Fast relaxation of photo-excited carriers in 2D transition metal dichalcogenides

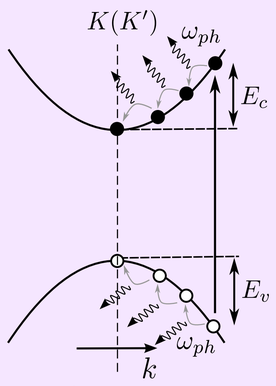
Mark Danovich[1], Igor L. Aleiner[2], Neil D. Drummond[3], Vladimir I. Fal'ko[1]

[1]National Graphene Institute, University of Manchester, Booth St E, Manchester M13 9PL, UK
[2]Physics Department, Columbia University, New York, NY 10027, USA
[3]Department of Physics, Lancaster University, LA1 4YB, UK

Introduction

Monolayer transition metal dichalcogenides (TMDCs) denoted by MX_2, consist of a transition metal atom M, covalently bonded to two chalcogen atoms X in the unit cell, and arranged in a hexagonal lattice. These materials possess unique properties [1], including: a direct-band-gap in the visible range at the two degenerate and inequivalent valleys of the Brillouine zone K and K', strong optical absorption, large exciton binding energies, and large spin splitting in the valence and conduction bands, making them ideal for optoelectronics applications [2]. Understanding the process of energy relaxation in these materials, which leads to radiative recombination, is of particular importance for optoelectronics applications.

Photo-excited carriers at the K/K' valleys, relax inelastically by emitting phonons, allowing them to reach the bottom of the conduction (c) and valence (v) bands where they can then radiatively recombine. We predict ps-scale relaxation of photo-excited carriers in TMDCs, which is mediated by the emission of longitudinal optical (LO), and homopolar (HP) phonons. We evaluate the Born effective charges for MoS_2, $MoSe_2$, WS_2, and WSe_2, and the corresponding LO phonon couplings, to calculate the cooling times for hot electrons and holes from excitation energies of several hundred meV.



Sketch of the relaxation process at the K/K'-valleys.

Phonon mediated relaxation in TMDCs

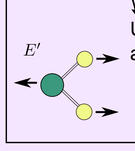
- We analyse the phonon mediated cooling of hot carriers in TMDCs, focusing on two optical phonon modes coupled to the intra-valley relaxation process: the in-plane longitudinal optical (LO), and the out of plane homopolar (HP) phonon modes, with a constant energy dispersion.
- These are the only two modes coupled to the intra-valley relaxation process, and having a finite coupling at the Γ-point, as dictated by the point group symmetry of the crystal, D_{3h}.
- Density functional theory calculations show a sufficiently large energy gap between the K and Q vallyes [3] (particularly for Mo based TMDCs), and weak carrier coupling with K-point phonons, allowing to focus only on the intra-valley scattering.
- At the K/K'-points, for energies up to 0.25 eV, the carriers can be approximated as having a parabolic energy dispersion with an effective mass.
- The carrier-phonon interaction Hamiltonian:

$$H_{e-ph} = \sum_{\substack{\vec{q},\vec{k} \\ \mu = LO,\, HP}} g_{\mu,\vec{q}} \underbrace{c^\dagger_{\vec{k}+\vec{q}} c_{\vec{k}}}_{\text{carriers}} \underbrace{(a^\dagger_{\mu,-\vec{q}} + a_{\mu,\vec{q}})}_{\text{phonons}}$$

Longitudinal Optical (LO)

$$g_{LO} = \frac{i}{A}\sqrt{\frac{\hbar}{2NM_r\omega_{LO}}}\frac{2\pi Ze^2}{1+qr_*}$$

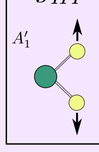
Effective charge; Screening length; Unit cell area; Reduced unit cell mass; Phonon frequency; Phonon wavevector



Homopolar (HP)

$$g^\alpha_{HP} = \sqrt{\frac{\hbar}{2NM\omega_{HP}}}D^\alpha, \qquad \alpha = c \text{ or } v$$

Deformation potential; Unit cell mass; Phonon frequency



TMDCs parameters used in the modelling of phonon emission rates

	$\frac{m_c}{m_0}$ [3]	$\frac{m_v}{m_0}$ [3]	A [3] [Å^2]	$\frac{M_r}{m_p}$	$\frac{M}{m_p}$	$\hbar\omega_{LO}$ [4] [meV]	$\hbar\omega_{HP}$ [4] [meV]	D_c [4] [eV/Å]	D_v [4] [eV/Å]	Z	r_* [5] [Å]
MoS_2	0.46	0.54	8.65	38.4	160	49	51	5.8	4.6	−1.08	41
$MoSe_2$	0.56	0.59	9.37	59.7	254	37	30	5.2	4.9	−1.80	52
WS_2	0.26	0.35	8.65	47.5	248	44	52	3.1	2.3	−0.47	38
WSe_2	0.28	0.36	9.37	85.0	342	31	31	2.3	3.1	−1.08	45

LO phonon coupling in 2D TMDCs

The LO mode couples to charge carriers through the polarization $\vec{P}_{op} = \frac{Ze}{A}\vec{u}$, which is induced by the lattice deformation given by the relative displacement $\vec{u}$, and the opposite effective charge on the two sublattices, given by the Born effective charge tensor,

$$Z_{ij} = \frac{1}{e}\frac{\partial F_j(s)}{\partial E_i}\bigg|_{E=0}$$

Partial derivative of the jth component of the force on atom s at zero-field equilibrium position, with respect to ith component of the electric field.

In 2D, unlike 3D, the resulting coupling has a finite value at the Γ-point, with a momentum dependent dielectric function. The coupling is obtained from the electrostatic interaction energy in 2D [6],

$$E_{int} = \frac{1}{2}\int \frac{d^2r d^2r'}{|r-r'|}\sigma(r)\sigma(r') + \underbrace{\frac{1}{2\kappa}}_{\substack{\text{in-plane} \\ \text{rigidity}}}\int d^2r(P_\perp^2 + P_{op}^2), \quad \sigma(r) = \underbrace{e\rho(r)}_{\substack{\text{2D charge} \\ \text{density}}} - \nabla\cdot\underbrace{\vec{P}_{op}}_{\substack{\text{optical phonon} \\ \text{induced} \\ \text{polarization}}} - \nabla\cdot\underbrace{\vec{P}_\perp}_{\substack{\text{other in-plane} \\ \text{polarization}}}$$

In the static approximation, integrating out the in-plane polarization $\vec{P}_\perp$, and Fourier transforming the integrand, we obtain the carrier-phonon interaction energy term composed of the phonon induced polarization and carrier density, from which we obtain the coupling coefficient,

$$E_{e-ph} = \int \frac{d^2\vec{q}}{(2\pi)^2}\frac{2\pi i e\hat{q}\cdot\vec{P}_{op,\vec{q}}\rho^*_q}{1+\underbrace{2\pi\kappa q}_{\text{screening length}}}$$

References

[1] Qing Hua Wang, et al., *Nature Nanotechnology*, 11, (2012), 699.
[2] Deep Jariwala, et al. *ACS Nano*, 2, (2014), 1102.
[3] Andor Kormnyos, et al., *2D Materials*, 2, (2015), 022001.
[4] Zhenghe Jin, et al., *Phys. Rev. B*, 4, (2014), 045422.
[5] Timothy C. Berkelbach, Mark S. Hybertsen, and David R. Reichman, *Phys. Rev. B*, 88, (2013), 045318.
[6] Bogdan Ganchev, Neil D. Drummond, Igor Aleiner, Vladimir Fal'ko, *Phys. Rev. Lett.*, 10, (2015), 107401.

Phonon emission rates

The emission rates are calculated using the Fermi golden rule:

$$\tau^{-1} = \frac{2\pi}{\hbar}\sum_{\vec{q},\mu}|\langle f|H_{e-ph}|i\rangle|^2\delta(E_f - E_i).$$

The phonon emission rates are valid only for carrier energies larger than the corresponding phonon energy.

HP phonon

The HP phonon emission rate is a constant independent of the carrier energy:

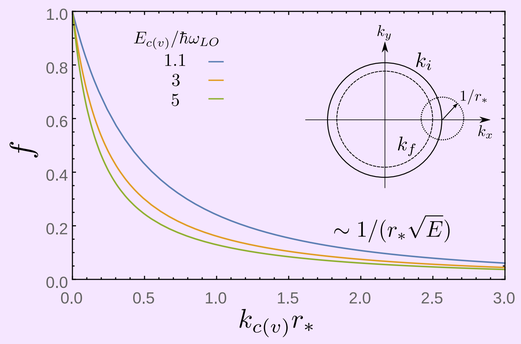
$$\tau^{-1}_{HP,\alpha} = \frac{m_\alpha A D^2_\alpha}{2M\hbar^2\omega_{HP}}, \qquad \alpha = c \text{ or } v$$

LO phonon

The LO phonon emission rate has dependance on both the carrier energy and the screening length. The screening length limits the dominantley contributing phonon wavevectors ($q \le 1/r_*$) to the scattering process:

$$\tau^{-1}_{LO,\alpha} = \tau^{-1}_\alpha f\left(\frac{E_\alpha}{\hbar\omega_{LO}}, k_\alpha r_*\right), \qquad \alpha = c \text{ or } v$$

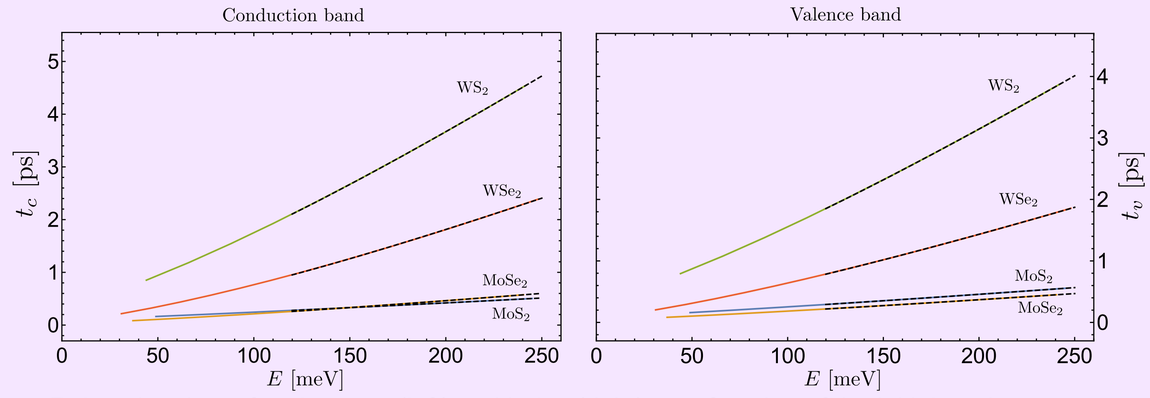
$\underbrace{\tau^{-1}_\alpha}_{\substack{\text{Emission rate with zero screening} \\ \text{(independent of the carrier energy)}}} = \frac{2\pi^2Z^2E_B}{\hbar}\frac{m_\alpha}{M_r}\frac{a_B^2}{A}\frac{E_B}{\hbar\omega_{LO}}$, $\underbrace{k_\alpha}_{\substack{\text{Carrier wavevector} \\ \text{corresponding to the} \\ \text{LO phonon energy}}} = \sqrt{\frac{2m_\alpha\omega_{LO}}{\hbar}}$



Relaxation times

The energy relaxation rate due to optical phonons emission:

$$\frac{dE}{dt} = -\frac{\hbar\omega_{LO}}{\tau_{LO}(E)} - \frac{\hbar\omega_{HP}}{\tau_{HP}}$$



Relaxation times for electrons (left) and holes (right) as a function of the initial carrier energy.

Asymptotic form of the relaxation time (dashed) for large carrier energies $(E \gg \hbar\omega_{LO}, \hbar\omega_{HP})$:

$$t(E) \approx aE - b\sqrt{E} + c$$

Values of derived and fitted parameters

	MoS_2	$MoSe_2$	WS_2	WSe_2
k_c [Å^{-1}]	0.077	0.074	0.055	0.048
k_v [Å^{-1}]	0.083	0.076	0.064	0.054
τ_c^{-1} [ps^{-1}]	112	296	11	45
τ_v^{-1} [ps^{-1}]	130	312	14	58
${\tau_{HP,c}}^{-1}$ [ps^{-1}]	6.8	7.7	0.69	0.54
${\tau_{HP,v}}^{-1}$ [ps^{-1}]	5.0	7.2	0.5	1.3
a_c [$\frac{\text{ps}}{\text{meV}}$]	$2.3\cdot10^{-3}$	$3.9\cdot10^{-3}$	0.029	0.017
b_c [$\frac{\text{ps}}{\sqrt{\text{meV}}}$]	0.012	0.033	0.24	0.17
c_c [ps]	0.14	0.15	1.27	0.70
a_v [$\frac{\text{ps}}{\text{meV}}$]	$2.7\cdot10^{-3}$	$2.6\cdot10^{-3}$	0.023	0.012
b_v [$\frac{\text{ps}}{\sqrt{\text{meV}}}$]	0.017	0.018	0.18	0.10
c_v [ps]	0.15	0.10	1.03	0.45

Summary

- The relaxation times of photo-excited carriers in 2D TMDCs due to emission of optical phonons, are of a few ps for all the materials studied.
- $MoSe_2$ and MoS_2 have the shortest sub-ps relaxation times for all carrier energies up to ~0.25 eV, which is attributed to their respective unit cell Born charges, and optical deformation potentials.
- The 2D LO phonon coupling has a finite value at the Γ-point, and a decreasing scattering rate with increasing carrier energy due to the lattice screening.
- The LO phonon typically dominates over the HP phonon mode, however for larger screening lengths and high carrier energies the two become comparable.
- The relaxation times obtained for WS_2 and WSe_2 are a lower bound, due to the energy allowed K→Q intervalley scattering in these materials.

Acknowledgments: We thank M. Calandra, T. Heinz, K. Novoselov, M. Potemski, A. Tartakovskii, and V. Zolyomi for useful discussions. This work was supported by the Simons Foundation, the ERC Synergy Grant Hetero2D and the ECFET European Graphene Flagship.

e-mail: mark.danovich@postgrad.manchester.ac.uk