: in Fig.2 we directly observe a change of electronic density of states $\Delta \rho_e$ after $b_q^\dagger |\Psi_G\rangle$. The phonon-induced off-diagonal terms $\langle \Psi_+ |b_q^\dagger |\Psi_G\rangle = t_{+q-G} \neq 0$ are precisely those neglected in the adiabatic approxima-
tion. Our result provides a direct access to a measure of non-adiabaticity in the system and furthermore, through \( \hat{\rho}_e = \hat{\rho}^{(0)} + \Delta \hat{\rho}_e \), all electronic observables can be computed. Here we have chosen to focus on one quantity, the thermoelectric conductivity, which is directly proportional to the entropy transfer between the two subsystems. Furthermore, we choose the simplest model, with a linear coupling to the TO mode (otherwise prohibited in the high symmetry structure) and all other ingredients (critical dynamics, anharmonic motion) obey exact analytical solutions. This is for the sake of transparency, to study a situation where non-adiabatic phenomena manifest particularly clearly.

In conclusion we have shown that close to a FE-QCP strong anharmonic fluctuations of atomic positions, described by a collective variable \( \xi_c \), lead to a new type of coupling between electrons and anharmonic phonons. It is a strong coupling effect that one is able to detect only by going not only beyond the standard adiabatic approximation for electrons but also beyond Ehrenfest dynamics for ionic motion. Our model is applicable in any distortive QCP where electronic polarizabilities are modified. Furthermore we have shown that the coupling through \( \xi_c \) can produce a finite net phonon drag effect, which substantially enhances thermoelectric transport coefficients. A superconducting phase, in an analogue material STO, is present even closer to the QCP and therein the source of a strong electron-TO phonon coupling remains an mystery. A possible extension of this work is to cover this intriguing regime.

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