Exciton-phonon relaxation bottleneck and radiative decay of thermal exciton reservoir in two-dimensional materials

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We study exciton radiative decay in a two-dimensional material, taking into account large thermal population in the non-radiative states, from which excitons are scattered into the radiative states by acoustic phonons. We find an analytical solution of the kinetic equation for the non-equilibrium distribution function of excitons in the radiative states. Our estimates for bright excitons in transition metal dichalcogenides indicate a strong depletion of radiative state population due to insufficient exciton-phonon scattering rate at low temperatures.

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I. INTRODUCTION

Exciton radiative decay in two-dimensional structures was first studied for excitons in molecular crystals [1, 2]. Later, it attracted much attention in the context of excitons in semiconductor quantum wells, whose fabrication became possible due to progress in semiconductor growth techniques [3–9]. The recent intense studies of monolayer transition metal dichalcogenides (TMDCs) have lead to a revival of research activity in the radiative dynamics of two-dimensional excitons, both experimental [10–23] and theoretical [22, 24–28].

In clean samples, the in-plane momentum $p$ is conserved during the photon emission. Then, only excitons with small momenta $p \sim \hbar \omega_{\text{ex}}/c$ can emit photons (here $\omega_{\text{ex}}$ is the excitonic resonance frequency and $c$ is the speed of light). The subsequent dynamics of the excitonic population and of the emitted light strongly depends on the exciton distribution over different momentum states. If the population was created by a resonant optical excitation, it is initially concentrated in the radiative region, so the excitons can quickly decay before being scattered into the non-radiative states. For a non-resonant optical excitation (excitation energy high above $\hbar \omega_{\text{ex}}$), or electrical pumping (excitons produced by binding free carriers injected electrically), the excitons may have time to thermalize before decaying. Sometimes, both contributions may be seen in photoluminescence [12, 14, 21].

If the excitons have thermalized, the excitonic population extends over a region of momenta, determined by the temperature $T$, usually much wider than the radiative region. Then, to relax the whole population, excitons from the non-radiative states must be scattered to the radiative region (Fig. 1), so radiative decay of a thermal excitonic population takes much longer than the recombination time $1/\Gamma_p$ of a radiative state with small momentum $p$. If the scattering is fast enough, the exciton distribution remains thermal, so the population decay rate is given by the simple thermal average of $\Gamma_p$, proportional to $1/T$ [6]. However, scattering typically slows down at low temperatures, which results in a depletion of the radiative region, so the overall population decay rate is slower than the thermal average. Numerical solution of the Boltzmann equation for excitons scattered by acoustic phonons in a GaAs quantum well has shown the importance of this relaxation bottleneck effect [29, 30].

In this paper, we revisit the problem of competition between the exciton radiative decay and the scattering by acoustic phonons, assuming the latter to be the dominant source of scattering. We do not include scattering by optical phonons, assuming the excitonic temperature to be much lower than the optical phonon energy. We also assume the exciton density to be sufficiently low, so that exciton-exciton scattering and annihilation is inefficient. We consider a clean undoped sample, so exciton scattering by impurities and free carriers can also be neglected. Under these conditions, acoustic phonons can dominate the exciton scattering.

Below, we show that the Boltzmann equation describ-
ing the exciton radiative decay and scattering by acousti-
cal phonons has a remarkably simple analytical solution, 
whose validity is guaranteed by the same separation of 
momentum scales that creates the problem: the large 
width of the excitonic thermal distribution as compared 
to that of the radiative region. This makes the exciton 
distribution in the non-radiative reservoir insensitive to 
what happens in the radiative region, and enables us to 
find the overall population decay rate in the bottleneck 
regime [Eqs. (6) and (14a), for $\Gamma_p$ being smaller or larger 
than the typical phonon frequency, respectively]. Applying 
our results to bright excitons in TMDCs, we find a 
strong bottleneck effect, leading to nanosecond popu-
lation decay times at $T \sim 10 - 100$ K (neglecting non-
radiative decay).

II. SINGLE EXCITON BAND

We start by considering the simplest case of a non-
degenerate exciton band with the mass $m_{ex}$ and the 
parabolic dispersion $\hbar \omega_{ex} + p^2/(2m_{ex})$, weakly 
coupled to two-dimensional acoustic phonons and to three-
dimensional phonons. At times longer than the dephas-
ing time, the coherent polarization can be neglected, and 
the exciton population can be characterized by the mo-
mementum distribution function $f_p$. Its time evolution 
is described by the kinetic equation:

$$\frac{\partial f_p}{\partial t} = -\Gamma_p f_p + I_{\text{in}}^p - I_{\text{out}}^p.$$  \hspace{1cm} (1)

Here $\Gamma_p$ is the exciton radiative decay rate, non-zero for 
momenta $p < \hbar k_{rad} \equiv (\sqrt{\varepsilon} \omega_{ex}/c)$, where $\varepsilon$ is the dielectric 
constant of the medium surrounding the excitonic layer, 
for simplicity assumed to be the same on both sides of 
the layer. We neglect non-radiative exciton decay, which 
can be straightforwardly incorporated. The last two terms in 
Eq. (1), $I_{\text{in}}^p$ and $I_{\text{out}}^p$, represent the in- and out-scattering 
parts of the exciton-phonon collision integral. Assuming 
$f_p$ to be non-degenerate, we write them as

$$I_{\text{in}}^p = \int \frac{d^2p'}{(2\pi\hbar)^2} W_{p' \rightarrow p} f_{p'},$$ \hspace{1cm} (2a)

$$I_{\text{out}}^p = \int \frac{d^2p'}{(2\pi\hbar)^2} W_{p \rightarrow p'} f_p \equiv \frac{f_p}{\tau_p}.$$ \hspace{1cm} (2b)

Here $W_{p' \rightarrow p}$ is the rate of exciton scattering from 
the state $p$ to the state $p'$, due to phonon absorption 
or emission. It includes the energy-conserving $\delta$ function, 
$\delta(p^2/(2m_{ex}) - (p')^2/(2m_{ex}) + u_s |p - p'|)$, where $u_s$ is the 
speed of sound. In Eq. (2b), we also defined the out-
scattering time $\tau_p$. We assume the phonons to be always 
in equilibrium with temperature $T$ (here and below mea-
sured in energy units), then the rates in Eqs. (2a), (2b) 
satisfy the detailed balance condition, $W_{p' \rightarrow p}/W_{p \rightarrow p'} = e^{(p' - p)/\tau_p}/T$. Then, the collision integral is nullified by the 
Maxwell-Boltzmann distribution,

$$f_{eq} = \frac{2\pi \hbar^2 n_{ex}}{m_{ex} T} e^{-p^2/(2m_{ex} T)},$$ \hspace{1cm} (3)

where $n_{ex} = \int f_p d^2p/(2\pi\hbar)^2$ is the total exciton density.

Generally, there are several ways to use the kinetic 
equation (1) to study relaxation kinetics. (i) One can 
take some initial condition $f_p(t = 0)$ and study its sub-
sequent evolution. (ii) One can look for stationary solu-
tions of Eq. (1), which must be supplemented by an 
exciton generation term. The explicit form of this gener-
ation term would be strongly dependent on the specific 
experimental situation, and we prefer to assume that ex-
citation has been performed in the past, and the excitons 
have had enough time to thermalize. (iii) One can look 
for decaying solutions of the form $f_p(t) = f_p e^{-\gamma t}$, where $-\gamma$ is an eigenvalue of the right-hand side of Eq. (1), 
which is a linear integral operator. Generally, this op-
erator has several eigenvalues, and we are interested in 
the smallest one (by the absolute value). It will also domi-
nate the solution of the initial value problem (i) at long 
times, and can be called the effective decay rate. Thus, 
in the following we will focus on problem (iii), and look 
for the effective decay rate $\gamma$.

The central question is how much the distribution in 
the radiative region is different from the equilibrium one. 
This distribution is determined by three processes: (i) ex-
citon radiative decay, (ii) exciton scattering from the 
radiative region to the non-radiative states with $p > \hbar k_{rad}$ 
by phonon absorption, and (iii) exciton scattering from 
the non-radiative states to the radiative region by phonon 
emission. The momenta $p'$ of the relevant states in the 
non-radiative region are fixed by the energy conservation:

$$\frac{(p')^2}{2m_{ex}} = \frac{p^2}{2m_{ex}} \pm u_s |p - p'|.$$ \hspace{1cm} (4)

For $p$ in the radiative region, we have $p \ll p'$, only the 
“$+$” sign is allowed, so $p'$ must lie in a narrow circular 
strip $|p'| - 2m_{ex} u_s |< \hbar k_{rad}$. It is only from this strip that 
excitons can scatter into the radiative region.

In turn, from which states can excitons be scattered 
to the circular strip? If $|p'| = 2m_{ex} u_s$, the set of all 
momenta $p'$ satisfying the energy conservation condi-
tion (4) forms a contour shown in Fig. 2 by the dashed 
line. Crucially, most of the contour lies outside the ra-
diative region. Thus, the population of exciton states 
in the strip $|p'| - 2m_{ex} u_s |< \hbar k_{rad}$ is determined by ex-
changing excitons with states in a broad energy interval, 
determined either by the largest allowed phonon energy, 
$4m_{ex} u_s^2$, or by the temperature $T$, whichever is smaller. 
In either case, this cutoff energy is much larger than that of 
the radiative window, $(\hbar k_{rad})^2/(2m_{ex})$. Thus, even 
if one sets $f_p = 0$ in all the radiative region (the ex-
treme case of very fast radiative decay), the effect on $f_p'$ 
in the strip $|p' - 2m_{ex} u_s |< \hbar k_{rad}$ is small by a factor 
$k_{rad}/\min \{\sqrt{m_{ex} T},m_{ex} u_s \} \ll 1$. Therefore, for $p$ in 
the radiative region, $f_{\text{in}}^p$ can be evaluated using $f_{eq}^p$. This is 
the key observation that enables us to solve the problem.

Then, looking for a solution $f_p(t) = f_p e^{-\gamma t}$ and setting 
$\partial f_p/\partial t = -\gamma f_p$ in Eq. (1), we readily find the exciton
distribution in the radiative region,

\[ f_p = \frac{I_p^{\text{in}}}{\gamma + \Gamma_p + 1/\tau_p}, \quad (5) \]

where \( I_p^{\text{in}} = A^{q\text{in}}/\Gamma_p \) is fixed by the detailed balance condition. Furthermore, in the radiative region we can neglect the momentum dependence of \( f_p^{\text{in}} \) and \( \tau_p \approx \tau_0 \). Then, integrating over \( p \), we obtain the following simple expression for the effective decay rate:

\[ \gamma = \frac{2\pi\hbar^2}{m_{\text{ex}}T} \int \frac{d^2p}{(2\pi\hbar)^2} \frac{\Gamma_p}{1 + \Gamma_p \tau_0 + \gamma \tau_0}. \quad (6) \]

In fact, \( \gamma \tau_0 \) in the denominator can be safely neglected, since from Eq. (6) it follows that \( \gamma \tau_0 \approx \hbar^2 k_{\text{rad}}^2/(2m_{\text{ex}}T) \). Since \( \tau_p \approx \tau_0 \) in the thermal region of momenta, the condition \( \gamma \tau_p \ll 1 \) is also satisfied, which justifies that the distribution at \( p > \hbar k_{\text{rad}} \) is thermal. Thus, these states indeed act as a quasistationary reservoir, from which the population is supplied to the radiative region. If the exciton-phonon relaxation is not fast enough, \( 1/\tau_0 \ll \Gamma_p \), then \( \Gamma_p \) drops out of Eq. (5), and the overall decay rate is governed by the exciton-phonon relaxation bottleneck.

In the following, we use the standard expressions for the radiative decay rates of the longitudinal and transverse excitons [6 32],

\[
\begin{align*}
\Gamma_p^L &= \Gamma_0^{\text{vac}} \theta(\varepsilon h^2 \omega_{\text{ex}} - c^2 p^2) \frac{\sqrt{\varepsilon h^2 \omega_{\text{ex}} - c^2 p^2}}{\varepsilon h \omega_{\text{ex}}} , \quad (7a) \\
\Gamma_p^T &= \Gamma_0^{\text{vac}} \theta(\varepsilon h^2 \omega_{\text{ex}} - c^2 p^2) \frac{h \omega_{\text{ex}}}{\sqrt{\varepsilon h^2 \omega_{\text{ex}} - c^2 p^2}} , \quad (7b)
\end{align*}
\]

where \( \Gamma_0^{\text{vac}} \) is the parameter characterizing the exciton-phonon coupling strength, determined by the excitonic transition dipole moment. Then, the integral in Eq. (6) can be straightforwardly evaluated:

\[
\begin{align*}
\gamma^L &= \frac{(\hbar \omega_{\text{ex}})^2}{m_{\text{ex}}c^2 T} \Gamma_0^{\text{vac}} \sqrt{\varepsilon} \mathcal{F}_L \left( \frac{\tau_0(T)}{\sqrt{\varepsilon}} \right) , \quad (8a) \\
\mathcal{F}_L(x) &= \frac{1}{2x} - \frac{1}{x^2} + \ln(1 + x) , \quad (8b) \\
\mathcal{F}_T(x) &= 1 - x \ln \left( 1 + \frac{1}{x} \right) , \quad (8c)
\end{align*}
\]

where we included explicitly the temperature argument of \( \tau_0(T) \), to emphasize that it determines the temperature dependence of \( \gamma \), together with the prefactor \( 1/T \).

The dependence \( \tau_0(T) \) is determined by the specific exciton-phonon coupling mechanism. We assume the main mechanism to be the deformation potential arising from the difference between conduction and valence band shifts under a local deformation of the crystal. We neglect the piezoelectric potential, which is due to the macroscopic electric polarization created by the deformation. Indeed, as the exciton is overall neutral, it can couple to an electric field only in the second order (Stark effect). For the deformation potential, we take a simple form assuming the phonons to be two-dimensional, with wave vectors \( q \) much smaller than the exciton radius:

\[
\hat{V}(r) = (D_c - D_v) \sum_q \sqrt{\frac{\hbar q}{2\rho S \rho_s}} (\hat{b} + \hat{\rho}^\dagger_q) e^{iqr} , \quad (9)
\]

where \( D_{c,v} \) is the deformation potential for the conduction/valence band, \( \rho_s \) and \( S \) are the surface mass density and the total area of the excitonic layer (so that \( \rho S \) is the sample mass), and \( \hat{b}, \hat{\rho}^\dagger_q \) are the creation and annihilation operators for a longitudinal acoustic phonon with wave vector \( q \). The Fermi Golden Rule gives the following phonon absorption rate [4 33]:

\[
\frac{1}{\tau_0} = \frac{2(D_c - D_v)^2 m_{\text{ex}}}{\rho \hbar^2 (\varepsilon h^2 u_{\text{ex}}^2/2T - 1)} \approx A \frac{T}{h} \quad (T \gg m_{\text{ex}} u_{\text{ex}}^2) , \quad (10a)
\]

\[
A \equiv \frac{(D_c - D_v)^2 m_{\text{ex}}}{\rho \hbar^2 u_{\text{ex}}^2} . \quad (10b)
\]

Eq. (10a), in combination with Eqs. (8a)–(8c), determines the temperature dependence of the radiative relaxation rate for the whole exciton population, both in the regime of full thermalization, \( 1/\tau_0 \gg \Gamma \), and for strong depletion of the radiative zone due to relaxation bottleneck, \( 1/\tau_0 \ll \Gamma \), which inevitably sets in at low temperatures.

In semiconductor quantum wells, the simple model used so far needs several modifications. The most important one is that while the exciton motion is confined to two dimensions, the phonons are three-dimensional, so their wave vector has also a perpendicular component \( q_z \) in addition to the in-plane \( q \). Also, one often has to take into account the finite values of the exciton radius \( a_{\text{ex}} \) and of the quantum well thickness \( d_{\text{QW}} \). The electron-phonon matrix element then also includes factors which
vanish for large \( q \gg 1/a_{\text{ex}} \) and \(|q_z| \gg 1/d_{QW} \) [34]. For most III-V and II-VI semiconductors, such as GaAs or ZnSe, the heavy-hole exciton mass \( m_{\text{ex}} \sim m_0 \), the free electron mass, and \( u_s \sim 5 \times 10^5 \text{ cm/s} \), which gives the phonon wave vector satisfying the energy conservation \( 2m_{\text{ex}}u_s/\hbar \sim 0.01 \, \text{ Å}^{-1} \). The typical values of \( 1/a_{\text{ex}} \) and \( 1/d_{QW} \) are often of the same order.

Then, phonons with more or less any \(|q_z|\) on the scale of Fig. 2 can be emitted or absorbed, so the radiative region cannot be supplied not just from the narrow strip around \( p' = 2m_{\text{ex}}u_s \), but from a wide region in the outer space \( p' > 2m_{\text{ex}}u_s \). A state with \( p \) in the outer region, in turn, can receive population from the whole inner area of the inner part of the dashed contour (phonon absorption), and from the whole outer area of its outer part (phonon emission). Thus, population depletion in the small radiative region still only weakly affects the supply region, so our key observation that \( I^p_\text{p} \) can be calculated using \( I^p_\text{p} \) for the termal states remains valid, together with Eqs. (6) and (8a–8c). What should be modified with respect to the simple two-dimensional model, is the phonon absorption rate \( 1/\tau_0(T) \). While the Fermi Golden Rule calculation with the simple Hamiltonian (9) gives a rate \( 1/\tau_0 \propto T^2 \), the model including the matrix element suppression at \( q \gg 1/a_{\text{ex}} \) and \(|q_z| \gg 1/d_{QW} \), yields \( 1/\tau_0 \propto T \) [29]. Both lead to relaxation bottleneck at low temperatures; more detailed investigation of this issue is beyond the scope of this paper.

III. APPLICATION TO TRANSITION METAL DICHALCOGENIDES

Exciton relaxation by scattering on acoustic phonons in monolayer TMDCs, such as MoS\(_2\), MoSe\(_2\), WS\(_2\), WSe\(_2\) was recently studied in Ref. [33], where three-dimensional phonons were considered. Here we assume the binding between the TMDC monolayer and the substrate not to be strong, so the acoustic phonons are taken to be two-dimensional. To extend the validity of Eq. (9) to phonon wave vectors comparable to inverse exciton radius, \( 1/a_{\text{ex}} \), the matrix element should be multiplied by the Fourier transform of the square of the excitonic wave function for the electron-hole relative coordinate \( r_{eh} \). For the hydrogen-like wave function, \( \propto e^{-r_{eh}/2m_{\text{ex}}} \), and equal electron and hole masses \( m_{\text{ex}} \), this amounts to an additional factor \( [1 + (q_{\text{ex}}/4)^2]^{-3/2} \) in Eq. (8). It is known that because of strong dielectric confinement in the TMDC monolayer, the interaction potential is not \( 1/r_{eh} \), so the bound state wave functions do not have a hydrogenic form [33, 34]. However, as will be seen below, the precise form of the cutoff factor does not matter, as the typical exciton radius in TMDC, \( a_{\text{ex}} \sim 1 \text{ nm} \) [35, 36], will turn out to be small enough for the cutoff effect not to play a significant role.

Another modification of the simple model studied in the previous section concerns the variety of excitonic species in TMDCs. The longitudinal and transverse bright excitons, degenerate at \( p = 0 \), become strongly split by the exchange interaction at \( p \gg \hbar k_{\text{rad}} \) [24, 25, 31]. Namely, in addition to \( p^2/(2m_{\text{ex}}) \), the longitudinal exciton energy contains a linear term, \( v_{\text{ex}}p \), with the group velocity, \( v_{\text{ex}} = c\Gamma_{0v}/(2\omega_{\text{ex}}) \), determined by the same parameter \( \Gamma_{0v} \) as the radiative rates (7a), (7b). Using the parameters from Table I and taking \( \varepsilon = 2.5 \), we obtain \( v_{\text{ex}} = (0.9–1.1) \times 10^5 \text{ cm/s} \) for all four materials. Not only \( v_{\text{ex}} \gg u_s \), but also the energy \( m_{\text{ex}}v_{\text{ex}}^2 \), at which \( v_{\text{ex}}p \) is overcome by \( p^2/(2m_{\text{ex}}) \), is 2–3 times larger than the room temperature. Thus, at low temperatures, the longitudinal exciton population is negligible compared to the transverse one. The matrix element of the deformation potential \( \Gamma_{\alpha p} \), which determines the rate \( W_{p'\rightarrow p} \), should also include the overlap \( \langle \alpha, p | \alpha', p' \rangle \) between states of the two exciton branches, \( \alpha, \alpha' = L, T \), determined by the angle \( \phi_{pp'} \) between \( p \) and \( p' \) [25, 31]:

\[
|\langle T, p | T, p' \rangle|^2 \lesssim \frac{1 \pm \cos(2\phi_{pp'})}{2}.
\]

Besides the two bright exciton species, in monolayer TMDCs there are six dark exciton species whose energies are in the same range (up to energy shifts of a few tens of meV, due to spin-orbit and exchange interactions). These excitons are formed by conduction and valence band states belonging to different valleys or/and having different spins, so their radiative decay is forbidden in the zero approximation. In molybdenum-based compounds, the bright excitons have a lower energy than the dark ones, while in tungsten-based ones, the situation is the opposite. This was used to explain the experimentally observed rise of the luminescence intensity in WSe\(_2\) with increasing temperature in terms of the increasing thermal population of the higher-energy bright excitons [14, 47]. Conversion between dark and bright excitons requires either a spin flip or an intervalley scattering which, in a clean crystal, can occur by phonon absorption or emission. The energy of intervalley phonons is of the same order as that of optical phonons, so these processes are slow at low temperature, as compared to scattering by acoustic phonons. Thus, conversion between dark and bright excitons leads to slow equilibration between different excitonic reservoirs but does not affect directly the population of the radiative states. In the following, we

| Parameter | MoS\(_2\) | MoSe\(_2\) | WS\(_2\) | WSe\(_2\) | Units |
|-----------|----------|----------|---------|---------|------|
| \( \hbar\omega_{\text{ex}} \) | 1.9 | 1.7 | 2.0 | 1.7 | eV |
| \( 1/\Gamma_0 \) | 0.23 | 0.24 | 0.19 | 0.22 | ps |
| \( m_{\text{ex}} \) | 1.09 | 1.35 | 0.73 | 0.90 | \( m_0 \) |
| \( D_e - D_v \) | 2.0 | 0.6 | 1.5 | 1.1 | eV |
| \( u_s \) | 6.6 | 4.1 | 4.3 | 3.3 | \( 10^5 \text{ cm/s} \) |
| \( \rho \) | 1.6 | 2.0 | 2.4 | 3.1 | \( 10^{-7} \text{ g/cm}^2 \) |
focus on the dynamics of exciton exchange between the bright radiative states and the reservoir from the transverse bright exciton band, leaving aside the problem of slow population exchange between different reservoirs. Still, one should keep in mind that this slow population exchange may contribute to dynamics at very long times.

For bright excitons in TMDs, the radiative rate is quite large, \( h\Gamma_0^{\text{rad}} \) being a few meV \cite{15, 19, 20, 22, 23, 27, 28}. For the coefficient \( \mathcal{A} \) in Eqs. (10a, 10b), the material parameters listed in Table 1 give a few \( \mu \text{eV/K} \). This is an order of magnitude smaller than experimentally measured values \cite{15, 19, 20, 22, 23, 27, 28}, probably due to a larger value of \( D_c - D_v \) than that given in Ref. \cite{43}. In any case, \( 1/\tau_0(T) < \Gamma_0^{\text{rad}} \) below several tens of Kelvins, so one can expect the bottleneck effect. It should be noted, that intravalley dark excitons can also decay radiatively at a rate about 100–1000 times slower than for the bright ones \cite{44}, so already above a few Kelvins, their population in the radiative region should be thermalized. For intervalley dark excitons, radiative decay is possible if assisted by phonon emission \cite{20}. We are not aware of any estimate for the rate of this process.

The large radiative decay rate \( \Gamma_p \) of the bright excitons leads to an energy broadening \( h\Gamma_0^{\text{rad}} \cong 2m_{ex}u_{\text{ex}}^2 \), the latter being 0.54, 0.27, 0.15, and 0.11 meV, for the four materials, respectively. This introduces a large energy uncertainty \( \sim h\Gamma_p \) in Eq. (1), so the image of Fig. 2 is not valid, and the radiative region is refilled from states \( p' \) with energies \( (p')^2/(2m_{ex}) \sim \min\{h\Gamma, T\} \) (Fig. 3). Still, outside the radiative region the states are not broadened, so the kinetic equation is applicable, and the effect of the depleted radiative region on \( I_{p'} \) at energies \( (p')^2/(2m_{ex}) \sim \min\{h\Gamma, T\} \) is relatively weak by the same phase-space argument as before (note that the total spectral weight of the radiative states is unchanged, it is only spread over a wide energy range). Thus, the population flow \( I_p \) into the radiative region can again be calculated assuming equilibrium distribution \( I_{p'}^0 \) outside, but not the detailed balance condition. Indeed, scattering of an exciton from the non-radiative region into a strongly broadened radiative state followed by fast radiative decay can equivalently be viewed as phonon-assisted radiative decay of a non-radiative state via a virtual intermediate state in the radiative region. Assuming \( m_{ex}u_{\text{ex}}^2/h/\tau_0 \ll \{h\Gamma, T\} \ll m_{ex}u_{\text{ex}}^2 \) \cite{49}, we can determine the average decay rate from the total incoming flux into the radiative region for the longitudinal and transverse excitons:

\[
\gamma = \int_{p < hkrad} \frac{d^2p}{(2\pi\hbar)^2} \frac{I_p^{\text{in,L}} + I_p^{\text{in,T}}}{n_{ex}}. \tag{12}
\]

The incoming fluxes \( I_p^{\text{in,L}}, I_p^{\text{in,T}} \) are, in turn, given by (we omit the labels “L,T” at \( I_p^{\text{in}} \) and \( \Gamma_p \) for brevity)

\[
I_p^{\text{in}} = \frac{n_{ex}}{2} \int_{hkrad} \frac{p'dp'}{m_{ex}T} \frac{e^{-(p')^2/(2m_{ex})}}{2p'u_0[1 + (p'/\hbar)^2(a_{ex}/4)^2]^3} \times \sum_{\pm} \frac{e^{\mp u_{p'}/(2T)}}{2 \sinh[u_{p'}/(2T)]} \Gamma_p \equiv \frac{\Gamma_p}{2} \left( e^{\mp u_{p'}/(2T)} - 1 \right),
\]

where we approximated \( |p - p'| \approx p' \), took into account the overlaps \cite{11} which amount to 1/2 upon angular integration, and denoted \( \epsilon_{p'} \equiv (p')^2/(2m_{ex}) \). The sum over the two signs in the second line corresponds to phonon absorption/emission for the upper/lower signs, respectively. The key ingredient of Eq. (13) is the Lorentzian density of final states for exciton scattering into the radiative region, which includes the radiative broadening. The \( p' \) integral is cut off at large \( p' \) by one of the three factors: the thermal exponential \( e^{-\epsilon_{p'}/T} \), the matrix element suppression \( [1 + (p'/\hbar)^2(a_{ex}/4)^2]^{-3} \), and the Lorentzian which imposes \( \epsilon_{p'} \lesssim \Gamma_p \). First, all of these imply \( u_{p'} \ll \epsilon_{p'}, T \), as illustrated by Fig. 3, so we approximate \( 2 \sinh[u_{p'}/(2T)] \approx u_{p'}/T \) and neglect \( u_{p'}/T \) everywhere else, which is equivalent to treating the phonon-induced potential \( V(r) \) as a quasistatic disorder of the strength \( V^2 \propto T \). Second, the cutoff imposed by the Lorentzian turns out to be more important than that due to the exciton radius: for \( \epsilon_{p'} = 3 \text{ meV} \sim h\Gamma_p \), \( m_{ex} = m_0, a_{ex} = 1 \text{ nm} \), we obtain \( p'_{ex}(4\hbar) \approx 0.07 \). Thus, the integral is dominated by \( \epsilon_{p'} \sim \hbar^2 \) for \( T \gg \hbar \), and by \( \epsilon_{p'} \sim T \) for \( T \ll \hbar \), while the cutoff due to the exciton radius is not important in either case.

Combining Eqs. (12, 13), and integrating first over...
with the same coefficient $A$ as in Eqs. (10a), (10b). The function $\mathcal{G}(\vartheta)$, defined in Eq. (14b) and plotted in Fig. 4, determines the temperature dependence of $\gamma$ in the appropriate units: for $\varepsilon = 2.5$, we obtain $\hbar \Gamma_{\text{vac}}^\text{ex} / (2 \sqrt{\varepsilon}) \sim 10$ K, while $\hbar k_{\text{rad}}^2 / (2 \pi m_{\text{ex}}) \approx 5$ ns$^{-1}$ (taking $m_{\text{ex}} = m_0$, $\hbar \omega_{\text{ex}} = 2$ eV). The dimensionless coefficient $A$ is in the range $0.03 - 0.13$ for the parameters in Table I while in experiments values approaching unity are reported [15,19,20,22,23]. Thus, the typical values of $\gamma$ at temperatures $T \sim 50$ K correspond to decay times of the order of nanoseconds.

In time-resolved photoluminescence experiments on TMDCs, two contributions to the luminescence are often observed [12,14,21]: a fast component, decaying on the picosecond time scale, and a slow one, which appears at temperatures above 100–150 K, and decays on time scales between 100 ps [12] and 2.5 ns [21]. It is this slow component that was attributed to the radiative decay of excitons from the reservoir, and the nanosecond decay time scale is similar to what we obtained above. At low temperatures, the slow component was not observed so far. It is likely that in the above experiments at low temperatures, the excitons quickly decay from the radiative states without populating the non-radiative reservoir at all. This is quite natural for quasiresonant optical excitation used in Refs. [11,21], but not totally clear for the non-resonant excitation in Ref. [12].

The overall temperature dependence of $\gamma$, given by Eqs. (14a), (14b), has quite simple qualitative explanation. At $T \ll \hbar \Gamma_{\text{vac}}^\text{ex}$, we have $\gamma \propto T / \Gamma_{\text{vac}}^\text{ex}$. Indeed, the whole thermal exciton population pumps the radiative region, where the density of states is $\propto 1 / \Gamma_{\text{vac}}^\text{ex}$ (the top of the Lorentzian), while the phonon occupation is proportional to $T$. At $T \gg \hbar \Gamma_{\text{vac}}^\text{ex}$, the whole Lorentzian in the radiative region is involved, which can be pumped only from states with energies $\epsilon_{\text{ex}} \sim \hbar \Gamma_{\text{vac}}^\text{ex}$ whose population is $\propto 1 / T$, while the pumping rate is proportional to $1 / \tau_0 (T) = \mathcal{A} T$, so the temperature drops out. Note that Eq. (13) is valid only when $\Gamma_\mathcal{p} \gg 1 / \tau_0$ [29], which sets the upper limit on the temperature to be a few tens of Kelvins. In particular, if $A \sim 1$, there is no room for the temperature-independent regime. At higher temperatures, when $\Gamma_\mathcal{p} \lesssim 1 / \tau_0$, the rate $\gamma$ should start decreasing with temperature, but the study of this regime is beyond the scope of the present paper.

![Image](image-url)

**IV. CONCLUSIONS**

To conclude, we analyzed radiative decay of thermalized exciton population subject to scattering by acoustic phonons. Assuming sufficiently low temperatures, we did not include scattering on optical phonons. Depending on the radiative decay rate $\Gamma_0$ of excitonic states with small momenta, on the phonon absorption rate $1 / \tau_0$ in these states, and on the frequency $2 m_{\text{ex}} u_s^2 / \hbar$ of the absorbed phonons, we identified several regimes. When $\Gamma_0 \ll 1 / \tau_0$, the excitons in the radiative region are strongly depleted, and $\gamma$ is determined by exciton scattering into the radiative region (the relaxation bottleneck). In this case, $\Gamma_0$ drops out from $\gamma$, and its temperature dependence is $\gamma \propto 1 / (T \tau_0 (T))$. In particular, if $1 / \tau_0 \propto T$, a curious situation may arise where $\gamma$ depends neither on temperature, nor on $\Gamma_0$. Finally, when $\Gamma_0 \gg 1 / \tau_0$, the radiative broadening of states in the depleted radiative region affects the exciton-phonon scattering rate itself. It is this strong-broadening case that we find to be relevant for bright excitons in TMDCs at low temperatures. Then, at lowest temperatures $T \ll \hbar \Gamma_0$ the effective population decay rate $\gamma \propto T$, while at $T \gg \hbar \Gamma_0$ it becomes temperature-independent.

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At this point, it does not matter whether $m_\text{ex}u_\text{ex}^2 \gg \hbar/\tau_0$ or not. Indeed, the main contribution to $\Gamma_\text{p}$ comes from the states with relatively high energies, $(p')^2/(2m_\text{ex}) \sim \{\hbar \Gamma, T\} \gg \hbar/\tau_0$, so the kinetic equation at these high energies is valid. However, at too high temperatures, when $1/\tau_0$ becomes comparable to $\Gamma$, our theory is no longer quantitatively valid. Qualitatively, the effect can be taken into account by replacing $\Gamma_\text{p} \rightarrow \Gamma_\text{p} + 1/\tau_0$ in the denominator of the Lorentzian in Eq. (13). However, the precise shape of the spectral function at the bottom of the exciton band will no longer be Lorentzian.