Nonequilibrium lattice dynamics in two-dimensional materials

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Surface Science 2021

Frontiers of Electronic-Structure Theory: Focus on Electron-Phonon Interactions

CAU
Christian-Albrechts-Universität zu Kiel

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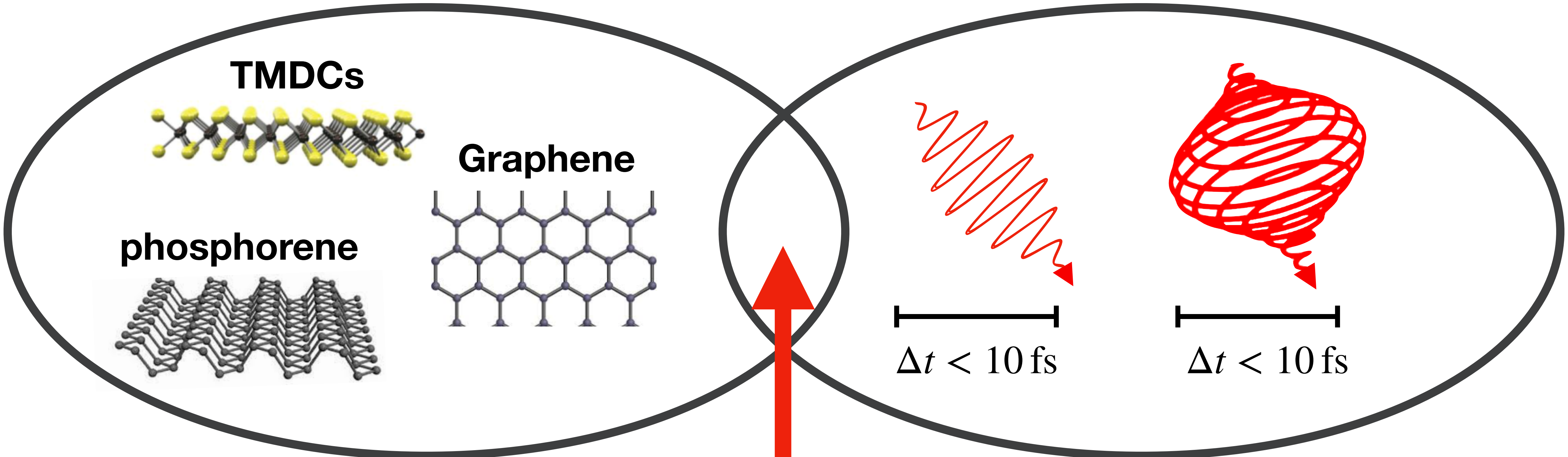
DFG Deutsche Forschungsgemeinschaft
German Research Foundation

Nonequilibrium dynamics in two dimensions

Materials science in 2D | **Advent of femto-second lasers**



- Reduced dielectric screening
- Quantum-confinement in 2D
- Strong light-matter interactions
- Non-trivial topological properties

- Pump-probe spectroscopies
- Electron and phonon dynamics
- Light-driven phenomena

Properties on-demand using light pulses

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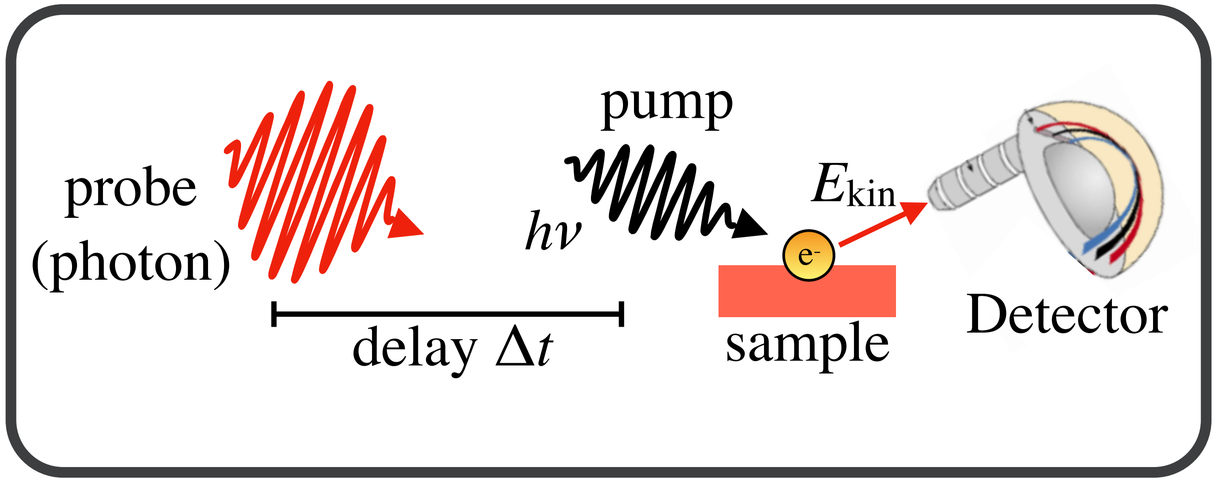
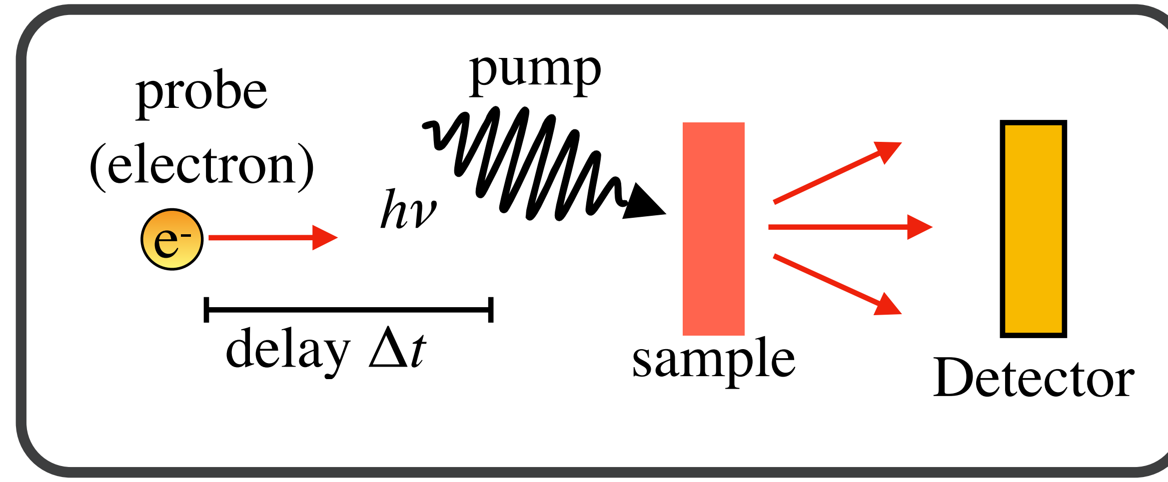
Nonequilibrium dynamics in two dimensions

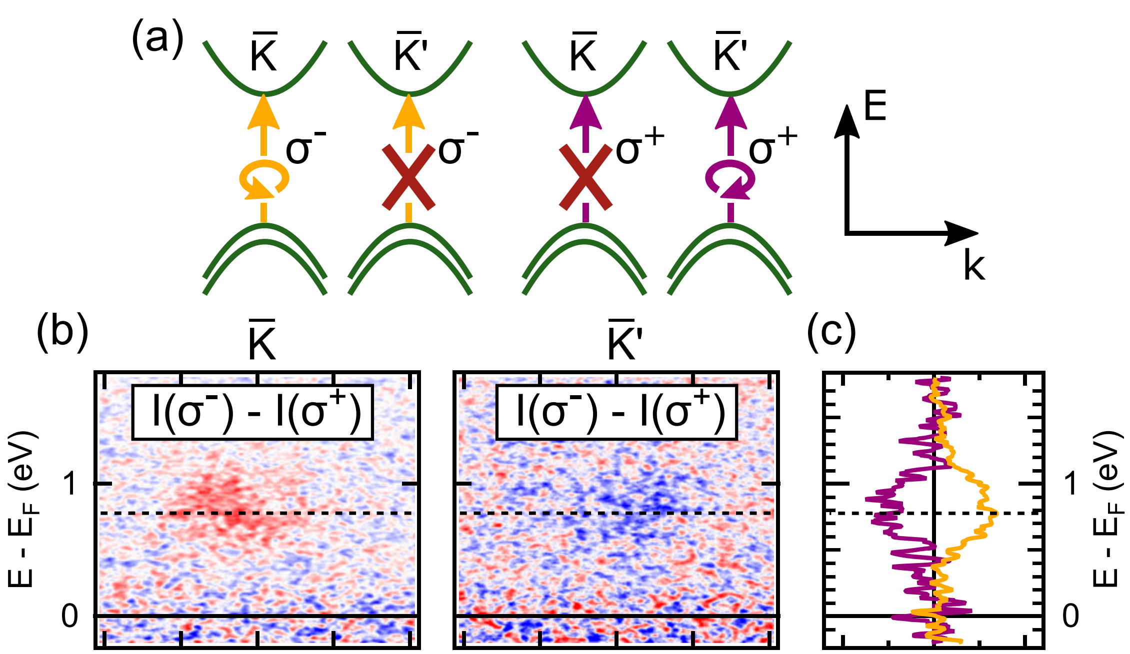
Time- and angle-resolved photoemission spectroscopy (trARPES)



Femto-second electron diffuse scattering (FEDS)

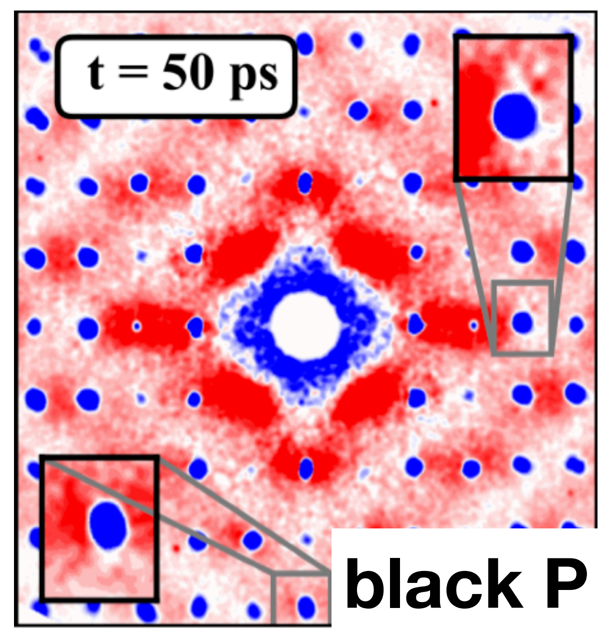


Circular Dichroism (WS_2)

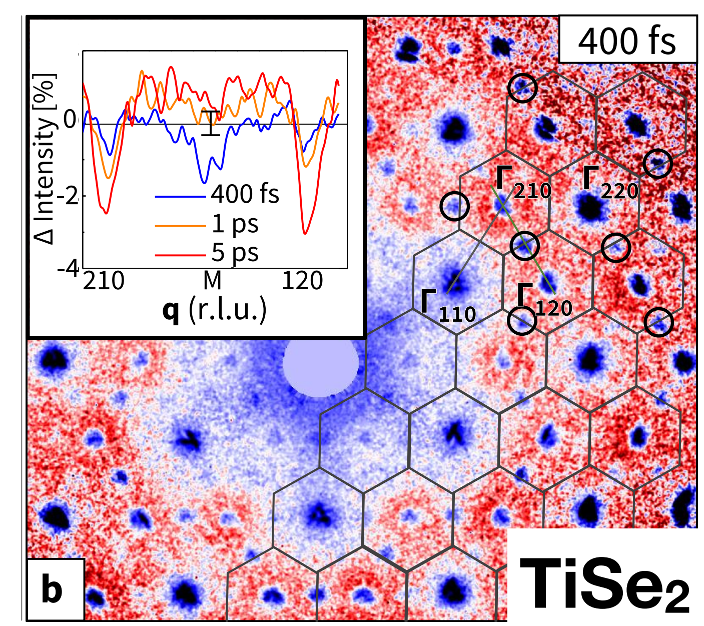


Beyer et al., PRL **123**, 236802 (2019)

Anisotropic lattice dynamic



Seiler et al.,
arXiv:2006.12873 (2020)



Otto et al.,
arXiv:1912.03559 (2020)

What is the role of phonons and electron-phonon interactions in the nonequilibrium dynamics?

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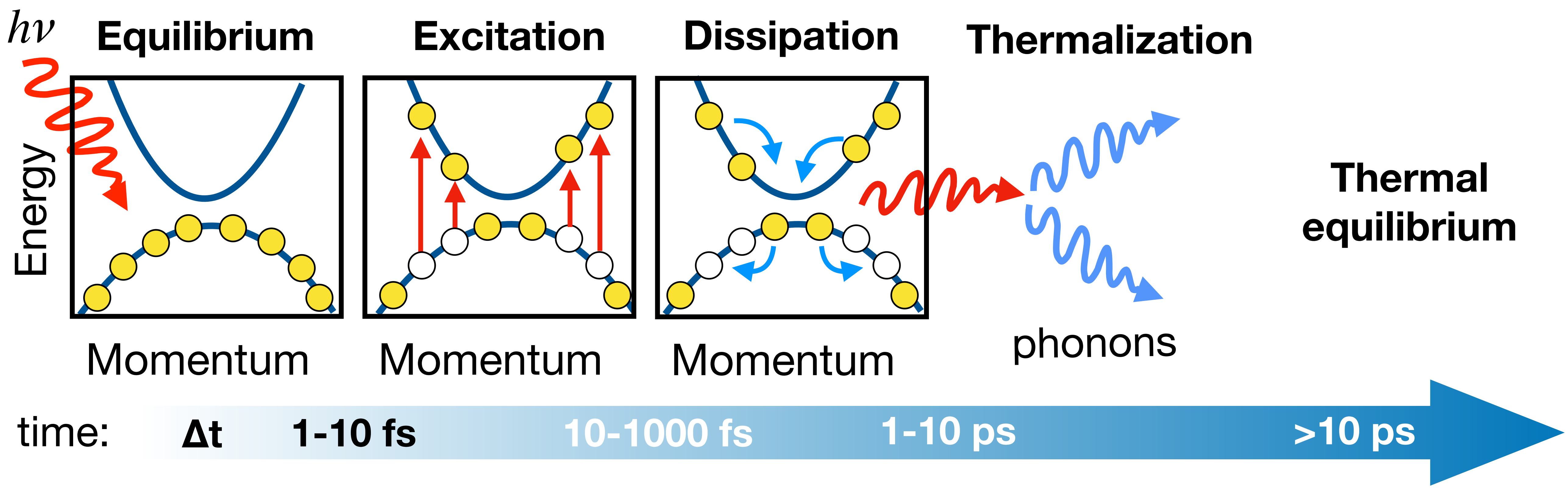
Ultrafast dynamics from first principles



Which level of theory?

- Nonequilibrium Green's functions (& DMFT)
- Time-dependent density-function theory
- Time-dependent Boltzmann equation
- Quantum Master equation
- Molecular dynamics / Path integrals
- Non-thermal lattice models

Check-list:

- ☑ Electron / phonon dynamics
- ☑ Electron-phonon coupling
- ☑ Full momentum resolution

Equilibrium and nonequilibrium regimes in a quantum system

Distribution function (occupation number):

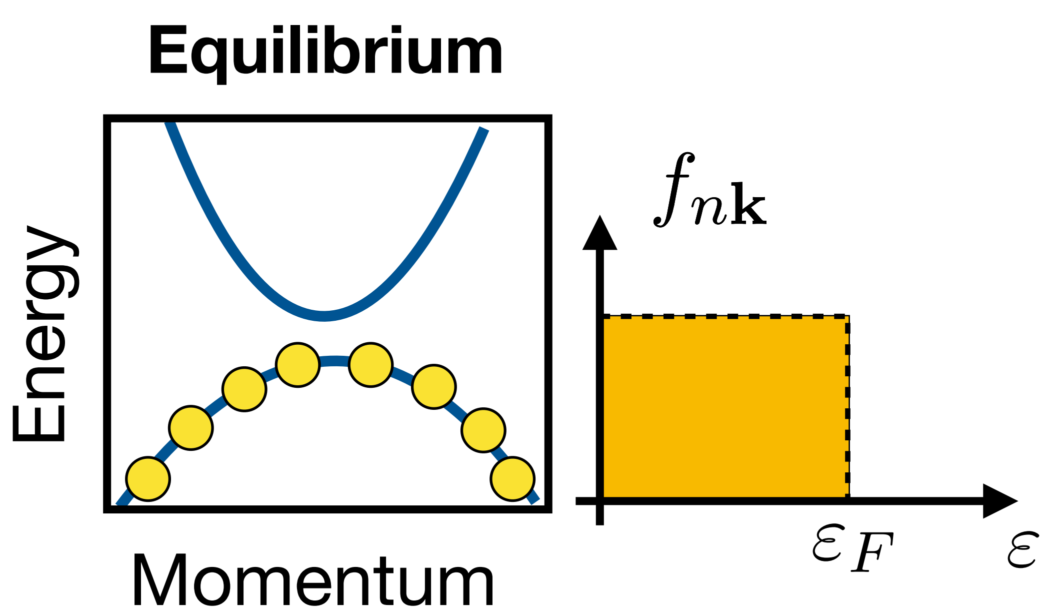
$f^{\sigma}_{n\mathbf{k}}$ Number of **electrons** in band n with momentum $\mathbf{k}$

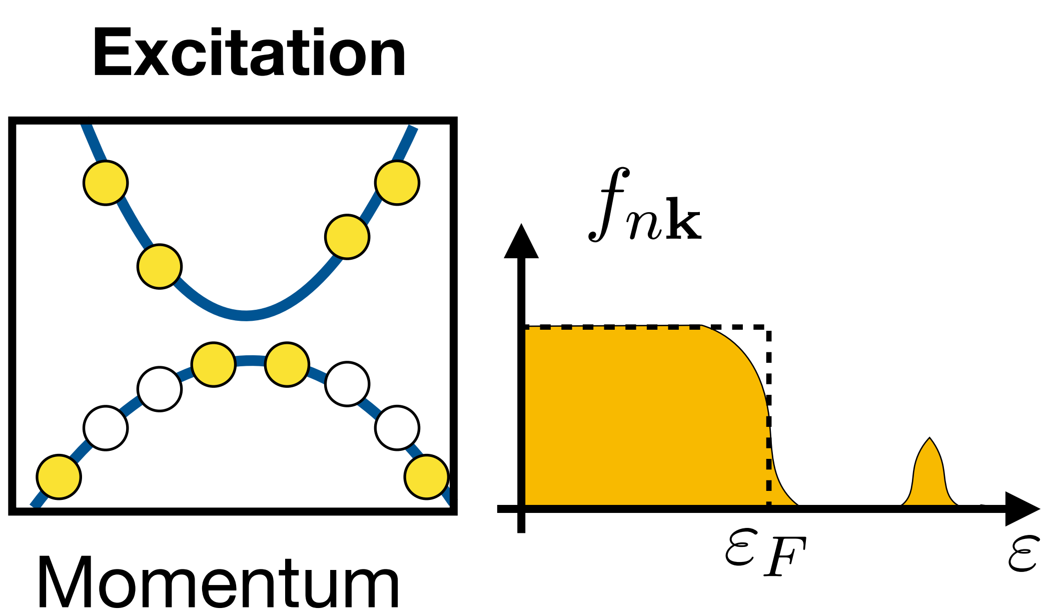
$n_{\mathbf{q}\nu}$ Number of **phonons** in branch ν with momentum $\mathbf{q}$

Equilibrium:

Fermi-Dirac statistics: $$f^{0}_{n\mathbf{k}}(\mu, T) = [e^{(\varepsilon_{n\mathbf{k}}-\mu)/k_{\mathrm{B}}T} + 1]^{-1}$$

Bose-Einstein statistics: $$n^{0}_{\mathbf{q}\nu}(T) = [e^{\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T} - 1]^{-1}$$





Out of equilibrium: $f_{n\mathbf{k}} \neq f^{0}_{n\mathbf{k}}$ and / or $n_{\mathbf{q}\nu} \neq n^{0}_{\mathbf{q}\nu}$

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The Boltzmann equation in solid-state physics

distribution function → $$\frac{\partial f}{\partial t} = \Gamma_{\text{collisions}}$$ ← collision integral

\+ other terms (fields, etc.)

(In a gas:)

Equilibrium is re-established via collisions

Books:
Ziman, Electrons and phonons, Oxford Universisty Press (1960)
Hang, Jauho, Quantum Kinetics in Transport and Optics of Semiconductors, Springer (1996)
Bonitz, Quantum Kinetic Theory (1998)

Charge and thermal Transport:
Poncé, Li, Reichard, Giustino, Rep. Prog. Phys. 83, 036501 (2019)
Li, Carrete, Katcho, Mingo, Comp. Phys. Comm.185, 1747 (2014)
Mizokami, Togo, Tanaka Phys. Rev. B 97, 224306, (2018)
Chaput, Phys. Rev. Lett 110, 265506 (2013)
Togo, Chaput, Tanaka, Phys. Rev. B 91, 094306 (2015)

Ultrafast dynamics:
Sadasivam, Chan, Darancet, Phys. Rev. Lett. 119, 136602 (2017)
Bernardi, Eur. Phys. J. B 89, 239 (2016)
Jhalani, Zhou, Bernardi, Nano Letters 17, 5012 (2017)
Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

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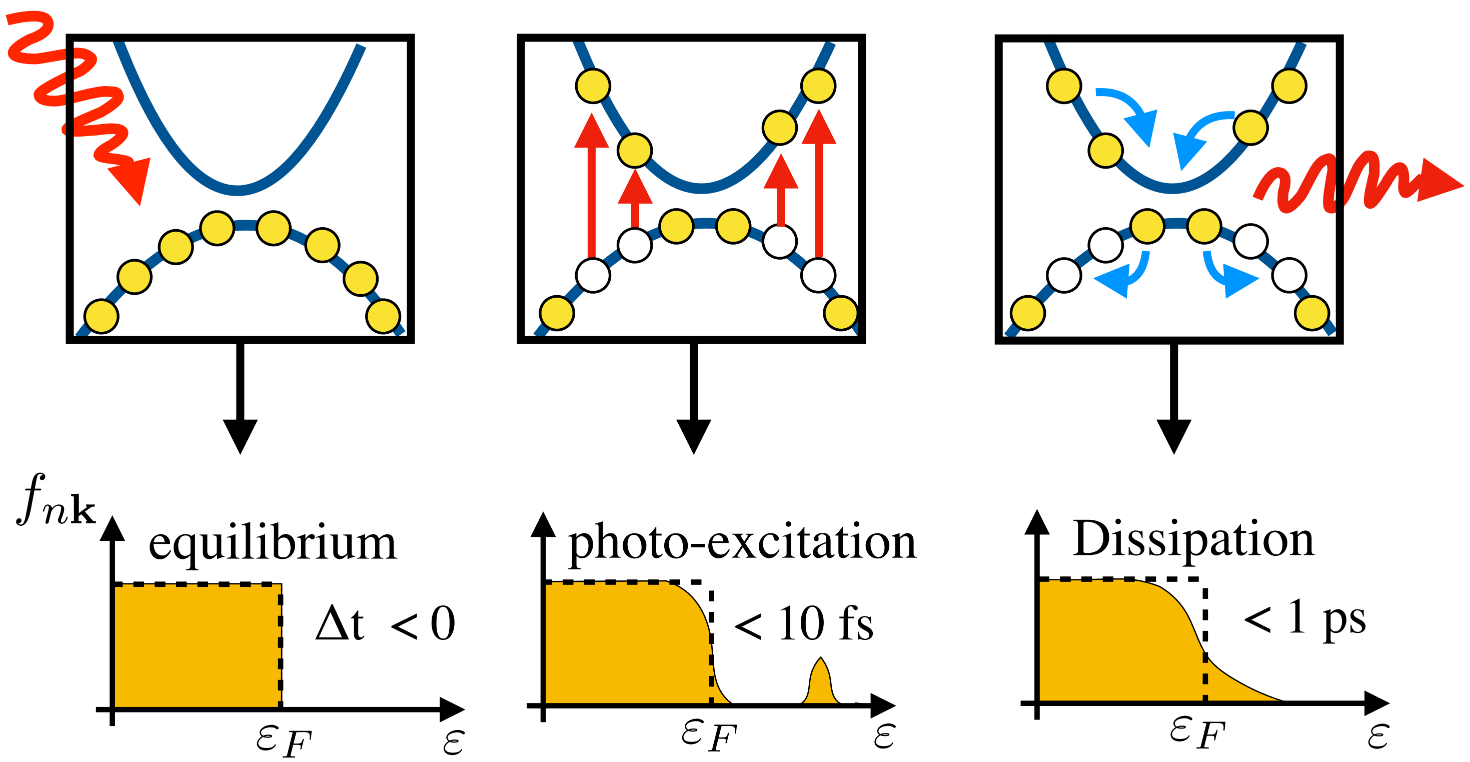
Time-dependent Boltzmann equation



Nonequilibrium states are described by

$$f^{\sigma}_{n\mathbf{k}} \qquad n_{\mathbf{q}\nu}$$

time-dependence of $f^{\sigma}_{n\mathbf{k}}$ $n_{\mathbf{q}\nu}$

time-dep. Boltzmann eq.:

electron-phonon

electron-photon (dipole int.)

electron-electron

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\mathrm{e-ph}}_{n\mathbf{k}}[f,n] + I^{\mathrm{light}}_{n\mathbf{k}}[f] + I^{\mathrm{e-e}}_{n\mathbf{k}}[f]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\mathrm{e-ph}}_{\mathbf{q}\nu}[f,n] + I^{\mathrm{ph-ph}}_{\mathbf{q}\nu}[n]$$

phonon-electron

phonon-phonon

First-principles approach to electron and lattice dynamics

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\mathrm{e-ph}}_{n\mathbf{k}}[f,n]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\mathrm{e-ph}}_{\mathbf{q}\nu}[f,n] + I^{\mathrm{ph-ph}}_{\mathbf{q}\nu}[n]$$

Boltzmann equation for the electron and phonon distribution function

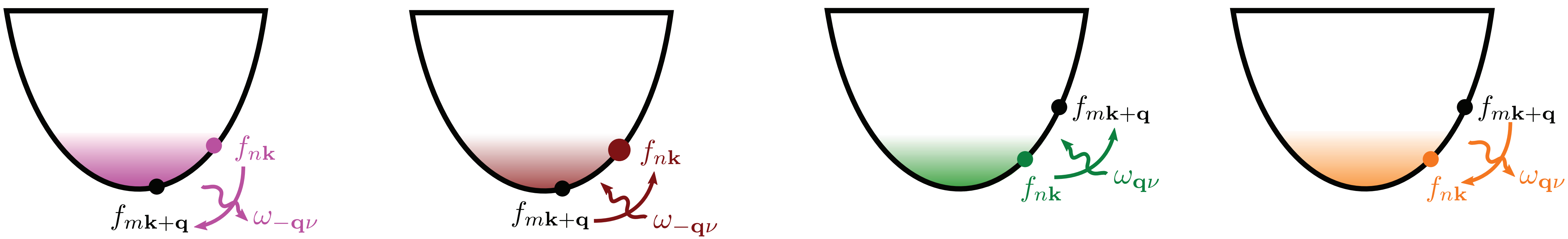
Poncé, et. al, Rep. Prog. Phys. (2019)

Example: electron-phonon scattering rate

$$I^{\mathrm{e-ph}}_{n\mathbf{k}}[f,n] = \frac{2\pi}{\hbar}\sum_{m\nu}\int\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2$$

$$\times\{(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})(1+n_{\mathbf{q}\nu})$$
$$+(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}$$
$$-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})(1+n_{\mathbf{q}\nu})$$
$$-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}\}$$

electron-phonon coupling matrix element



Ultrafast dynamics from first principles

Wannier-function interpolation

G. Pizzi et al.,
J. Phys. Cond. Matt. 32, 165902 (2020)

Electron-phonon coupling

S. Poncé et al.,
Comp. Phys. Comm. (2017)

Coupled-dynamics of electrons and phonons

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\mathrm{e-ph}}_{n\mathbf{k}}[f,n]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\mathrm{e-ph}}_{\mathbf{q}\nu}[f,n] + I^{\mathrm{ph-ph}}_{\mathbf{q}\nu}[n]$$

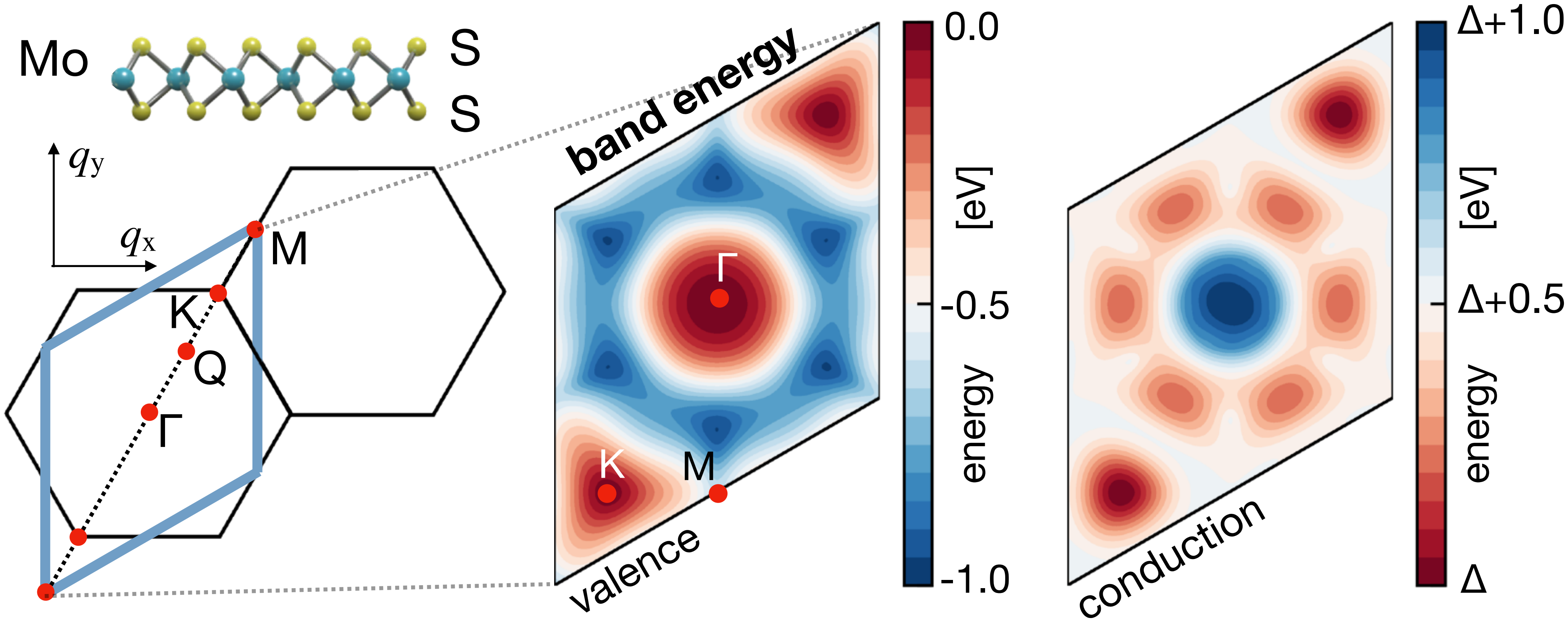
Density functional theory

P. Giannozzi et al.,
J. Phys.: Condens. Matter 29, 465901 (2017)

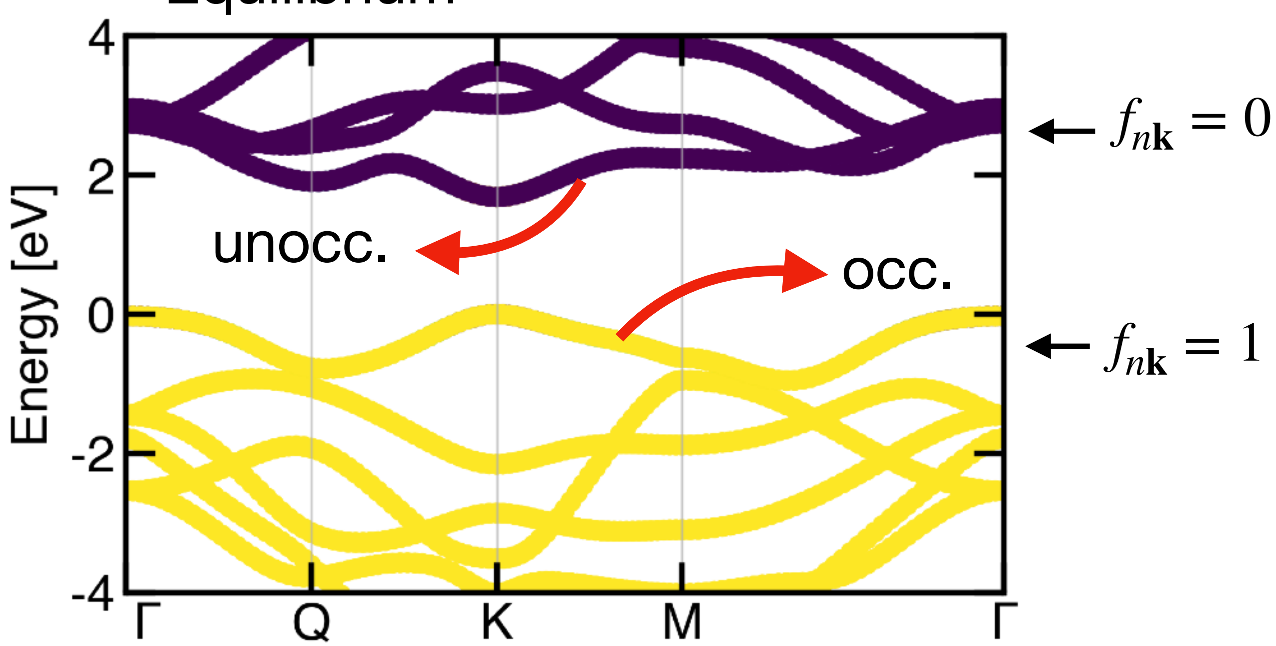
Third-order force constant

W. Li et al., Comp. Phys. Comm. 185, 1747 (2014)

Nonequilibrium electron dynamics in monolayer MoS_2

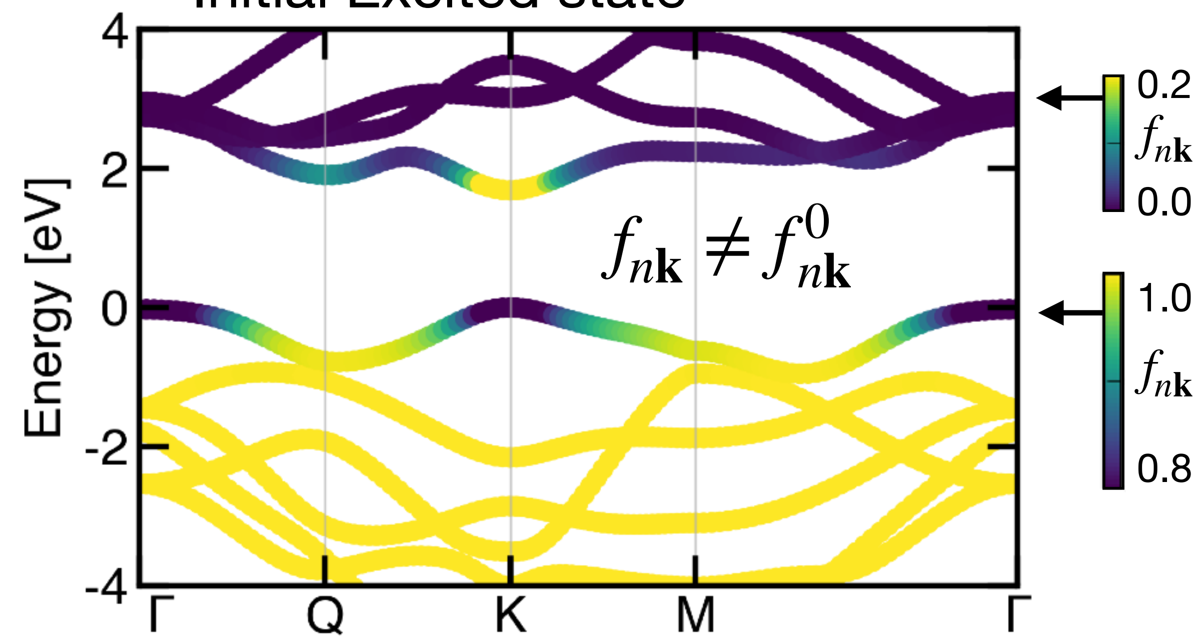


Equilibrium



$$f^0_{n\mathbf{k}}(\mu, T) = [e^{(\varepsilon_{n\mathbf{k}}-\mu)/k_BT} + 1]^{-1}$$

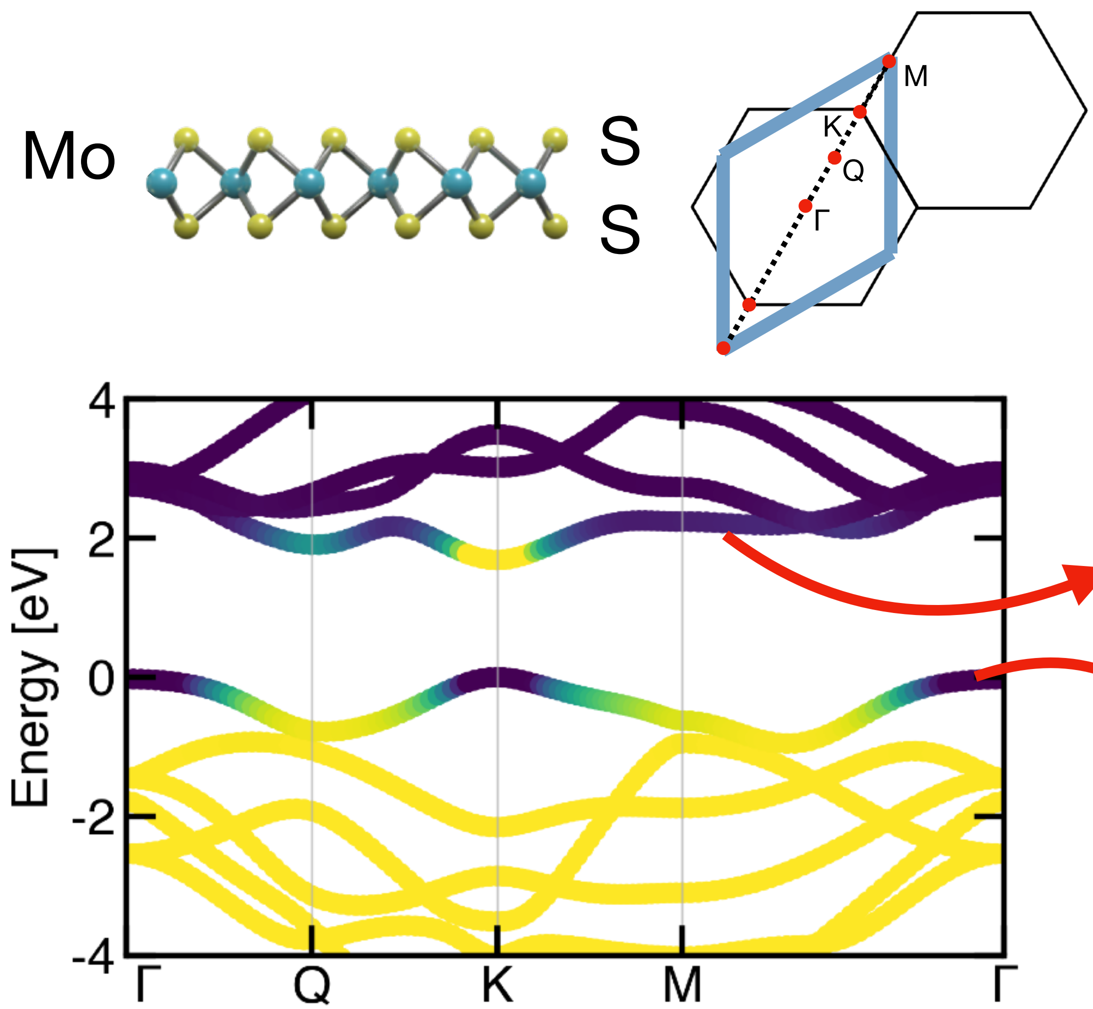
Initial Excited state

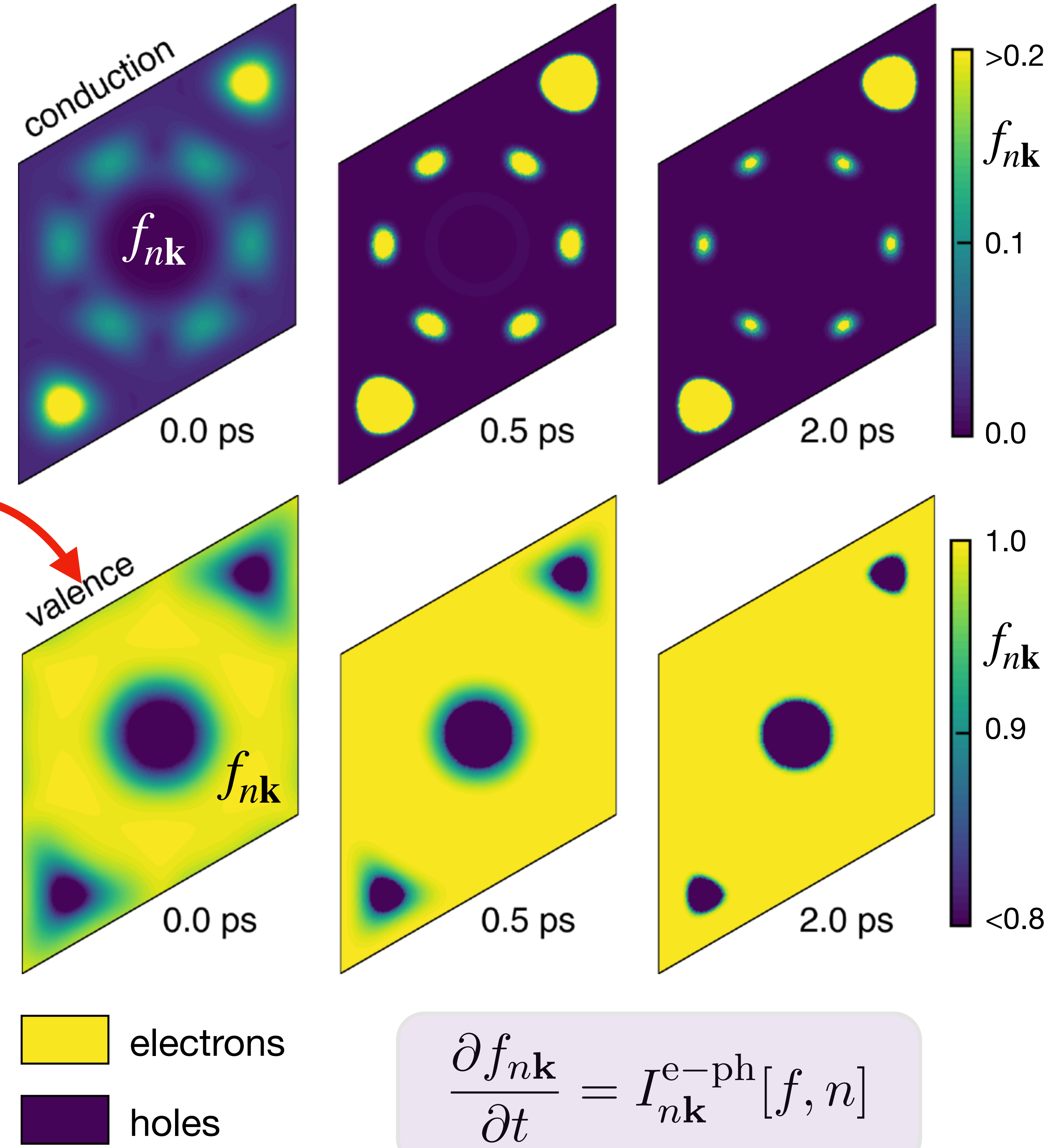


Excited carrier density: $n=10^{14}$ cm^{-2}

Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

Nonequilibrium electron dynamics





Estimated timescales for electron relaxation: $< 2\,\mathrm{ps}$

Experiments from (*) (fs-electron diffraction): $1.7 \pm 0.3\,\mathrm{ps}$

(*) Mannebach et al., Nano Lett. 15, 6889 (2015)

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\mathrm{e-ph}}_{n\mathbf{k}}[f, n]$$

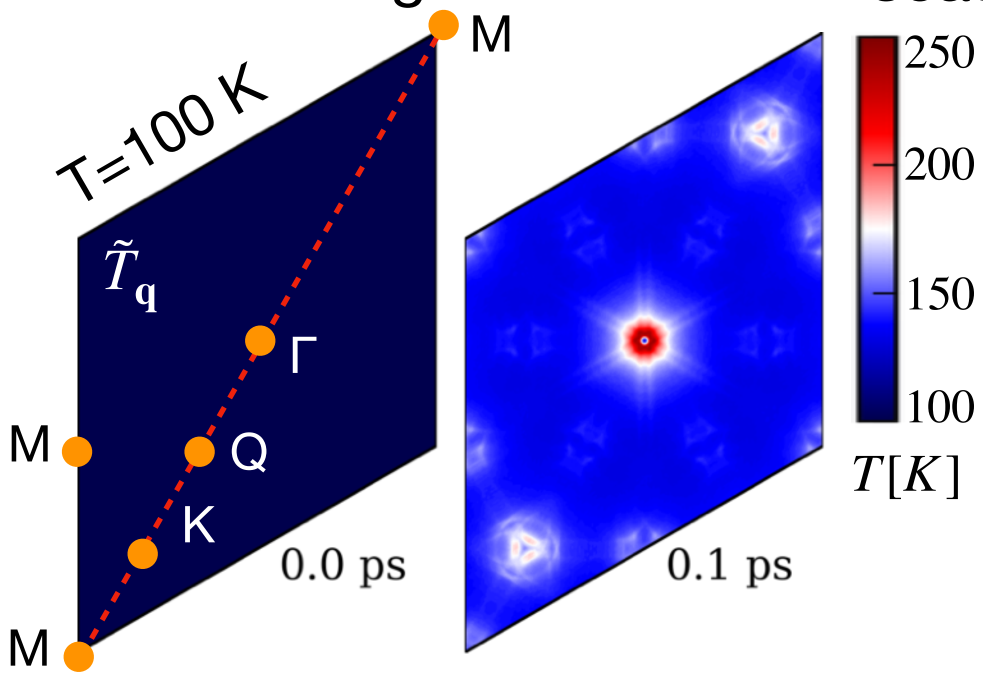
Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

Nonequilibrium phonon dynamics

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\mathrm{e-ph}}_{\mathbf{q}\nu}[f,n] + I^{\mathrm{ph-ph}}_{\mathbf{q}\nu}[n]$$

electron-phonon scattering

phonon-phonon scattering

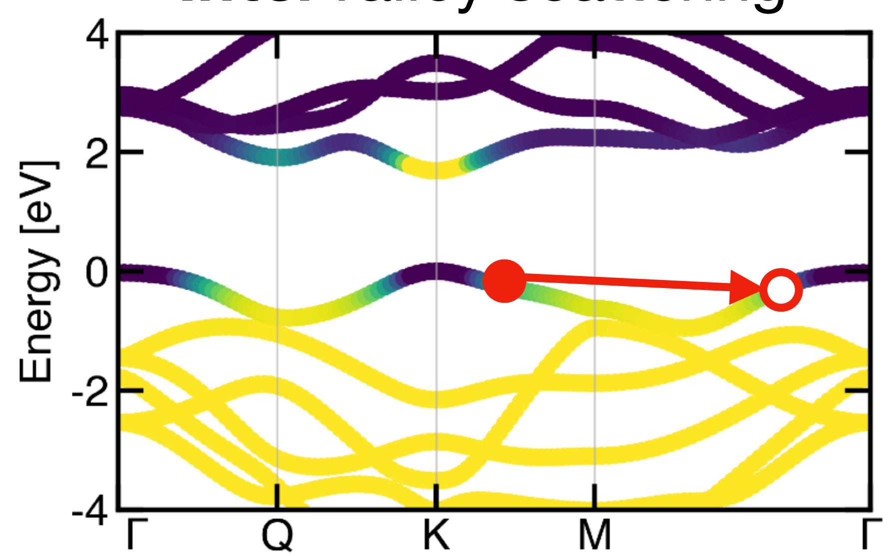


vibrational temperature

effective vibrational temperature

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu}[k_{\mathrm{B}} \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$

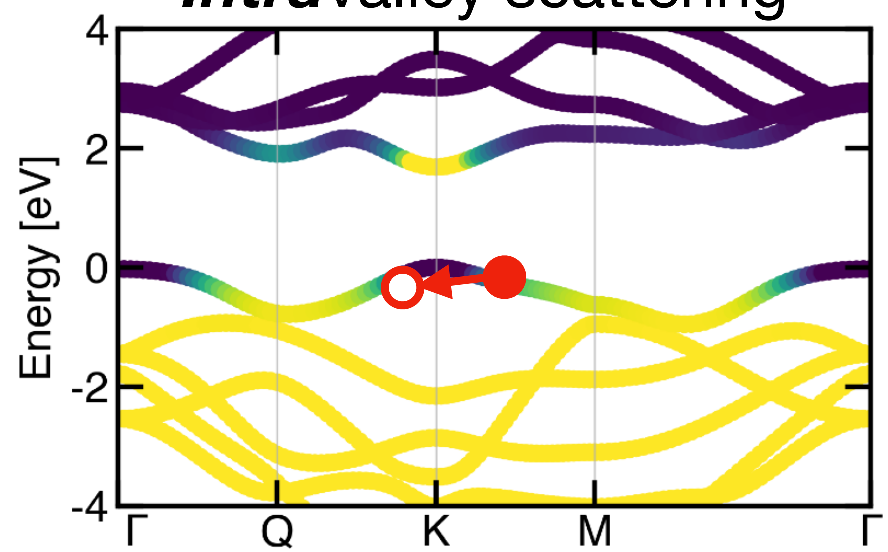
***Inter*valley scattering**



allowed phonon momenta:

$$\mathbf{q} \simeq \mathrm{K}$$

***Intra*valley scattering**



allowed phonon momenta:

$$\mathbf{q} \simeq \Gamma$$

Energy cons.: $\hbar\omega_{\mathbf{q}\nu} = \varepsilon_{n\mathbf{k}} - \varepsilon_{n\mathbf{k}'}$

Momentum cons.: $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

Nonequilibrium phonon dynamics

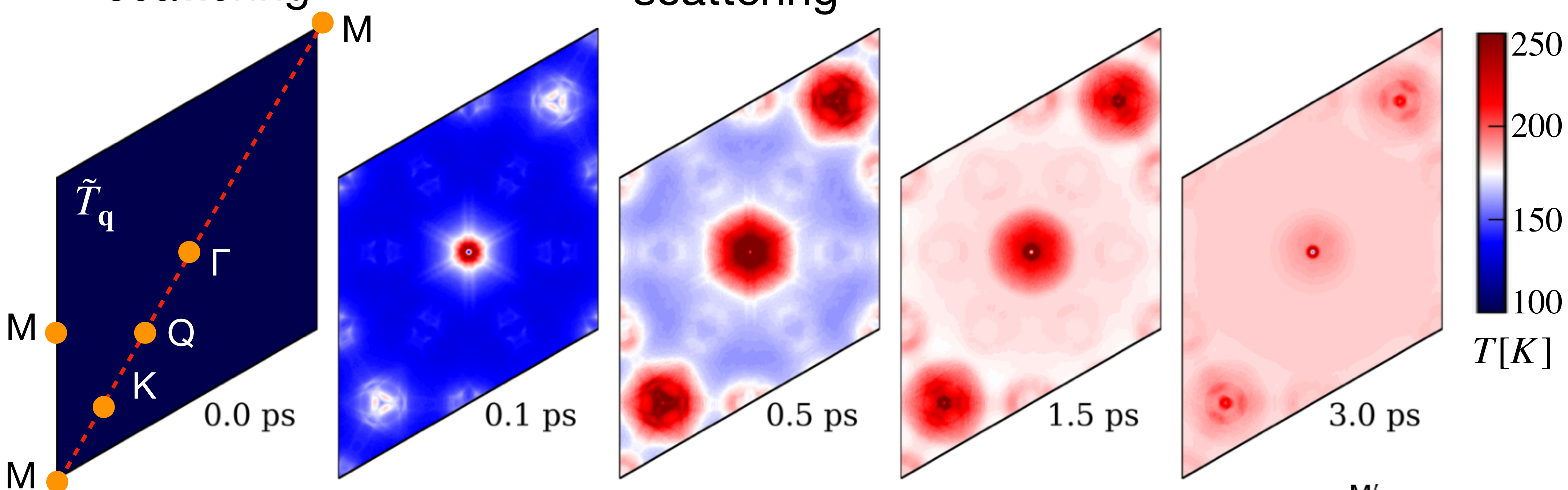
$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\mathrm{e-ph}}_{\mathbf{q}\nu}[f,n] + I^{\mathrm{ph-ph}}_{\mathbf{q}\nu}[n]$$

electron-phonon scattering

phonon-phonon scattering

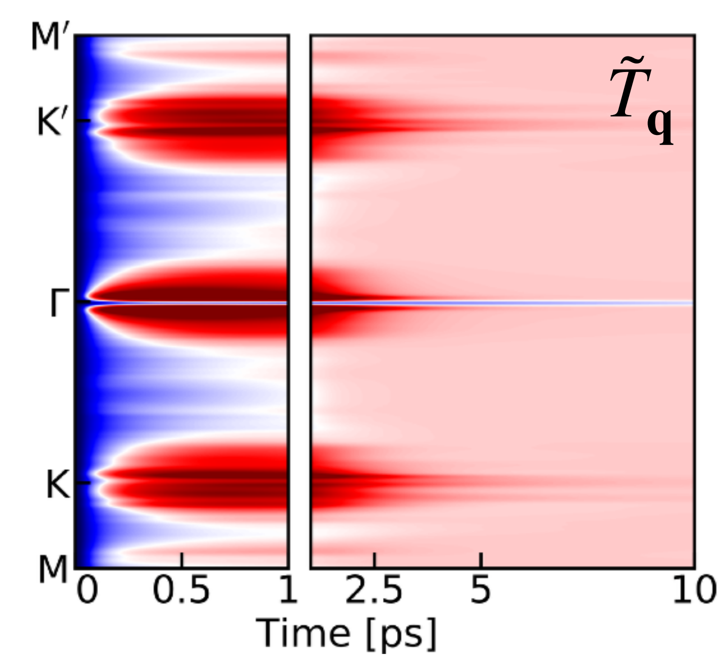
effective vibrational temperature

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu}[k_{\mathrm{B}} \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$



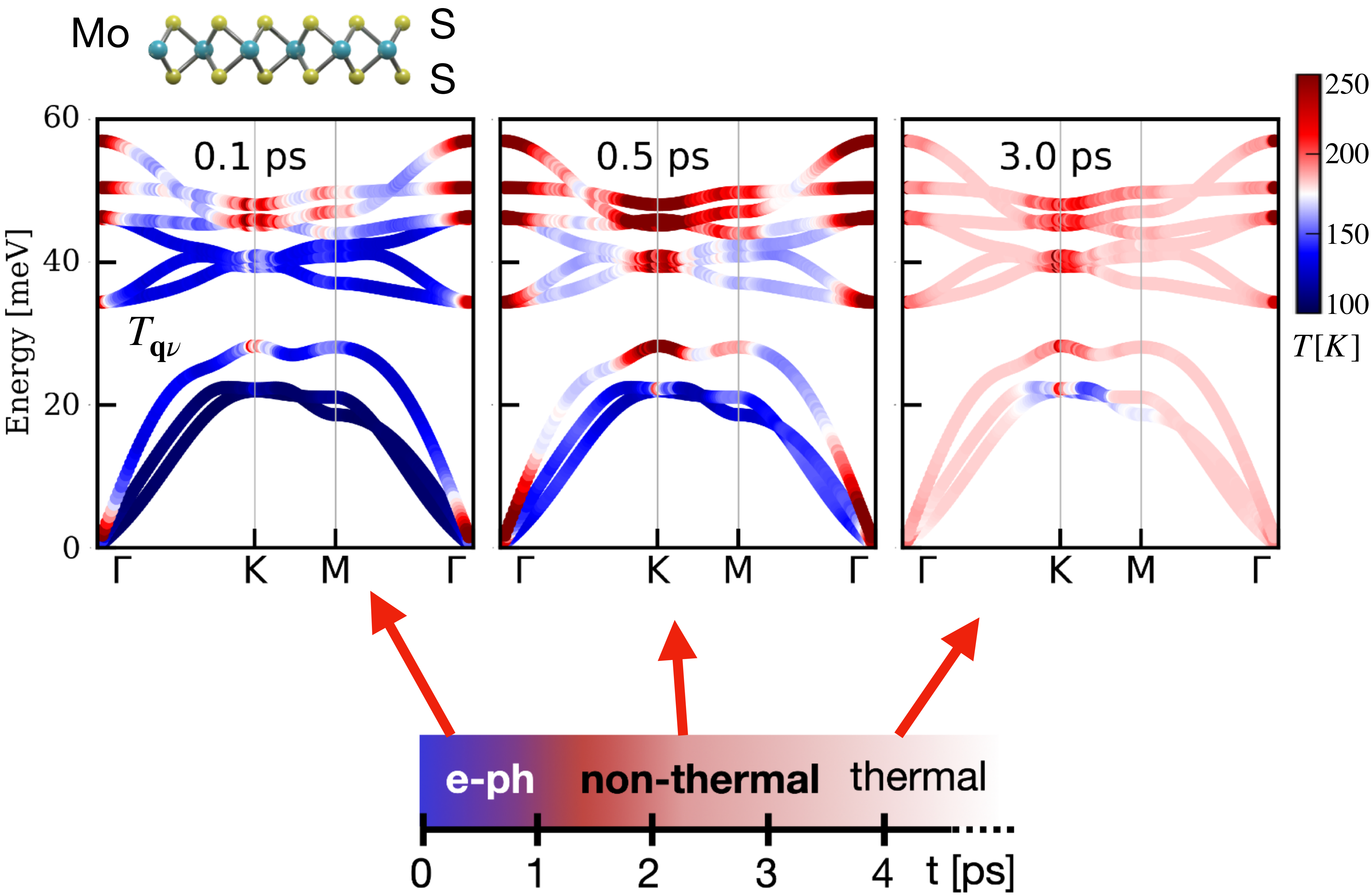
Energy cons.: $\hbar\omega_{\mathbf{q}\nu} = \varepsilon_{n\mathbf{k}} - \varepsilon_{n\mathbf{k}'}$

Momentum cons.: $\mathbf{q} = \mathbf{k}' - \mathbf{k}$



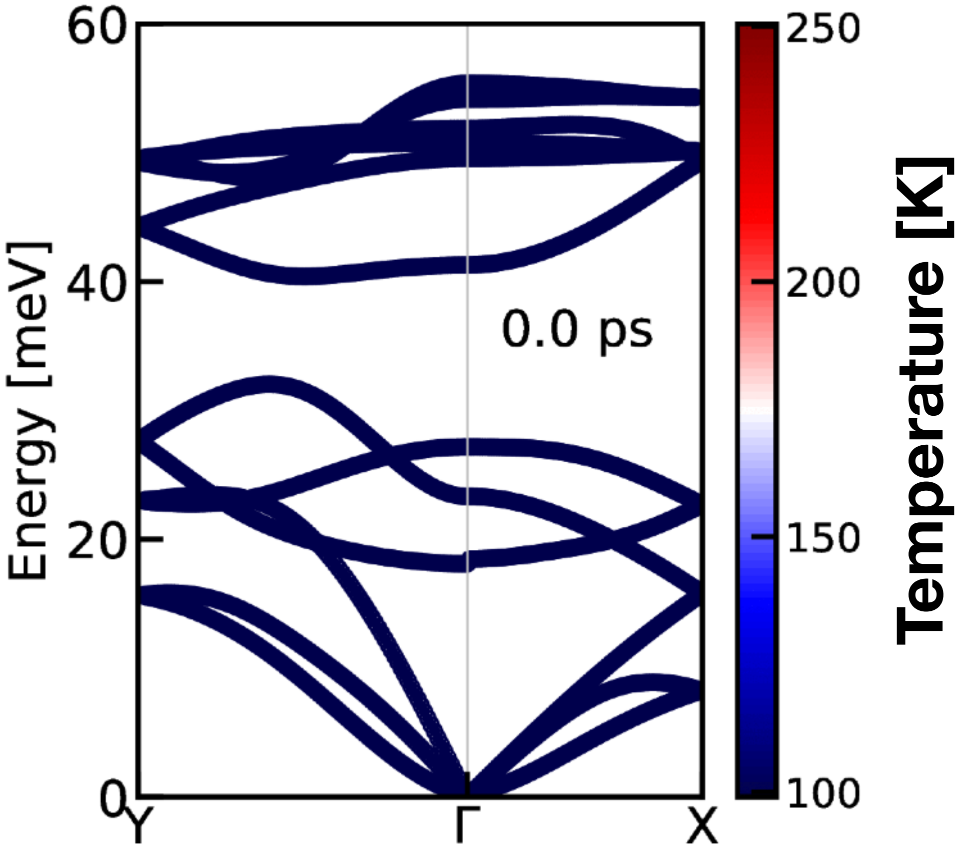
Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

Regimes of nonequilibrium phonon dynamics



Caruso, J. Phys. Chem. Lett. 12, 1274 (2021)

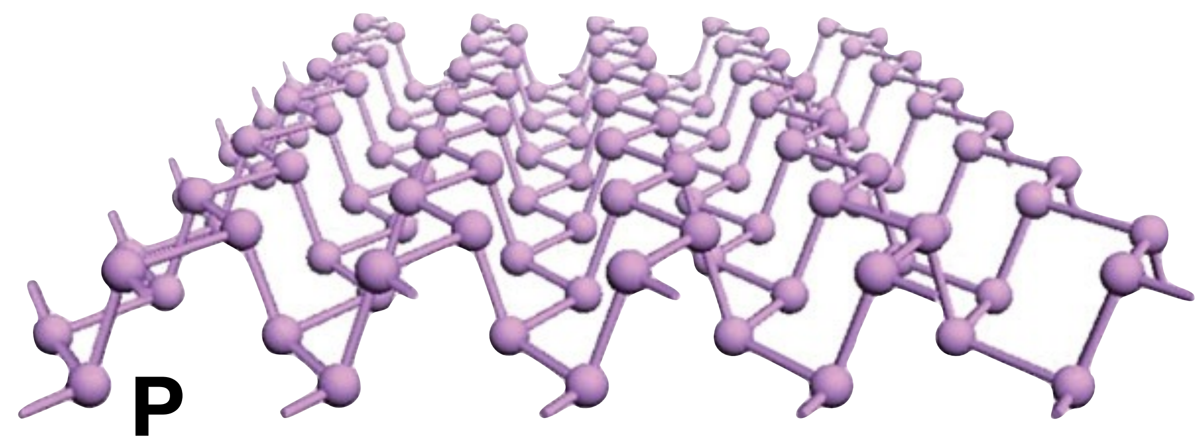
Nonequilibrium lattice dynamics: phosphorene

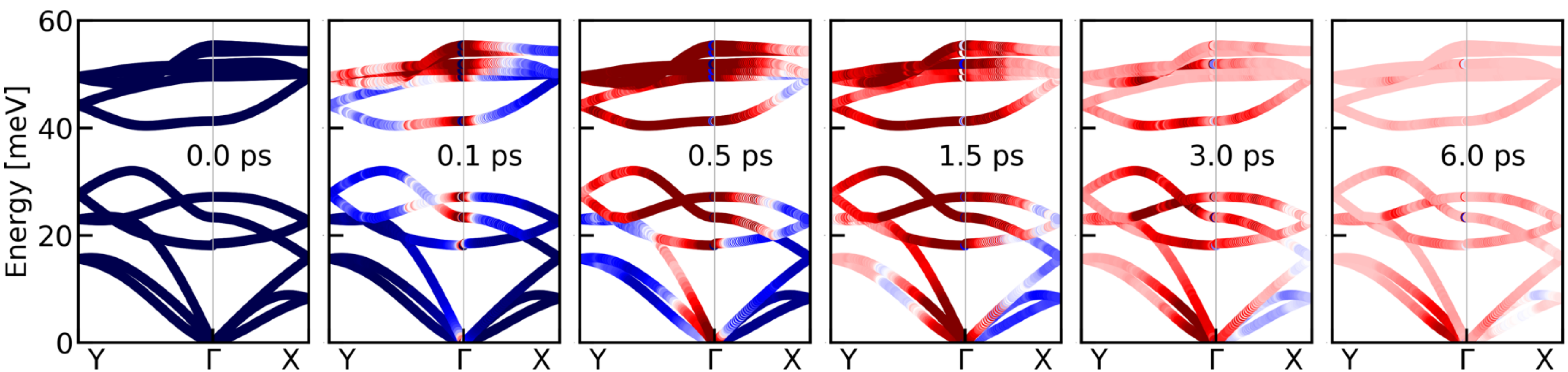


nonequilibrium dynamics of the lattice

↕

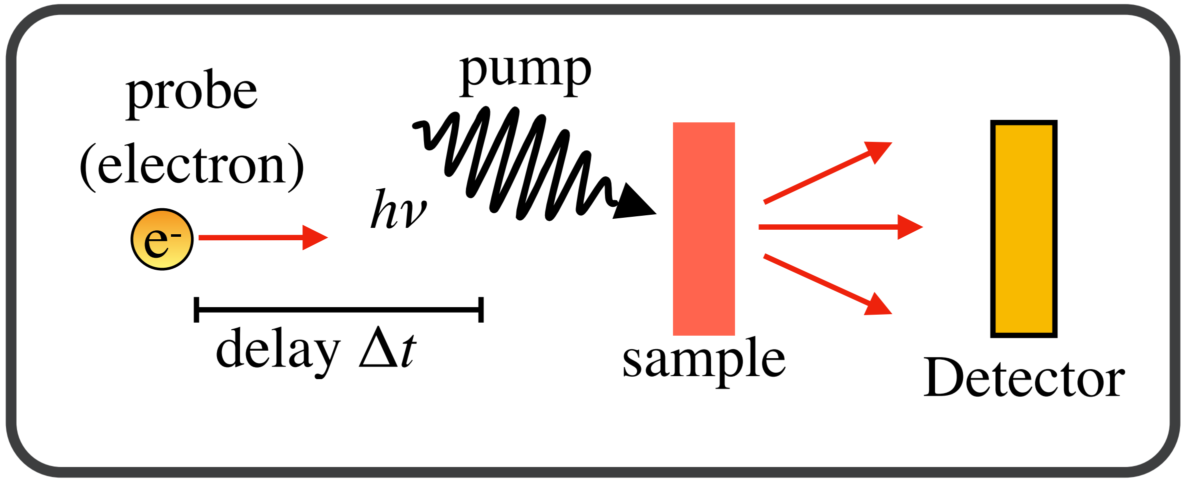
phase space for electronic transitions



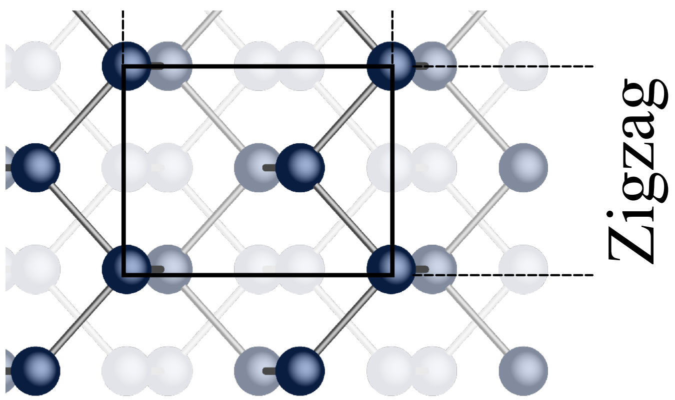


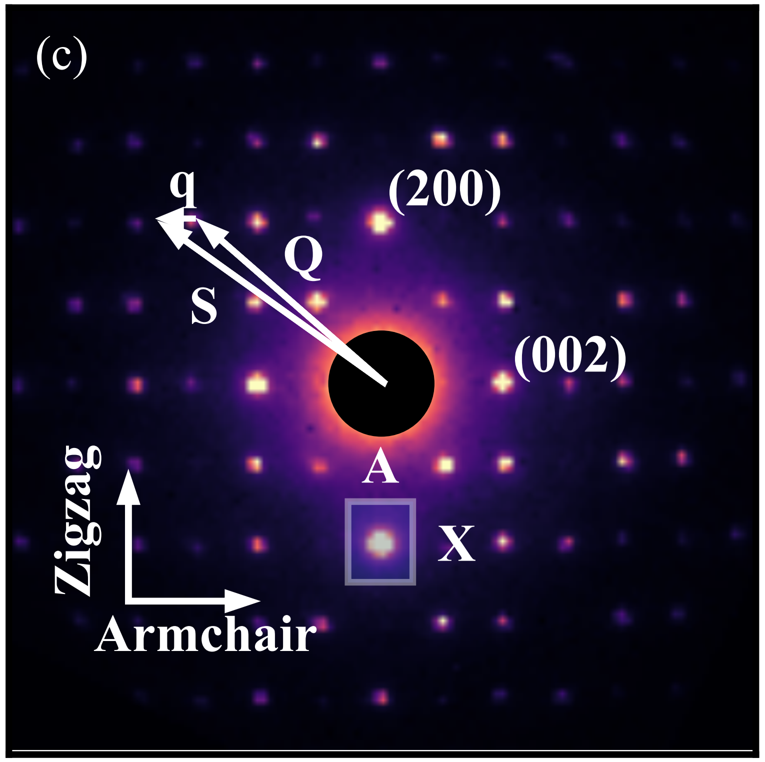
Electron diffuse scattering: black Phosphorus

Femto-second electron diffuse scattering (FEDS)



Black phosphorus



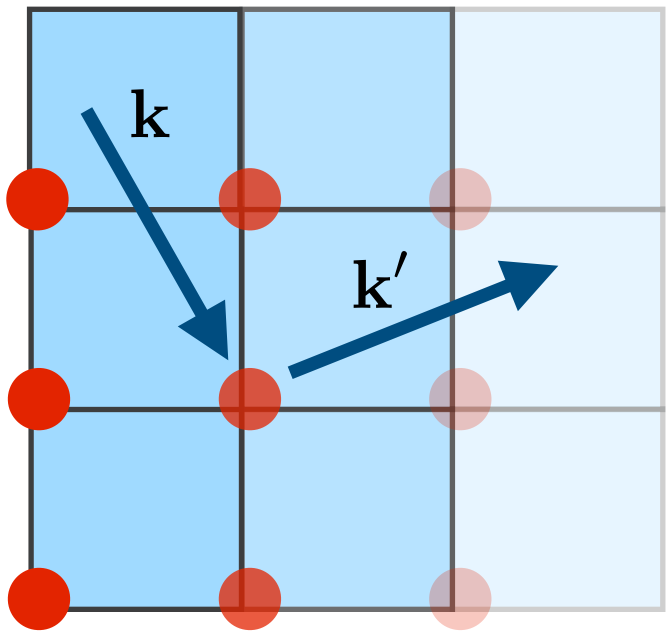


Experiments: FHI Berlin

Helene Seiler

Ralph Ernstorfer

Diffraction from a lattice

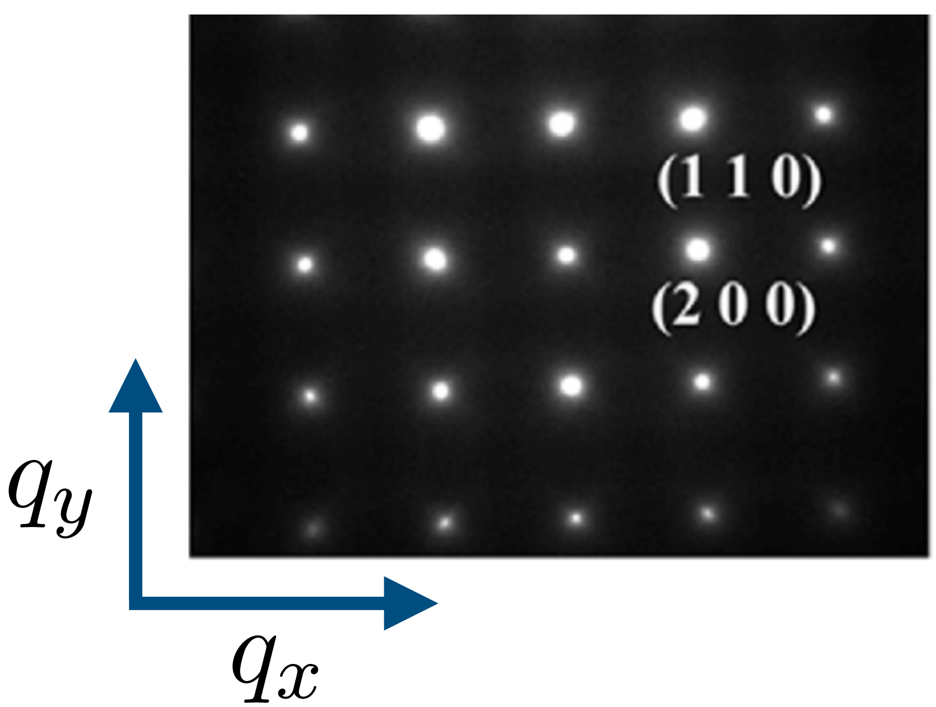


Bragg's law for interference condition:

$$A(\mathbf{q}) = \sum_{p}^{N_p} f_0 \exp\left[i\mathbf{q}\cdot\mathbf{R}_p\right]$$

- $A(\mathbf{q})$: amplitude
- f_0: Scattering cross section
- $\mathbf{q} = \mathbf{k}' - \mathbf{k}$: Transferred momentum
- $\mathbf{R}_p$: Lattice vector

example: Cubic lattice

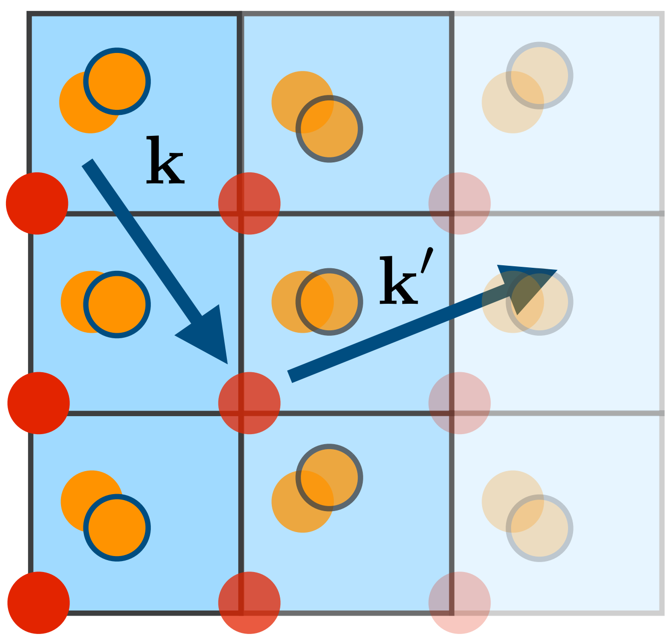


Scattering intensity for a perfect lattice:

$$I(\mathbf{q}) = |A(\mathbf{q})|^2 \simeq \delta_{\mathbf{q},\mathbf{G}}$$

- $\mathbf{G}$: Reciprocal lattice vector

Diffraction from a vibrating lattice



Zero-phonon term:

$$\langle I_0(\mathbf{S})\rangle_T = N_p^2|f_0|^2\exp(-2W_T)\delta_{\mathbf{S},\mathbf{G}}$$

Debye-Waller factor:

$$2W_T = \frac{1}{M_\kappa N_p}\sum_{\mathbf{q}\nu}\left[\sum_{\alpha\alpha'} S_\alpha S_{\alpha'} e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu *}_{\kappa\alpha'}(\mathbf{q})\right] E_{\mathbf{q}\nu,T}$$

One-phonon (dynamical) structure factor

$$\langle I_1(\mathbf{S},E)\rangle_T = |f_0|^2\exp(-2W_T)\frac{\hbar^2 N_p}{2M_\kappa}\sum_{\mathbf{q}\nu}\left[\sum_{\alpha\alpha'} S_\alpha S_{\alpha'} e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu *}_{\kappa\alpha'}(\mathbf{q})\right]\frac{1}{\hbar\omega_{\mathbf{q}\nu}} \times \left[\delta(\mathbf{S}+\mathbf{q})n_{\mathbf{q}\nu,T}\delta(E+\hbar\omega_{\mathbf{q}\nu}) + \delta(\mathbf{S}-\mathbf{q})(n_{\mathbf{q}\nu,T}+1)\delta(E-\hbar\omega_{\mathbf{q}\nu})\right]. \quad (16)$$

from the time-dependent Boltzmann equation

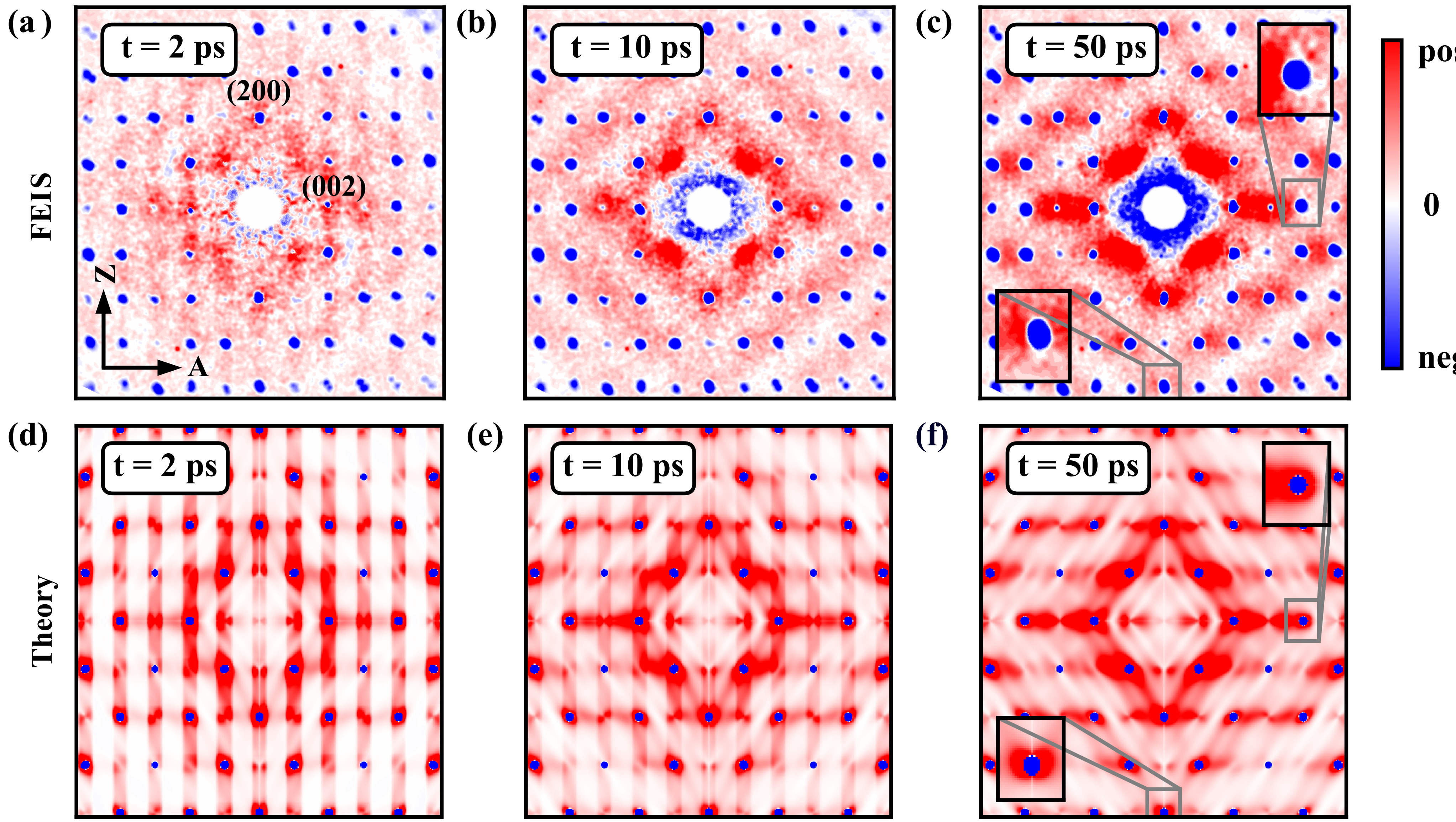
First-principles approach to Femto-second electron diffuse scattering (FEDS)

Microscopic origin of non-equilibrium lattice dynamics in bP

Intensity difference: $I(\mathbf{S},t) - I(\mathbf{S},t < t_0)$

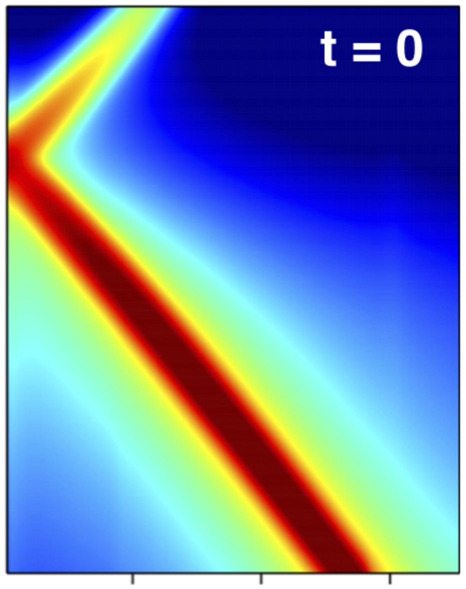
Experiment:

Theory:



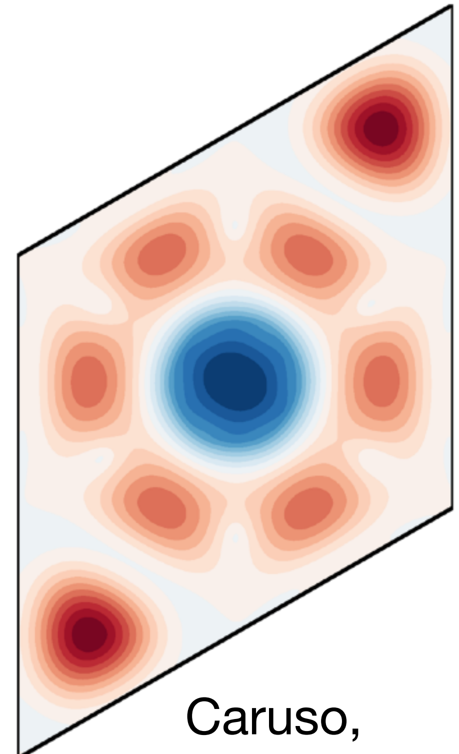
Marios Zacharias

Ultrafast dynamics of electrons and phonons



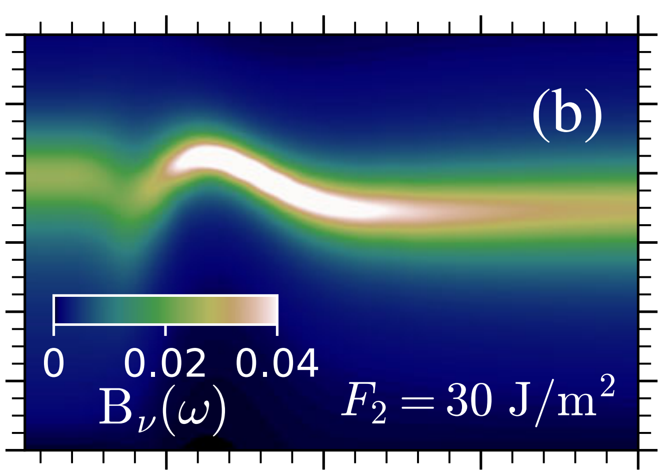
Nonequilibrium carrier dynamics in graphene

Caruso, Novko, Draxl,
Phys. Rev. B **101** 035128 (2020)



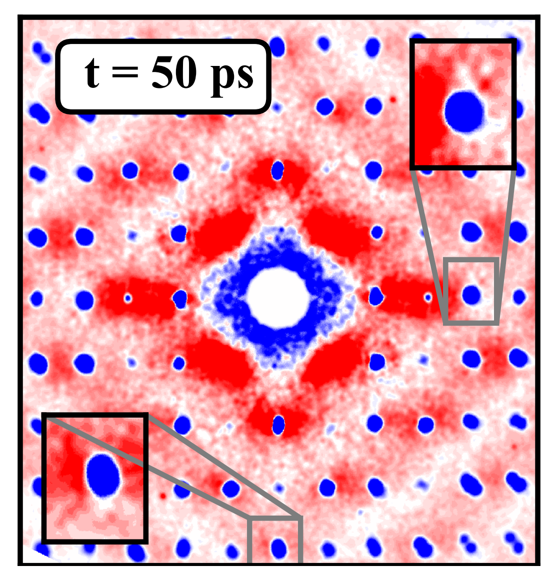
Nonequilibrium lattice dynamics in MoS_2

Caruso,
J. Phys. Chem. Lett. 12, 1274 (2021)



Transient phonon renormalization in MgB_2

Novko, Caruso, Draxl, Cappelluti,
Phys. Rev. Lett. **124** 077001 (2020)



Signatures of nonequilibrium lattice dynamics in phosphorene

Seiler, Zahn, Zacharias, et al.
arXiv (2020)

Acknowledgements

THEORY

Humboldt-Universität zu Berlin

- Claudia Draxl
- Pasquale Pavone
- Ignacio Gonzales-Oliva
- Maximilian Schebek
- Sebastian Tillak

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- Marios Zacharias

Institut of Physics, Zagreb

- Dino Novko

EXPERIMENTS

Fritz Haber Institute, Berlin

- Helene Seiler
- Daniela Zahn
- Ralph Ernstorfer

EPW:
S. Poncé et al.,
Comp. Phys. Comm. (2017)

Quantum Espresso:
P. Giannozzi et al., J. Phys.:
Condens. Matter 29, 465901 (2017)

Wannier90: G. Pizzi et al., J. Phys.
Cond. Matt. 32, 165902 (2020)

ShengBTE:
W. Li et al., Comp. Phys.
Comm. 185, 1747 (2014)

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