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Supporting Information: Negative effective excitonic diffusion in monolayer transition metal dichalcogenides

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November 13, 2019

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1 Wannier Equation and exciton-phonon scattering

The energetic position of the excitonic energies E_v is given by $E_v = E_v^{\text{single}} - E_v^{\text{binding}}$, where E_v^{single} is the single-particle separation between top of valence band in valley K and bottom of conduction-band dispersion relation in valley K, K' and Λ for $v = KK, KK', K\Lambda$, respectively. The exciton binding energy E_v^{binding} is obtained from the solution of the Wannier equation

$$\frac{\hbar^2 k^2}{2m_v} \Psi_v(\mathbf{k}) - \sum_{\mathbf{q}} W_{\mathbf{q}} \Psi_v(\mathbf{k} + \mathbf{q}) = E_v^{\text{binding}} \Psi_v(\mathbf{k}) \quad , \tag{1}$$

where m_v is the reduced exciton mass in valley v, i.e. $1/m_v = 1/m_v^e + 1/m_v^h$, with $m^{e,h}$ denoting the effective mass of electrons and holes in excitonic valley v. Furthermore $\Psi_v(\mathbf{k})$ is the excitonic wave function in momentum space while $W_{\mathbf{q}}$ is the Coulomb interaction, for which we have used a modified form of the potential for charges in a thin film of thickness d surrounded by a dielectric environment (see [1] for more details). Taking into account anisotropic dielectric tensors and solving the Poisson equation with the above described boundary conditions yields $W_q = V_q/\epsilon_{scr}(q)$, with the bare 2D-Fourier transformed Coulomb potential V_q and a non-local screening, $\epsilon_{scr}(q) = \kappa_1 \tanh\left[\frac{1}{2}\left[\alpha_1 dq - \ln\left(\frac{\kappa_1 - \kappa_2}{\kappa_1 + \kappa_2}\right)\right]\right]$, where $\kappa_i = \sqrt{\epsilon_i^{\parallel} \epsilon_i^{\perp}}$ and $\alpha_i = \sqrt{\epsilon_i^{\parallel}/\epsilon_i^{\perp}}$ account for the parallel and perpendicular component of the dielectric tensor ϵ_i of monolayer (i = 1) and environment (i = 2). The key parameters adopted for obtaining the dispersion relation are then listed below.

Parameter	Value	Reference
$E_{KK'}^{\text{single}}$ - E_{KK}^{single}	-31 meV	[2]
$E_{K\Lambda}^{\text{single}}$ - E_{KK}^{single}	$27~{\rm meV}$	[2]
m_K^h	$0.36 m_0$	[2]
m_K^e	$0.27 m_0$	[2]
$m^e_{K'}$	$0.36 m_0$	[2]
m^e_Λ	$0.64 m_0$	[2]
$\epsilon_{WS_2}^{\parallel}$	13.6	[3]
$\epsilon_{WS_2}^{\perp}$	6.3	[3]
κ_{hBN}	4.5	[4]

Table 1: Key parameters adopted, m_0 being the free-electron mass and m_{Λ}^e being the average over x and y directions.

The rates $\Gamma_{\mathbf{QQ'}}^{vv'}$ of the exciton-phonon coupling can in general be written as (see also [5])

$$\Gamma_{\mathbf{Q}\mathbf{Q}'}^{vv'} = \frac{2\pi}{\hbar} \sum_{\xi \pm} \left| G_{\xi|\mathbf{Q}'-\mathbf{Q}+\mathbf{Q}_{v'}'-\mathbf{Q}_{v}|}^{vv'} \right|^2 \left(n_{\xi,\mathbf{Q}'-\mathbf{Q}+\mathbf{Q}_{v'}'-\mathbf{Q}_{v}} + \frac{1}{2} \pm \frac{1}{2} \right) \delta \left(\epsilon_{\alpha} \pm \hbar \omega_{\xi,\mathbf{Q}'-\mathbf{Q}+\mathbf{Q}_{v'}'-\mathbf{Q}_{v}} - \epsilon_{\alpha'} \right) \quad ,$$

where \mathbf{Q}_{v} address the position in the Brillouin zone of the bottom of valley v, \pm refers to emission/absorption, ξ labels the phonon modes, $\hbar\omega_{\xi\mathbf{q}}$ provides the energy of phonon ξ with momentum \mathbf{q} and $n_{\xi,\mathbf{q}}$ is the phononic Bose-Einstein distribution. The exciton-phonon scattering coefficients G can be written as (see also [1]) $\left|G_{\xi\mathbf{q}}^{vv'}\right|^2 = \sum_{p=e,h} \left|g_{p\xi\mathbf{q}}^{vv'}\mathcal{F}_p^{vv'}(\mathbf{q})\right|^2$, where p distinguishes between electron/holes, \mathcal{F} is the form factor $\mathcal{F}_p^{vv'}(\mathbf{q}) = \sum_{\mathbf{k}} \Psi_{v'}^*(\mathbf{k})\Psi_v(\mathbf{k}+\alpha_v^p\mathbf{q})$, with $\alpha_v^p = (m_v^e + m_v^h)^{-1} \left[\pm m_v^{h/e}\right]$ for p = e, h, respectively, while g are the carrier-phonon scattering coefficients which are approximated with the generic form of a deformation potential,

$$g_{p\xi\mathbf{q}}^{vv'} = \sqrt{\frac{\hbar}{2\rho A\omega_{\xi\mathbf{q}}}} \mathcal{D}_{p\xi\mathbf{q}}$$

Here ρ denotes the surface mass density of the monolayer and A the area of the system. For the coupling constant $\mathcal{D}_{p\xi\mathbf{q}}$ we adopt the approximations deduced from DFPT calculations in Ref. [6], where long range acoustic phonons couple linear in momentum $\mathcal{D}_{\xi\mathbf{q}} \equiv \mathcal{D}_{\xi}^{(1)}q$, while optical phonons and short range acoustic modes couple with a constant strength $\mathcal{D}_{\xi\mathbf{q}} \equiv \mathcal{D}_{\xi}^{(0)}$ in vicinity of high symmetry points. The phonon energies as well as constants $\mathcal{D}^{(0)}$ and $\mathcal{D}^{(1)}$ for all possible intra and intervalley scattering channels are listed in Ref. [6], including longitudinal and transverse acoustic (LA, TA) and optical (LO, TO) modes as well as the out-of-plane A₁ optical mode, i.e. the mechanisms providing the most efficient scattering channels.

Finally, for describing the radiative decay [1, 7] we use a value of γ corresponding to a decay rate of null momentum excitons of 8 meV, in accordance with the decay-induced broadenings for WS₂ reported in Ref. [8, 9], although we stress that the radiative recombination rate has a negligible role on the qualitative aspects of the here-proposed effective diffusion in h-BN encapsulated WS₂.

2 Scattering-induced diffusion coefficient

We now explicitly derive two equations concerning the so-called *scattering-induced diffusion coefficient* shown in Fig. 5 of the manuscript for describing the role of intervalley scattering in the remarkable evolution of D_{KK} at low temperature. We first show why $D_v^{\text{scat}} = \frac{1}{4} \partial_t \left(\langle \mathbf{r}^2 \rangle |_{\mathbf{r}}^v \right) \Big|_{scat} \approx \frac{\int \mathbf{r}^2 \eta_v(\mathbf{r},t) d\mathbf{r}}{\int 4N_v(\mathbf{r},t) d\mathbf{r}}$. To this purpose we write the derivative $\partial_t \left(\langle \mathbf{r}^2 \rangle |_{\mathbf{r}}^v \right) \Big|_{scat}$ as difference quotient, i.e. we evaluate the expectation value of \mathbf{r}^2 provided by $N_v(\mathbf{r},t)$ at a generic time t as well as by $N_v(\mathbf{r},t+\Delta_t)|_{scat}$, the latter being the scatteringinduced evolution of $N_v(\mathbf{r},t)$, i.e. the evolution when it is considered only the scattering-induced density dynamics $\partial_t N_v(\mathbf{r},t)|_{scat}$. The scattering-induced infinitesimal evolution can be written as $\lim_{\Delta_t\to 0} N_v(\mathbf{r},t+\Delta_t)|_{scat} = N_v(\mathbf{r},t) + \lim_{\Delta_t\to 0} \Delta_t \partial_t N_v(\mathbf{r},t)|_{scat}$: Similarly to how the effective diffusion coefficient can be seen as (proportional to) the derivative of w^2 , the scattering-induced diffusion coefficient is a measure of the variation of w^2 when only the scattering-induced density dynamics is considered. Inserting $N_v(\mathbf{r},t+\Delta_t)|_{scat}$, with $\partial_t N_v(\mathbf{r},t)|_{scat} = \eta_v(\mathbf{r},t) + c_v N_v(\mathbf{r},t)$ from Eq. (4) of the manuscript, in the definition of D_v^{scat} via infinitesimal difference quotient one has

$$D_{v}^{\text{scat}} = \lim_{\Delta_{t} \to 0} \frac{1}{4\Delta_{t}} \left\{ \frac{\int \mathbf{r}^{2} (1 + c_{v} \Delta_{t}) N_{v}(\mathbf{r}, t) d\mathbf{r}}{\int (1 + c_{v} \Delta_{t}) N_{v}(\mathbf{r}, t) d\mathbf{r}} + \frac{\int \mathbf{r}^{2} \Delta_{t} \eta_{v}(\mathbf{r}, t) d\mathbf{r}}{\int (1 + c_{v} \Delta_{t}) N_{v}(\mathbf{r}, t) d\mathbf{r}} - \frac{\int \mathbf{r}^{2} N_{v}(\mathbf{r}, t) d\mathbf{r}}{\int N_{v}(\mathbf{r}, t) d\mathbf{r}} \right\}$$
$$= \lim_{\Delta_{t} \to 0} \frac{1}{4\Delta_{t}} \frac{\int \mathbf{r}^{2} \Delta_{t} \eta_{v}(\mathbf{r}, t) d\mathbf{r}}{\int (1 + c_{v} \Delta_{t}) N_{v}(\mathbf{r}, t) d\mathbf{r}} = \frac{\int \mathbf{r}^{2} \eta_{v}(\mathbf{r}, t) d\mathbf{r}}{\int 4N_{v}(\mathbf{r}, t) d\mathbf{r}} \quad \text{q.e.d.} \quad ,$$
(2)

where in the first equality we used $\int \eta d\mathbf{r} = 0$ in the denominator, in the second we noticed that the first and third term of first line cancel out (by definition of space-independent c_v) and finally we used the limit $\lim_{\Delta_t \to 0} c_v \Delta_t \ll 1$.

We now derive the relation $|D_{v_1}^{\text{interv}}| \approx |D_{v_2}^{\text{interv}}|n_{v_2}/n_{v_1}$ for the simplified case of two only valleys v_1 and v_2 (the extension is trivial). First we not that from the relation $\partial_t N_v|_{scat} = \sum_{v'} \partial_t N_v|_{v'}$ it follows that in the simplified case of two valleys $\partial_t N_{v_1}|_{scat} = \partial_t N_{v_1}|_{v_2} = -\partial_t N_{v_2}|_{scat}$, where we used twice the relation $\partial_t N_v(\mathbf{r},t)|_{v'} = -\partial_t N_{v'}(\mathbf{r},t)|_v$. Remembering Eq. (4) in the manuscript, this implies that $\eta_{v_1} =$ $-\eta_{v_2} + \int d\mathbf{r} \partial_t N_{v_2}|_{scat} [N_{v_1}(\mathbf{r})/n_{v_1} - N_{v_2}(\mathbf{r})/n_{v_2}]$. In most situations one has $|N_{v_1}(\mathbf{r})/n_{v_1} - N_{v_2}(\mathbf{r})/n_{v_2}| \ll$ $N_{v_2}(\mathbf{r})/n_{v_2}$ (even at low temperatures, while $N_{v_1}(\mathbf{r})/n_{v_1}$ is identically equal to $N_{v_2}(\mathbf{r})/n_{v_2}$ when there is no spatial separation between different valleys). As a consequence, it follows that $\eta_{v_1} \approx -\eta_{v_2}$: Inserting the latter in the definition of $D_{v_1}^{\text{scat}}$ [see also Eq. (2)] one has

$$D_{v_1}^{\text{scat}} = \frac{\int \mathbf{r}^2 \eta_{v_1}(\mathbf{r}, t) d\mathbf{r}}{4n_{v_1}} \approx -\frac{\int \mathbf{r}^2 \eta_{v_2}(\mathbf{r}, t) d\mathbf{r}}{4n_{v_1}} = -D_{v_2}^{\text{scat}} \frac{n_{v_2}}{n_{v_1}} \qquad \text{q.e.d.} \quad .$$
(3)

3 Spatiotemporal dynamics of absolute intravalley densities and photoluminescence

While in the manuscript we focused on normalized spatial distributions (see photoluminescence in Fig. 2 of the manuscript), squared width w^2 or effective diffusion coefficients D (see Figs. 3-5 in the manuscript), which provide a direct measure of the spatiotemporal dynamics, in this section we focus on absolute quantities such as the excitonic population of different valleys or the absolute intensity of the PL.

In Fig. 1 we show the spatiotemporal dynamics of the spatial densities N_{KK} , $N_{KK'}$ and $N_{K\Lambda}$ in terms of absolute populations (first to third column) normalizing w.r.t. to the maximal value reached by the mostlypopulated valley ($K\Lambda$ at 300 K and KK' in the other two cases). In view of the energetic misalignment, the population of valley KK is much smaller than the one of the other valleys, hence it is rather complicated to observe its profile in the first column of Fig. 1 (if not in the sub-picosecond timescale or at higher temperatures): For this reason its profile is also shown in logarithmic scale (column 4). In this way, one can observe a temporal dependence of the population in the center of the spatial density $N_v(\mathbf{r} = 0, t)$ as well as a different total population of different valleys. While the latter stems from the energy misalignment of different excitonic valleys combined with temperature and degeneracy of valley $K\Lambda$, the former has multiple causes: First, one can have a change of the total excitonic density due to e.g. direct recombination or intervalley energy thermalization, the latter being very strong directly after the optical excitation (see also [7] for the case of spatially-homogeneous optical excitation). When the total excitonic density is almost constant, i.e. at later stages of the evolution, the main dependence comes from the diffusion because $N_v(\mathbf{r} = 0, t)$ is roughly proportional to $1/w_v^2(t)$ for quasi-Gaussian distributions.



Figure 1: Spatiotemporal dynamics of absolute values (columns one to three) of the intravalley spatial densities in valley KK, KK' and $K\Lambda$, respectively, at three different temperatures. For valley KK we also plot the same results in logarithmic scale (column four) with different ranges in order to observe the spatiotemporal dynamics for occupations changing abruptly with temperature.

In Fig. 2 we focus on the spatiotemporal dynamics of the absolute values of the PL stemming from incoherent excitons. First, in panel (a) we focus on the dynamics of the PL intensity in the center of the excited spatial density. One finds behaviours very similar to the ones shown in previous studies of spatiallyhomogeneous optical excitation of W-based materials [7]: One can see a first strong decrease induced by the intervalley thermalization following the polarization-to-population transfer (which in W-based materials tend to overpopulate valley KK followed by a subsequent much slower decay induced by the radiative recombination. Similarly to what has been observed in those previous studies, as far as the temperature decrease i) the initial fast decrease of intensity with time becomes less steep but ii) lasts much longer, resulting iii) in a reduced ratio of intensity at later vs earlier stages. Points i) and ii) stem from the reduced effectiveness of the exciton-phonon scattering (which drives the thermalization) while point iii) stems from the interplay of overpopulation of valley KK after optical excitation and its low population at smaller temperatures after the thermalization. In panels (b-d) we plot the spatiotemporal dynamics of the absolute value of the PL keeping in mind the results of panel (a), i.e. choosing a logarithmic scale with different range depending on temperature. One can observe a very similar behaviour between Fig. 2(b-d) and the fourth column of Fig. 1: This indicates once again that the PL spatial density follows the behaviours of N_{KK} , as already shown in Fig. 3 of the main manuscript by looking at squared width and effective diffusion coefficient. Note that the sharp decrease of intensity [see 2(a)] together with the color-map plot may give the impression of a negative effective diffusion at 77K: This is however not the case once the spatial distribution is properly normalized, as shown in Fig. 2(b) of the manuscript. Analogously, the interplay between steep increase of second moment [see Fig. 2(c) and 3(c) in the manuscript] and strong decrease of the intensity in the center [see Fig. 2(a)] leads to an apparently interesting behaviour in the first 10 ps in Fig. 2(d).



Figure 2: Evolution of the logarithm of the PL from incoherent excitons (a) in the center of the spatial density $\mathbf{r} = 0$ for three different temperatures considered in the manuscript and associated spatiotemporal dynamics (b-d). In view of the different ratio of PL intensity at later vs earlier stages for different temperatures shown in panel (a), three different ranges and color scales have been adopted in panels (b-d).

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