Unifying explanation for carrier relaxation anomaly in gapped systems

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We develop a theory to describe energy relaxation of photo-excited carriers in low-temperature ordered states with band gap opening and formulate carrier relaxation time \( \tau \) near and below transition temperature \( T_c \) by quantifying contributions from different carrier-phonon scatterings to the relaxation rate. The theory explains anomalous experimental observations of \( \tau \) in gapped systems. Transverse acoustic (TA) phonon modes play a crucial role in carrier relaxation; their heat capacity determines \( \tau \)-divergence near \( T_c \). The theory is validated by fitting \( \tau \) of fullerene polymers onto a theoretical curve.

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The nonequilibrium dynamics of photo-excited carriers in solids has attracted considerable research interest in the field of condensed matter physics. These dynamics are governed by multiple scatterings of carriers and energy transfer to the phonon field, both of which are quantified by the carrier relaxation time \( \tau_{\text{exp}} \) and its temperature \( (T) \) dependence. Usually anomalous \( T \)-dependence of \( \tau_{\text{exp}} \) is observed in many gapped systems, for example, phase-ordered systems showing an energy gap opening in the electron band below the transition temperature \( T_c \). It has been found that a wide variety of superconductors \[1\,\text{[12]}\] and density-wave compounds \[13\,\text{[19]}\] show diverging behavior of \( \tau_{\text{exp}} \) near \( T_c \), as confirmed by femtosecond time-resolved optical spectroscopy \[1\,\text{[4, 5, 7–17, 19]}\]. The divergence of \( \tau_{\text{exp}} \) in these gapped systems is believed to result from recursive energy transfer between electrons and phonons. Photo-excited electrons having high energy emit a number of phonons through relaxation from above to below the energy gap. Conversely, relaxed electrons can be re-excited above the gap by absorbing phonon energy. This phonon emission-reabsorption process becomes efficient near \( T_c \) because of the small gap energy, and thus, it suppresses the relaxation of carriers, extending \( \tau_{\text{exp}} \) significantly. This anomalous phonon-mediated relaxation in gapped systems is called the phonon bottleneck effect. This bottleneck enables the reproduction of these experimental observations of \( \tau_{\text{exp}} \) in various gapped systems that exhibit \( \tau_{\text{exp}} \)-divergence at \( T_c \).

In this Letter, we develop a theory of photo-excited carrier relaxation dynamics with the objective of resolving the above-mentioned issues. We postulate that the lack of \( \tau_{\text{exp}} \)-divergence even in gapped systems can be ascribed to the presence of transverse acoustic (TA) phonon modes. Further, we state that an ensemble of TA modes in gapped systems serves as a high-capacity thermal sink, and energy release to the sink from other phonon modes facilitate efficient cooling of carriers, in other words, a significant reduction in \( \tau_{\text{exp}} \) close to \( T_c \). The proposed theory is validated by the quantitative agreement with experimental data of \( \tau_{\text{exp}} \) for peanut-shaped \( C_{60} \) polymers, a typical charge density wave (CDW) material that does not show any carrier relaxation anomalies.

First, we briefly review the conventional bottleneck concept for \( \tau_{\text{exp}} \)-divergence. It is based on the assumption that photo-excited carrier relaxation in gapped systems is regulated by the anharmonic slow decay of phonons \[1\,\text{[20]}\]. By the absorption of a pump laser photon, electrons in the valence band are excited far above the initial states, and they rapidly accumulate in the upper end of the gap through carrier-carrier and carrier-phonon interactions. Then, the carriers emit high-energy phonons (HEPs) whose energies are higher than the gap width \( 2\Delta \) to relax into the lower end of the gap. The HEPs produced can be reabsorbed to create new carriers above the gap [see Fig. 1(a)] or they can decay in an anharmonic manner into low-energy phonons (LEPs) that no longer excite carriers because their energy is lower than \( 2\Delta \) [see left-hand side panel in Fig. 1(b)]. If the reabsorption probability per unit time is much larger than the inverse of the anharmonic decay time (\( \tau^{-1} \)), photo-excited carriers and HEPs settle in nearly steady states that obey the Fermi and Bose distribution functions, respectively, with temperature \( T' \) that is higher than the lattice temperature \( T \). Meanwhile, LEPs obey the Bose distribution function with \( T \), because they remain unperturbed after the laser pulse incident. Consequently, the carrier relaxation is dominated by the energy transfer from HEPs to LEPs, that is, \( \tau_{\text{exp}} \simeq \tau \), which is described
with $\omega$ three-phonon scattering processes through which HEPs dissipate. Here, $\omega$ TA modes are considered. Only the scatterings that involve TA modes are relevant to the lack of divergence in $\tau$. (c) Phonon density of states of TA modes with cutoff frequency $\Omega_{TA}$, and those of LA modes with $\Omega_{h}$. The maximum frequency of the LEP is $\Omega_{l}$ (see text for its definition).

by the time evolution of the two temperatures, that is, $T' = T'(t)$ and $T = T(t)$.

It should be emphasized that in the conventional bottleneck concept, only longitudinal acoustic (LA) phonon modes are considered. Here, we point out the unnoticed but important role of TA phonon modes in the HEP’s decay [see right-hand side panel in Fig. 1(b)]. Because TA phonon modes generate no density modulation in the lattice, they cannot interact with photo-excited carriers within the deformation potential theory. This fact implies that TA modes serve as a thermal receiver into which HEPs dissipate, as a result of which the $\tau$-divergence vanishes even at $T_c$. Below, we prove that this holds true in certain gapped systems.

To formulate the anharmonic decay time $\tau$ of HEPs, we consider the time evolution of the phonon distribution function. Following the above discussion, we divide phonon excitations into two groups. One group consists of HEPs ($\Omega_{l} < \omega_{q,LA} < \Omega_{h}$) in equilibrium temperature at $T'$ that can participate in the reabsorption process. The other group involves TA modes ($\omega_{q,TA} < \Omega_{TA}$) and LEPs [$\omega_{q,LA} < 2\Delta/\hbar (\equiv \Omega_{l})$] in equilibrium at $T$ that do not participate in the reabsorption process. Here, $\omega_{q,TA}$ and $\omega_{q,LA}$ represent the phonon dispersion relations, where $q$ is the wavevector. $\Omega_{h}, \Omega_{l}$, and $\Omega_{TA}$ are the cutoff frequencies for the HEP, LEP, and TA modes within the Debye approximation, respectively. The distribution functions for the two groups are given by

$$n(\omega_{q,j}) = \left[ \exp \left( \frac{\hbar \omega_{q,j}}{k_B T} \right) - 1 \right]^{-1},$$

with an appropriate variable $x = T$ or $T'$.

The rate of change in $n(\omega_{q,j})$ due to phonon-phonon collisions is written as [21]

$$\frac{\partial n(\omega_{q,j})}{\partial t} = J_{col}[n(\omega_{q,j})].$$

The collision integral $J_{col}[n(\omega_{q,j})]$ describes three-phonon scattering, and it is defined by

$$J_{col}[n(\omega_{0})] = \frac{2\pi}{\hbar N^2} \sum_{q_1,q_2,j_1,j_2} |w_{i\rightarrow f}|^2 \left( \frac{1}{2} S_A + S_B \right),$$

where

\begin{align}
S_A &= \{ [n(\omega_0) + 1]n(\omega_1)n(\omega_2) - n(\omega_0)[n(\omega_1) + 1][n(\omega_2) + 1] \} \delta(\omega_0 - \omega_1 - \omega_2), \\
S_B &= \{ [n(\omega_0) + 1][n(\omega_1) + 1]n(\omega_2) - n(\omega_0)n(\omega_1)[n(\omega_2) + 1] \} \delta(\omega_2 - \omega_0 - \omega_1). \tag{5}
\end{align}

Here, $\omega_s (s = 0, 1, 2)$ is an abbreviation of $\omega_{q,j_s}$, and $w_{i\rightarrow f}$ is the matrix element between the initial and the final state [22].

Note that $J_{col}$ regulates the time evolution of the total energy through the relationship

$$\frac{\partial}{\partial t} (E_{LA} + E_{TA}) = \sum_{q(LA)} \hbar \omega_{q,LA} J_{col} + \sum_{q(TA)} \hbar \omega_{q,TA} J_{col},$$

where the first and second summations on the right-hand side run over $q$s satisfying $0 < \omega_{q,LA} < \Omega_{l}$ and $0 < \omega_{q,TA} < \Omega_{TA}$, respectively. The energy $E_j$ is defined by

$$E_j = \sum_{q(j)} \hbar \omega_{q,j} n(\omega_{q,j}) \int_0^y \hbar \omega n(\omega) \rho_j(\omega) d\omega,$$

where $y = \Omega_{TA}(\Omega_{l})$ for $j = TA$ (LA). $\rho_j$ is the density of states defined by

$$\rho_j(\omega) = \alpha_j \omega^2 \theta(z - \omega), \quad \alpha_j = \frac{3\nu_j N}{z^3 \sum \nu_j'},$$

where $z = \Omega_{TA}(\Omega_{h})$ for $j = TA$ (LA), $\nu_{j'}$ is the number of phonon branches participating in the three-phonon
scattering, \(N\) is the number of unit cells, and \(\theta\) is the Heaviside step function; the total density of states is given by \(\rho = \rho_{TA} + \rho_{LA}\) [see Fig. 1(a)], satisfying the normalization condition \(1 = \int \rho(\omega) d\omega / N\). The Debye approximation we have used in Eq. (5) is valid when \(k_B T < \hbar \Omega_{TA}(< \hbar \Omega_h)\), which holds for many gapped systems below \(T_c\). We simplify \(n(\omega)\) in Eq. (7) as \(k_B T / \hbar \omega\) [1] to obtain \(E_j = C_j T\), where \(C_j = k_B C_j \gamma_j^3 / 3 \) \((k_B\) is the Boltzmann constant). In addition, we focus on the fact that each sum in Eq. (6) gives a non-zero value only when \(I_{TA}\) is attributed to the reduced phonon population, \(\Delta\) decreases at \(T_c\). This result implied the possibility of \(\Delta\) to \(0\), \(I_{LA}\) vanishes (irrespective of \(p\)) but \(I_{TA}\) converges to a finite value as long as \(p \neq 0\). Therefore, we obtain a non-diverging \(\Delta\) at \(T_c\) if \(p \neq 0\), which readily follows from Eq. (9). When \(p = 0\), on the other hand, \(I_{TA} \sim 0\) for arbitrary \(T\) (because \(I_{TA} \sim \omega^2\); see Eq. (12)). In this case, \(I_{LA} = I_{TA} \sim 0\) at \(T_c\) so that \(\tau \rightarrow \infty\) at \(T_c\). We thus conclude that the anharmonic decay of HEPs to TA modes plays a prominent role in the efficient cooling of HEPs as well as in determining the significance of the \(\Delta\)-divergence at \(T_c\).

Upon reducing the temperature to zero, the energy dissipation of HEPs gradually reduces due to monotonic decreases in \(I_{LA}\) and \(I_{TA}\) [see Fig. 2(c)]. The decrease in \(I_{LA(TA)}\) is attributed to the reduced phonon population, which results in a monotonic increase in \(\Delta\) at low \(T\), as shown in Fig. 2(a). A similar increase has been found in various gapped systems [2, 3, 10, 12, 13, 14], and it is attributable to the inefficient cooling of HEPs.

Now, we apply the proposed theory to photo-excited carrier relaxation in quasi one-dimensional C\(_{60}\) polymers. It was previously observed in experiments [22] that the C\(_{60}\) polymers undergo the CDW transition [22] at \(T_c = 60K\), forming a well-defined energy gap at the Fermi level. This result implied the possibility of the \(\Delta\)-divergence at \(T_c\) to \(60K\); nevertheless, optical pump-probe investigations [18] of the C\(_{60}\) polymers revealed a monotonic variation in \(\tau_{\text{exp}}\) near \(T_c\), whose origin has yet to be clarified. This problem is solved by considering that the twisting phonon modes of the C\(_{60}\) polymer [20] play the same role as the above-described TA modes. Figure 3 shows the numerical reproduction (indicated by lines) of the experimental data [18] (indicated by circles) of the \(T\)-dependent \(\tau_{\text{exp}}\) of the C\(_{60}\) polymers. An over-


all agreement between the theory and the experiments is obtained by assuming $p \sim 0.3$. The other parameters we used are $\Omega_{TA} = 220$ cm$^{-1}$, $\Omega_p = 360$ cm$^{-1}$, and $2\Delta(0) = 360$ K; the first two values were estimated from the phonon model for 1D C$_60$ polymers [26], and the last value gives $2\Delta(0)/k_BT_c = 6$ consistent with many CDW compounds [27].

The generality of Eq. (10) is of great importance. It is applicable to $\tau_{\text{exp}}$ in other gapped systems such as TI-based cuprate superconductors [2, 6] and the solid fullerenes K$_3$C$_{60}$ and Rb$_3$C$_{60}$ [3]. Even these materials show a lack of $\tau_{\text{exp}}$-divergence; however, no theoretical studies have attempted to clarify their relaxation anomalies. We believe that the proposed theory will serve as a unified framework for nonequilibrium carrier dynamics in gapped systems.

In conclusion, we have developed a theory to describe the energy dissipation from HEPs ($\hbar\omega_{q,LA} > 2\Delta$) to LEPs ($\hbar\omega_{q,LA} < 2\Delta$) and TA modes in gapped systems below $T_c$. This theory enables the evaluation of the $T$-dependence of $\tau$ as a function of the coupling strength $p \equiv w_2/w_1$ between the HEPs and the TA modes, and it explains the crossover between the diverging and the non-diverging behaviors of photo-excited carrier relaxation. The latter behavior can quantitatively account for the anomalous carrier relaxation time in C$_60$ polymers, as measured by recent pump-probe laser experiments. The coupling between the HEPs and the TA mode also suggests the variation of $\tau_{\text{exp}}$-divergence in typical gapped systems.

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[22] For example, the first term in the curly brackets in Eq. (5) implies that one phonon with $\omega_0$ decays into two phonons with $\omega_0$ and $\omega_1$.
[23] In the calculation, we assume that $T'$ is fixed [that is, $T'(0) \approx T'(\infty)$] in order to derive the analytical expres-
sion of $\tau$. A similar assumption has been used in Ref. [1] for the case of the absence of the TA mode.

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