Resonant electron-lattice cooling in graphene

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Controlling energy flows in solids through switchable electron-lattice cooling can grant access to a range of interesting and potentially useful energy transport phenomena. Here we discuss a unique switchable electron-lattice cooling mechanism arising in graphene due to phonon emission mediated by resonant scattering on defects in crystal lattice, which displays interesting analogy to the Purcell effect in optics. This mechanism strongly enhances the electron-phonon cooling rate, since non-equilibrium carriers in the presence of momentum recoil due to disorder can access a larger phonon phase space and emit phonons more efficiently. Resonant energy dependence of phonon emission translates into gate-tunable cooling rates, exhibiting giant enhancement of cooling occurring when the carrier energy is aligned with the electron resonance of the defect.

In 1946 Purcell discovered that bringing the energies of atoms in alignment with resonances in optical cavities can dramatically enhance the rate of spontaneous emission [1]. One way of understanding the enhancement is provided by Fermi’s Golden Rule that mandates that the transition rate is proportional to the density of final states. The latter is enhanced in a cavity at resonance compared to a free-space density of states, providing means for controlling the light-matter coupling [2,3]. Here we discuss an electron-phonon analog of Purcell effect arising due to phonon emission being resonantly enhanced when carrier energies align with electron resonances at defects. We show that on resonance electrons can emit phonons more efficiently, enhancing the electron-lattice cooling rate and making it gate-tunable.

While this effect is completely generic, we will see that it becomes particularly dramatic in graphene, a material in which energy relaxation pathways of non-equilibrium hot carriers are uniquely sensitive to minute amounts of disorder. In pristine graphene electron cooling is suppressed due to the phonon “momentum surplus” bottleneck for electron-phonon scattering, arising because electron Fermi momentum values are much smaller than the typical momenta of thermal phonons for relevant carrier densities and temperatures. Momentum mismatch greatly constrains the available phase space for momentum-conserving scattering that involves thermal phonons, which leads to a suppression of cooling rates [4,5]. However, theoretical and experimental studies indicate that disorder, through breaking translation symmetry and allowing for momentum non-conserving scattering, relieves the momentum surplus bottleneck and enhances the cooling rates [6]. Microscopically, the enhanced disorder-assisted electron-phonon scattering originates from so-called “supercollisions” in which the excess recoil momentum is being absorbed by the impurity whereas the energy is carried away by a thermal phonon [7,11].

Recently impurity-assisted electron-lattice cooling in graphene was imaged using nanoscale thermometry scanning probe technique [12,13]. It was found that the dominant contribution to cooling arises from resonant scatterers with the energies of the resonances positioned near the Dirac point. It was conjectured that resonant scatterers mediate phonon emission and cooling through the process of trapping band carrier in a localized state (LS) as illustrated in the inset of Fig. 1.

While this picture seems plausible, the study reported in...
Refs. [12, 13] left a number of key questions unanswered, in particular the origin of the resonances and the extent to which resonant scattering can enhance the cooling rates. Below we present a microscopic picture of cooling due to phonon emission mediated by resonant scattering and evaluate the electronic cooling cross-section. The cooling rate is sharply enhanced when the Fermi energy is close to the resonance energy of one the scatterer, turning off quickly when the Fermi level is detuned from the resonance. Disorder-assisted resonant cooling is found to dominate over the intrinsic contribution due to momentum-conserving electron-phonon processes. This, along with the ON/OFF switching behavior seen near the resonance, presents the novel possibility of gate-tunable cooling.

Graphene is known to host a wide variety of atomic-scale defects which can act as resonant scatterers, trapping electrons in quasibound states [14–17]. Ab initio and STM studies [18–20] have shown that quasi-bound states with energies near the Dirac point arise in a robust manner when adatoms or polar groups like H, F, CH$_3$ or OH bind covalently to carbon atoms, transforming the Dirac point. The three terms in Eq. (4) correspond to resonant scattering shown in Fig. 2: (a) - (c), scattering at the defect occurs before, after, and both before and after a phonon emission process. In these processes the excess recoil momentum is absorbed by the defect, opening up a large phase space of final states for phonon emission. Process (c), which describes trapping of a carrier on the localized state followed by phonon emission, gives a dominant contribution to the cooling rate.

Here we shall consider phonon emission by carriers in the presence of such resonant scatterers, assuming that the lattice is at a constant temperature of $T_p$, forming a thermal phonon bath. We show that the resonance in the local density of states gives rise to enhanced phonon emission in a manner similar to how spontaneous photon emission is enhanced by the optical cavity resonances in the Purcell effect. The Hamiltonian is given by a sum of the electron and phonon parts, and the electron-phonon interaction, $H = H_{el} + H_{ph} + H_{el-ph}$, where

$$H_{el-ph} = \sum_{k, p} g \sqrt{\omega_k} b_k^\dagger a_p^\dagger a_p + h.c.$$  
$$H_{el-ph} = \sum_{n, p} g \sqrt{\omega_p} b_p^\dagger a_p + h.c. $$

and the electron Hamiltonian $H_{el}$, describing free carriers and their interaction with the defects, is discussed below. From the above Hamiltonian, we can calculate the energy dissipation rate as

$$P = \sum_{p, p', k} \omega W_{p, p', k}(1 - n') n (N_k + 1) \delta(\epsilon' + \omega - \epsilon)$$

where $n$, $n'$ and $N_k$ are Fermi and Bose distributions for electrons and phonons with momenta $p$, $p'$ and $k$, and with energies $\epsilon = \epsilon_p$, $\epsilon' = \epsilon_{p'}$, and $\omega = \omega_k$ respectively. To calculate the scattering cross-section, we use Fermi’s golden rule:

$$W_{p, p', k} = \frac{2\pi}{\hbar} |M_{p, p', k}|^2$$

where an incoming electron $|p\rangle$ is scattered into the outgoing state $|p'\rangle$, emitting a phonon with momentum $k = p - p'$.

The matrix element $M_{p, p'}$, describing phonon emission in the presence of a defect, can be written as a sum of three terms, corresponding to three different types of scattering shown in Fig. 2

$$M_{p, p'} = |p'\rangle M(k) G_0 |p\rangle$$

where $t$ is the T-matrix for the defect, evaluated at the energies of the in and out states as discussed below, $G_0$ is the bare electronic Green’s function, and

$$M(k) = \langle p', k | H_{el-ph} | p \rangle = g \sqrt{\omega_k} \delta(p - p' - k)$$

is the bare electron-phonon scattering matrix element. The three terms in Eq. (4) correspond to resonant scattering at the defect before, after, and both before and after a phonon emission process.

We will eventually find that the contribution to the cooling rate due to resonant scattering, taken on-resonance, is large compared to the contribution from scattering through processes (a) - (c).
The bare electron propagator is given by
\[ G_0(\mathbf{p}, \epsilon) = \frac{1}{\epsilon - H_0(\mathbf{p}) + i0} \]  
with the free-particle tight-binding Hamiltonian given by a 2 × 2 matrix in the A/B sublattice pseudospin basis
\[ H_0 = \begin{pmatrix} 0 & tf(\mathbf{p}) \\ tf^*(\mathbf{p}) & 0 \end{pmatrix}, \quad f(\mathbf{p}) = \sum_{i=1}^{3} e^{i\mathbf{p}\mathbf{e}_i}. \]  
Here \( \mathbf{e}_i \) are vectors connecting neighboring C atoms and \( t \) is the nearest-neighbor hopping parameter.

To describe resonant scatterers, we introduce diagonal on-site disorder potential \( V(x) = \sum_{j} V_j (1 + \sigma_j) \delta(\mathbf{x} - \mathbf{x}_j) \) with the signs plus and minus corresponding to defects positioned on sites A or B, respectively. Resonant character of this disorder potential becomes prominent in the limit \( V \gg W \), where \( W \approx 6eV \) is the graphene bandwidth. This is evident from the T-matrix, describing the defect potential renormalized by multiple scattering processes. For a single defect, taken without loss of generality on an A site at \( \mathbf{x} = 0 \), T-matrix equals
\[ t(\epsilon) = \frac{\tilde{V}}{1 - V \sum_{\mathbf{p}} G_0(\epsilon, \mathbf{p})} = \frac{\pi \nu_2^2}{\epsilon \ln(W/\epsilon) + \delta} \frac{1 + \sigma_z}{2} \]  
where \( \tilde{V} = \frac{1}{2}(1 + \sigma_z)V \) and \( \delta = \pi \nu_2^3/V \ll W \). The T-matrix has a resonance centered at \( \epsilon_{LS} \approx -\delta/\ln(W/\delta) \), which corresponds to the energy of localized states. The energy of the resonance \( \epsilon_{LS} \) is small, with \( \delta \) parameterizing the detuning from the Dirac point.

When the defect concentration is low and defect potential \( V \) is large compared to \( W \), each defect hosts a single resonance state with energy \( \epsilon_{LS} \) close to the Dirac point, broadened due to hybridization with the states in the Dirac continuum. For a strong defect potential \( V \gg W \) the energy \( \epsilon_{LS} \) is much smaller than the bandwidth \( W \) and it has an opposite sign to that of \( V \). This resonance has a half-width of \( \gamma \approx \pi \delta/(2 \ln(W/\delta)) \), and is thus small when \( \delta \) is small.

The contribution of defect to the single-particle density of states is given by
\[ \frac{1}{\pi} \text{Im} \ t(\epsilon) = \frac{\pi \nu_2^2 |\epsilon|/2}{(\epsilon \ln(W/|\epsilon|) + \delta)^2 + (\pi \epsilon/2)^2} \]  
where we used the identity \( \ln(iW/\epsilon) = \ln(W/|\epsilon|) + i\pi \text{sgn}(\epsilon)/2 \). This expression can be viewed as the density of states of pristine graphene \( \sim |\epsilon| \) modulated by a resonant energy dependence due to the peak. The peak in the energy dependence of \( \text{Im} \ T(\epsilon) \), positioned near the Dirac point, corresponds to the defect resonance state.

Next we proceed to calculate the cooling power spectrum. It will be shown that in realistic regimes the cooling power spectrum is proportional to the defect density of states, with a prefactor that depends on the electron and phonon energy distributions. Heuristically, a resonant scatter traps band electrons on the quasi-bound state found in the previous section, and the energy difference is released to phonons. Due to breaking of translation symmetry by the presence of defects, momentum does not have to be conserved as these defects can absorb recoil momentum from the phonons, thus enlarging the available phase space for the outgoing states. To evaluate the cooling power spectrum, we need to first evaluate the matrix element in Eq. (4).

We will focus on the experimentally relevant regime of electron and phonon temperatures small compared to the resonance energy \( \epsilon_{LS} \) and width \( \gamma = \pi \delta/(2 \ln(W/\delta)) \). In this case, since the change of electron energy is small compared to \( \epsilon_{LS} \) and \( \gamma \), the process is quasi-elastic. Also, at not too low temperatures the phonon momentum values \( \mathbf{k} \) are typically large compared to electron in and out momentum values \( \mathbf{p} \) and \( \mathbf{p}' \), which are of order \( k_F \). This allows us to approximate \( G(\epsilon, p) \sim \pm 1/\sigma e k \). The first two terms of Eq. (4) then combine to give a commutator
\[ -M(k)t(\epsilon) \frac{[\sigma \cdot \mathbf{k}, \sigma_3]}{2k^2} = M(k)t(\epsilon) \frac{i\sigma \times \mathbf{k}}{v k^2} \]  
Here \( M(k) = g \sqrt{\omega_k} \) is the electron-phonon interaction matrix element. The third term in Eq. (4) can be evaluated by integrating the product of two Greens functions over internal electron momenta \( k < q < k_0 = W/v_F \), giving
\[ tG_0M_0G_0t \approx \frac{M(k) 1 + \sigma_3}{2} - \frac{\nu_2^2}{2\pi v_F} \ln \frac{W}{v_F k} \left[ 1 + \frac{\sigma_3}{2} \right] t'(\epsilon) \]  

Summing the three terms in Eq. (4) gives
\[ M_{\mathbf{p}\mathbf{p}'} = M(k) \frac{i\sigma \times \mathbf{k}}{v_F k^2} t(\epsilon) + M(k) \frac{2}{2\pi v_F} \ln \frac{k_0 1 + \sigma_3}{2} - \frac{\nu_2^2}{2\pi v_F} \ln \frac{k_0 1 + \sigma_3}{2} t'(\epsilon) \]  

The two contributions in Eq. (12) can be compared directly by ignoring the matrix structure. Since the process is quasi-elastic, the difference between \( \epsilon \) and \( \epsilon' \) is essential and the second term, which is “more resonant” than the first term, must dominate. To investigate the competition between the two terms in more detail we consider their ratio
\[ \frac{M_1}{M_2} \approx \frac{2s \epsilon \ln \frac{W}{\epsilon} + \delta}{v_F k g T \ln \frac{k_0}{k}} \]  
where \( s \) is the acoustic sound velocity \( s \approx 2 \times 10^4 \text{m/s} \). Since the velocity ratio \( s/v \) is quite small, the second term in Eq. (12) will indeed dominate for the energies near
resonance, $\mu \sim \epsilon_{LS}$ and at not too low temperatures. However, a different behavior is expected for energies away from the resonance, since the second term fall off faster than the first term ($1/e^2$ vs. $1/e$). As a result the first term can win at large enough $\epsilon$. For a crude estimate, taking the detuning from resonance on the order of $\epsilon_{LS}$ we see that the first term becomes relevant when $k_B T \gtrsim (s/v_F) \epsilon_{LS}$. Taking $\epsilon_{LS} \sim 30$ meV gives $T > 5$ K, which is close to the measurement temperature in [12, 13]. This analysis indicates that the second term dominates at resonance, whereas the first term dominates away from resonance.

Next we show that resonant energy dependence of phonon emission translates into a resonant dependence of cooling rate as a function of carrier doping. After plugging the matrix element given in Eq. [12] into the expression for the cooling power spectrum, Eq. [2], and averaging over $\mathbf{p}$ and $\mathbf{p}'$ angles, we find that the contributions of the first and second terms separate whereas the cross terms vanish under trace. To evaluate the second term, we make use of the identity: $\sum_{\mathbf{p}, \mathbf{p'}} = N \int d\epsilon d\epsilon' \nu(\epsilon) \nu(\epsilon')$, where $\nu(\epsilon)$ is the density of states per spin per valley and $N = 4$ is the spin and valley degeneracy, assuming unit area. The energy conservation delta function can be used to evaluate one of the integrals, the other integral can be evaluated by using the quasi-elastic approximation: $\int_{-\infty}^{\infty} d\omega \delta(\epsilon(n(\epsilon) - n(\epsilon - \omega))) \approx -f(\mu) \omega$, where $g(\epsilon)$ is an arbitrary smooth function of $\epsilon$, and the identity $n(\epsilon)(1 - n(\epsilon - \omega)) = N^0(\nu(\epsilon - \omega) - n(\epsilon))$, with $N^0$ being the Bose function evaluated at the electronic temperature. The final integral over $\omega_k$ is of the form

$$\int_{0}^{\infty} d\omega \omega^4(N^0 - N^p) = 24\zeta(5)k_B^5 T^5 (T_e - T_p)$$

where $N^0$ is the Bose function evaluated at the lattice temperature. Putting everything together, we arrive at

$$P_2(\mu) = A(\mu) k_B^5 T^5 (T_e - T_p)$$

for the cooling power per defect. Here $\mu$ is the Fermi energy and

$$A(\mu) = \frac{48\zeta(5)}{\pi^2} \frac{D^2}{\hbar^3 ps^2} \frac{(\pi/2)^4 \mu^2 \ln^2 \frac{h \omega}{k_B T} }{[\mu \ln \frac{W}{|\mu|} + \delta]^2 + \frac{\pi^2}{4} \mu^2 t^2}$$

where $k_p \approx k_B T_e/s$ is the typical momentum of emitted phonon and we used the relation between the electron-phonon coupling constant and graphene deformation potential $g^2 = D^2/2p_s \hbar^2$ with $D \approx 50 \text{meV}$. The quantity $P_2(\mu)$ vanishes in equilibrium as a result of detailed balance, but is non-zero when the system is driven out of equilibrium, as expected. For numerical estimate we use the value $D^2/\hbar^2 ps^2 v_F^2 = 1.86 \times 10^{10} \text{eV}^{-1}$. After scaling Fermi energy by 1 meV and temperature by 1 K, we evaluate the numerical factors to obtain

$$P_2(\mu) = \frac{\mu^2 \ln^2 \frac{h \omega}{k_B T} (T_e - T_p) |\text{meV}|^2}{[\mu \ln \frac{W}{|\mu|} + \delta]^2 + \frac{\pi^2}{4} \mu^2 t^2} [\text{1K}^5] \times 260 \text{fW.}$$

This contribution peaks near the resonance energy, falling off as $1/\mu^2$ at large detuning.

The contribution of the first term in Eq. [12] can be evaluated in a similar manner, giving

$$P_1(\mu) = 9.62 \frac{g^2 k_B^3 (T_e^3 - T_p^3)}{2h^3 v_F^2} \nu(\mu) \frac{\nu(\mu)|t(\mu)|^2}{\mu^2}$$

where $\nu(\mu) = |\mu|/2\pi h^2 v_F^2$ is the density of states. After scaling Fermi energy by 1 meV and temperature by 1 K this expression becomes

$$P_1(\mu) = \frac{\mu^2 (T_e^3 - T_p^3)}{(\mu \ln \frac{W}{|\mu|} + \delta)^2 + \frac{\pi^2}{4} \mu^2 t^2} \times 0.28 \text{fW}$$

The total cooling rate per defect is then given by $P(\mu) = P_1(\mu) + P_2(\mu)$.

It is instructive to compare the cooling rates due to resonant scattering with the intrinsic contribution of pristine graphene[4, 5]. The cooling power per unit area due to momentum-conserving processes is given by $P_0(\mu) = B(\mu) k_B (T_e - T_p)$, with $B(\mu) = \pi N_h g^2 \hbar^2 (\mu) k_F^3 s^2$. The numerical factors can be evaluated to give

$$P_0(\mu) = 9.2 \times 10^{-3} (T_e - T_p) \mu^4 [\text{1K}][\text{1meV}]^4 \text{fW} \mu \text{m}^{-2}$$

To compare $P_0(\mu)$ to the resonant scattering contribution, Eq. [17], we choose a value for the defect concentration $n_d \approx 10^3 \text{m}^{-2}$. In Fig. [4] we plot the quantity

$$P(\mu) = P_0(\mu) + n_d (P_1(\mu) + P_2(\mu))$$

for three different values of $\epsilon_{LS}$, and with the parameters $\ln(k_0/k_p) = 5.6$, $T_e = 5.2$ K, $T_p = 4.2$ K. Experimental curve from [13] is plotted in Fig. [1] for comparison (not to scale). The data is consistent with the theoretical prediction for $\epsilon_{LS} \approx -22$ meV. The sharp peaks near $\epsilon_{LS}$ come from the contribution of $P_2$ while $P_1$ affects the tails of the peak. The intrinsic contribution $P_0$ is smaller than that of the defects at all energies shown in Fig. [4]. More significantly, the resonant peak in the local density of states of the defects translates into a peak in the cooling rate as a function of carrier density.

The sharp peak in $P(\mu)$ near $\epsilon_{LS}$ results in switching of electron cooling on and off through precise tuning of Fermi energy. In direct analogy with how the Purcell effect is used to control photon emission in optics, resonantly enhanced phonon emission, occurring around the localized defects, can be used to control cooling. One can envision the design of specific cooling pathways and, through defect engineering, developing new approaches to control heat flow in nano-systems.
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