Introduction to energy transport and chemical models for highly excited insulators

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Queen's University Belfast

- Established in 1845, 9th oldest in the UK.
- Research-intensive, world-class university.
- Over 25,000 students: 17,000 UG and 8,000 PG.

85th most impactful university globally tackling the UN Sustainable Development Goals *(THE Impact Rankings 2023)*

99% of our research environment is world-leading or internationally excellent *(REF 2021)*

15 subjects in the global top 200 *(QS World Rankings 2023)*

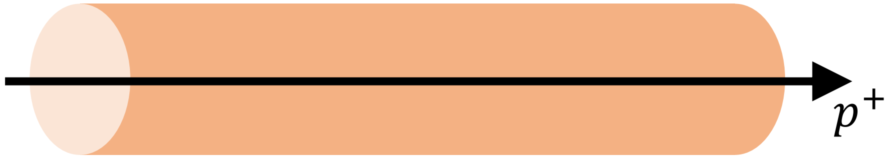
#1 University in the UK for entrepreneurial impact *(Entrepreneurial Impact Ranking, Octopus Venues*

Outline of the talk

- ❑ Experimental and theoretical motivations.
- ❑ From Boltzmann transport equation to hydrodynamic models.
- ❑ From hydrodynamic models to (simplified) energy transport models.
- ❑ Electrons (an holes) as a fluid.
- ❑ Generation & recombination in highly excited insulators.
- ❑ Excitons and band gap renormalisation.

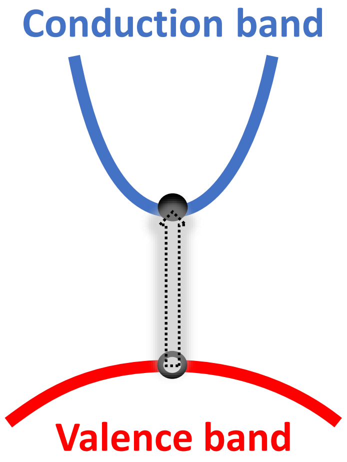
Highly excited insulators

- For instance, upon proton irradiation of a-SiO_2.



$$r_c = \frac{\hbar v_{ion}}{2E_{gap}}$$

- **Very localised** excitation of electron-holes pairs.



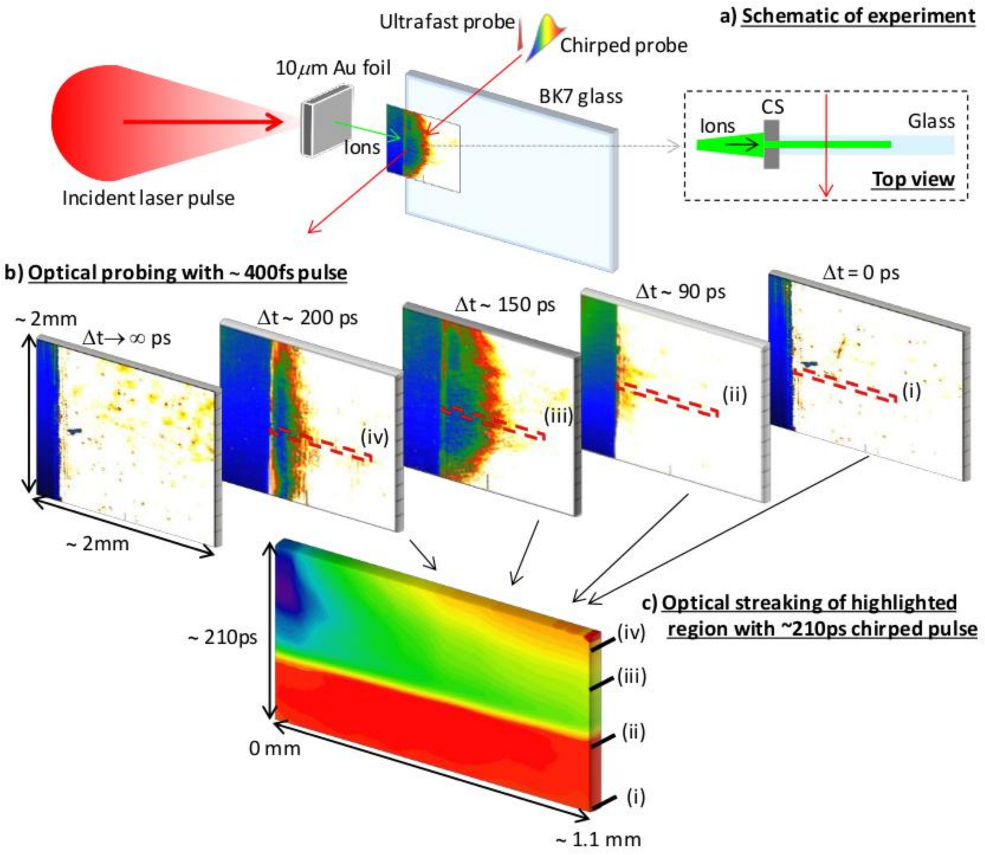
$$E_g = 8.7 \text{ eV}$$

- **Question**: How does the excited insulator relax?

What do we want to achieve?

- ❑ Model the relaxation of highly excited insulators.
- ❑ Use a model that is good for both bulk and nanostructure materials.
- ❑ Capitalise on the know-how from semiconductor modelling.
- ❑ Explain some unexpected experimental results.

Experimental background



Proton "pump" + IR (1053 nm) "probe"

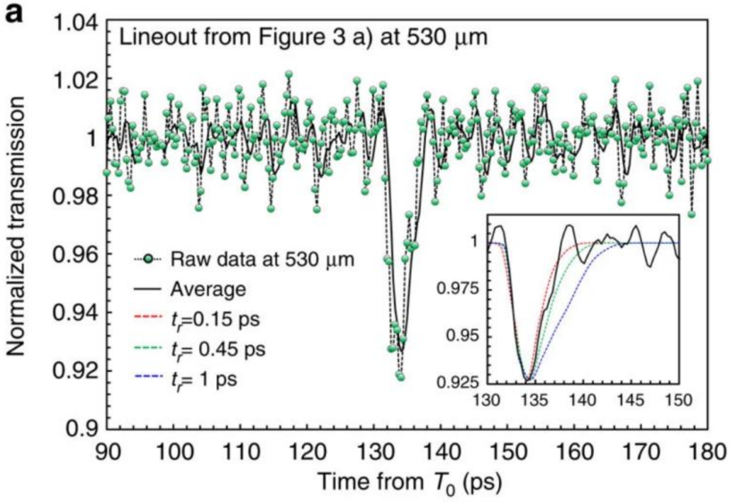
- ❑ **Ultrashort proton pulses (~3.5 ps)**
- ❑ **Optical streaking (chirped IR pulse ~ 1.2 ns)**

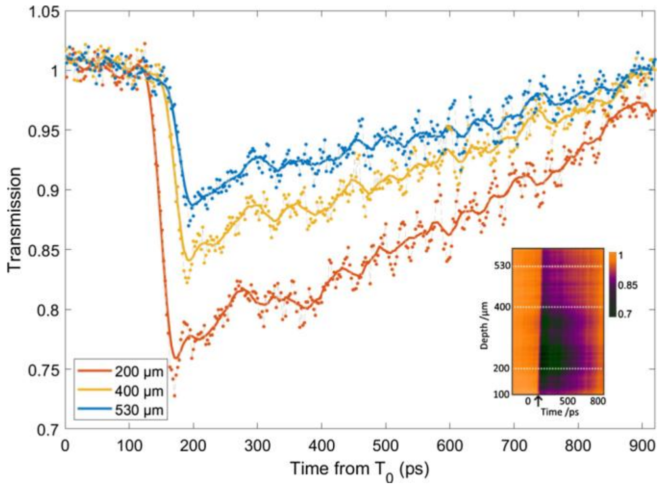
Spatially resolved (<1 mm) transient absorption

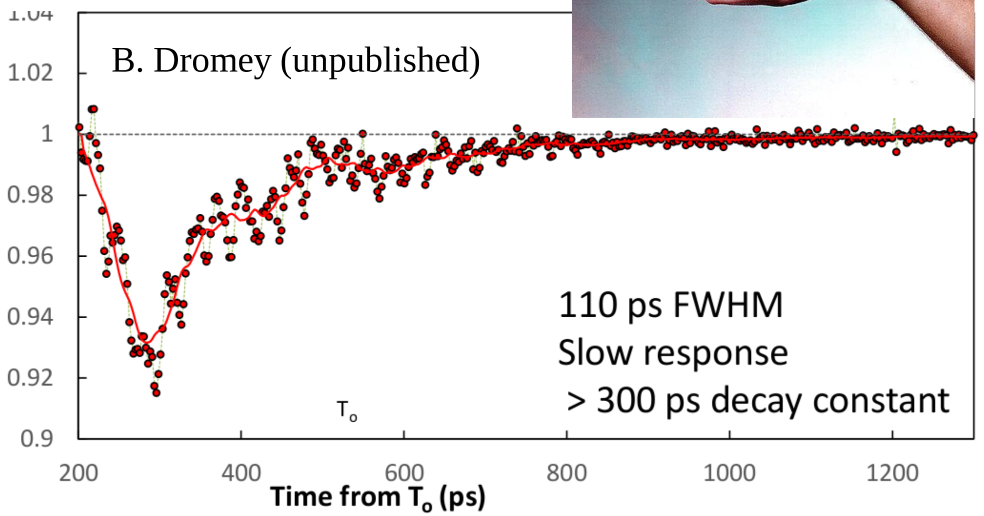
M. Coughlan *et al.* New J. Phys. **22** 103023 (2020)
B. Dromey *et al*. Nature Comm. **7** 10642 (2016)

Experimental background

Image: NASA







Fused silica (a-SiO_2)

Decay constant ~ 3.5 ps

Band gap: 8.7 eV

Density: 2.66 g/cm^3

Borosilicate glass (BK7)

Decay constant ~ 620 ps

Band gap: 4 eV

Density: 2.23 g/cm^3

Silica aerogel (10%)

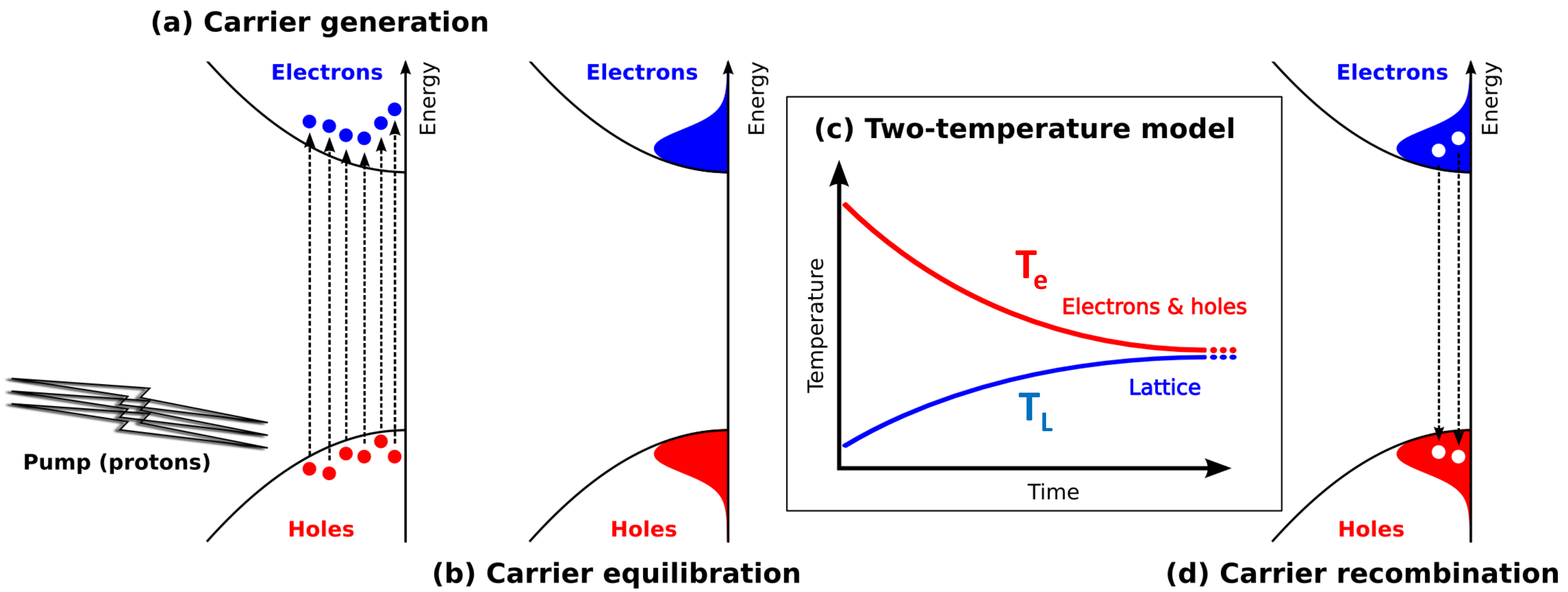
Decay constant ~ 300 ps

Band gap: 8.7 eV

Density: 0.26 g/cm^3

M. Coughlan *et al.* New J. Phys. **22** 103023 (2020)
B. Dromey *et al.* Nature Comm. **7** 10642 (2016)

Electron-hole generation & recombination



~ 10 fs

~ 0.1–1 ps

Exciton, Auger, SRH, radiative…

Knowledge transfer

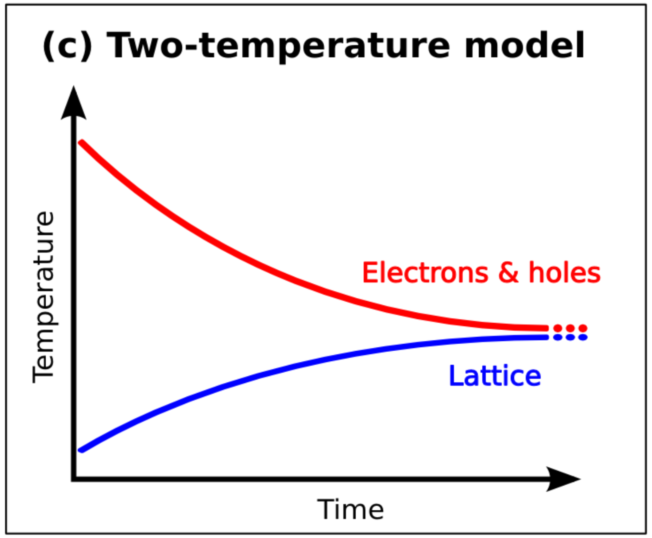
- An inspiring paper: S. Klaumünzer, *Thermal-Spike Models for Ion Track Physics: A critical Examination*, 2006.

> *"Thermal-spike models are only not used in ion-track physics, but also to describe the behaviour of excited carriers generated by femtosecond lasers or by strong electrical fields in submicron semiconductor devices. Though these various models deal with similar physical problems, they do not take too much notice of each other.* ***The consequence is that knowledge, which has been gained in one field, is not transferred to the others****."*

- The rest of this talk is just my attempt to explore this "Klaumünzer's programme".

The Thermal-spike model

- An established model of track formation.



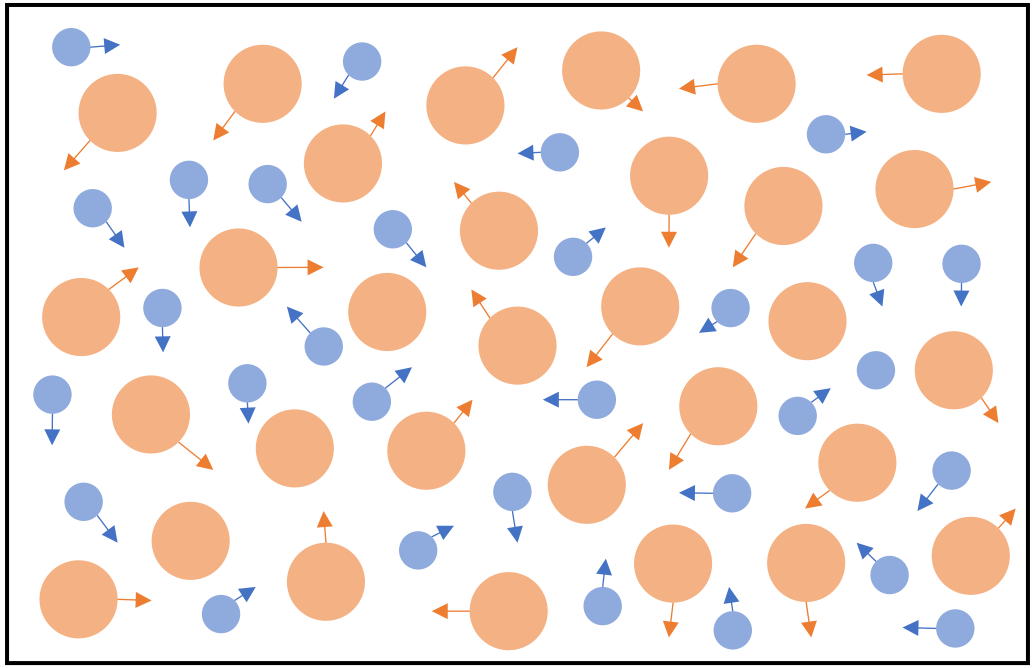
$$C_{v,e}\frac{\partial T_e}{\partial t} + \nabla \cdot \boldsymbol{q}_e = -g(T_e - T_L) + B(\boldsymbol{r}, t) \qquad \boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$C_{v,L}\frac{\partial T_L}{\partial t} + \nabla \cdot \boldsymbol{q}_L = g(T_e - T_L) \qquad \boldsymbol{q}_L = -\kappa_L \nabla T_L$$

"A severe deficiency of the currently used thermal-spike models in ion track physics is the missing distinction between the two kinds of excitations in semiconductors and insulators, namely electrons in the conduction bands and holes in the valence band. However, ***this distinction is essential to exploit the wealth of information available in the physics of semiconductors and insulators****."*

Statistical description

- Atomistic approaches are very accurate for bulk properties, *e.g.*, transport coefficients.
- For nanostructure materials, *e.g.*, aerogels, it is more convenient to model continuous media, *e.g.*, fluids.
- We don't look at the properties of the individual atoms, but at their "average properties".



Boltzmann transport equation

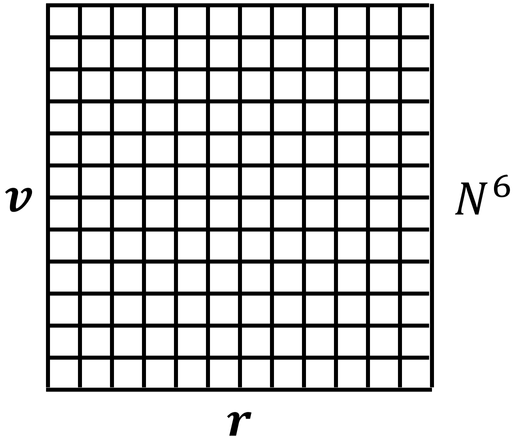
Source: Wikipedia

- ❑ Equation of motion for the distribution function, $f_\alpha(\boldsymbol{r},\boldsymbol{v},t)$, of species α:

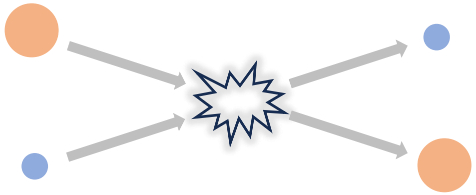
$$\frac{\partial f_\alpha}{\partial t} + \boldsymbol{v}\cdot\nabla f_\alpha + \boldsymbol{a}\cdot\nabla_v f_\alpha = \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

- ❑ Without collisions, the distribution is just “transported”.

$$f_\alpha(\boldsymbol{r},\boldsymbol{v},t) \simeq f_\alpha(\boldsymbol{r}-\boldsymbol{v}\Delta t,\boldsymbol{v}-\boldsymbol{a}\Delta t,t-\Delta t)$$

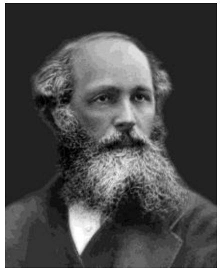


- ❑ For gases: kinetic energy ≫ potential energy.
- ❑ Only binary collisions (default).



Bittencourt, *Fundamentals of Plasma*, 3rd edition, 2004 --- Chapter 5

Method of Moments


Source: Wikipedia

- Velocity moments of the distribution function, $f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)$, of species α.
- The microscopic velocity, $\boldsymbol{v}$, does not have a fixed value (stochastic variable).


Source: L.S.

$$\langle \chi(\boldsymbol{v}) \rangle_\alpha = \frac{\int d^3\boldsymbol{v}\, \chi(\boldsymbol{v}) f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)}{\int d^3\boldsymbol{v}\, f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)}$$

Average

$$\int d^3\boldsymbol{v}\, f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t) = \frac{N_\alpha}{V} = n_\alpha$$

Normalisation

$$\langle v_i \rangle_\alpha = \frac{\int d^3\boldsymbol{v}\, v_i f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)}{n_\alpha} = u_{\alpha,i}$$

Average velocity

$$\langle v_i v_j \rangle_\alpha = \frac{\int d^3\boldsymbol{v}\, v_i v_j f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)}{n_\alpha} = \frac{\Pi_{\alpha,ij}}{m_\alpha n_\alpha} = \frac{\Pi_{\alpha,ij}}{\rho_\alpha}$$

Momentum transfer tensor

Bittencourt, *Fundamentals of Plasma*, 3rd edition, 2004 --- Chapter 6

Momentum flux tensor

- The microscopic velocity, $\boldsymbol{v}$, does not have a fixed value (stochastic variable).
- The macroscopic velocity field, $\boldsymbol{u}_\alpha(\boldsymbol{r}, t)$, is well-defined (average).

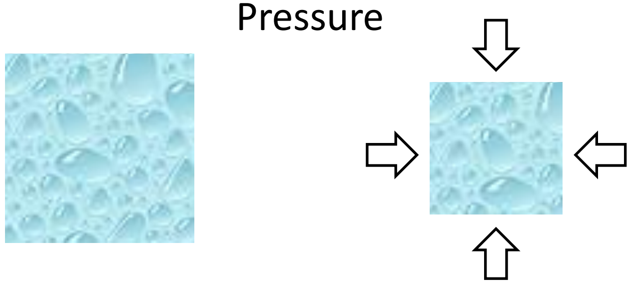
$$\boldsymbol{v} = \boldsymbol{u}_\alpha(\boldsymbol{r}, t) + \boldsymbol{c}_\alpha$$

$$\Pi_{\alpha,ij}(\boldsymbol{r}, t) = \rho_\alpha(\boldsymbol{r}, t)\langle v_i v_j\rangle_\alpha = \rho_\alpha(\boldsymbol{r}, t)\langle c_{\alpha,i} c_{\alpha,j}\rangle_\alpha - \rho_\alpha(\boldsymbol{r}, t) u_{\alpha,i}(\boldsymbol{r}, t) u_{\alpha,j}(\boldsymbol{r}, t)$$

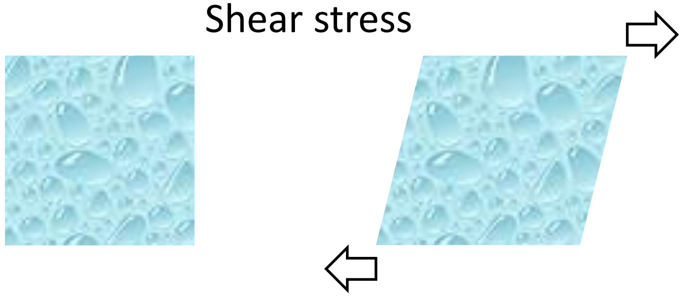
$$\boldsymbol{P}_{\alpha,ij} = \rho_\alpha(\boldsymbol{r}, t)\langle c_{\alpha,i} c_{\alpha,j}\rangle_\alpha$$

Pressure tensor

Pressure

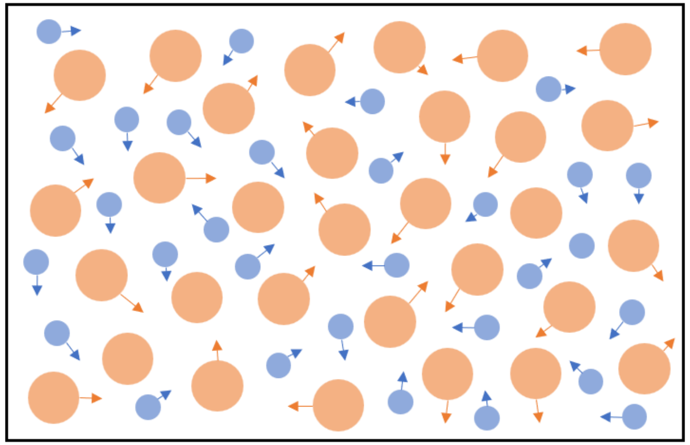


Shear stress



Kinetic energy density

- The microscopic velocity, $\boldsymbol{v}$, does not have a fixed value (stochastic variable).
- The macroscopic velocity field, $\boldsymbol{u}_\alpha(\boldsymbol{r},t)$, is well-defined (average).
- Both contribute to the kinetic energy (classical).



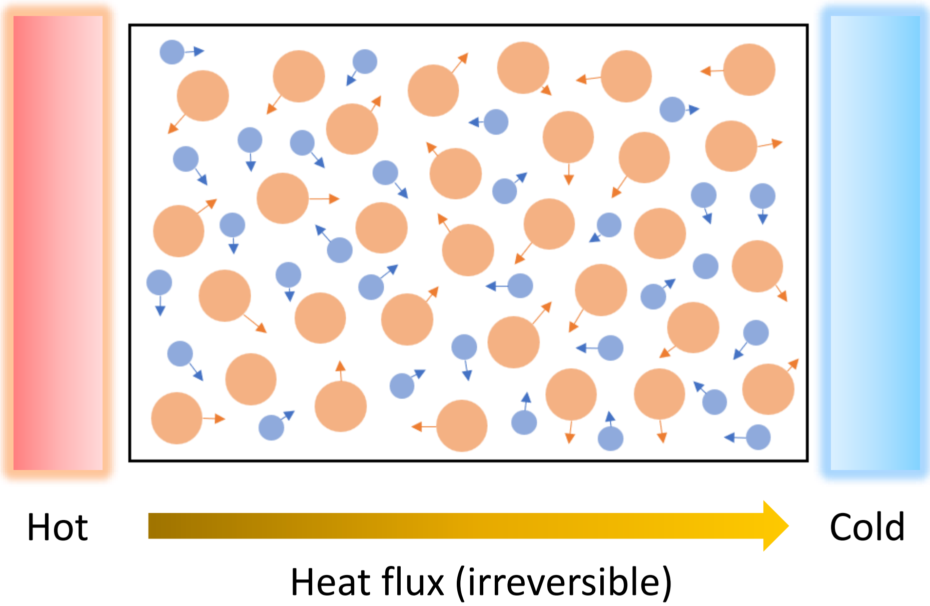
$$W_\alpha = n_\alpha(\boldsymbol{r},t)\left\langle \frac{m_\alpha}{2}\boldsymbol{v}_\alpha^2 \right\rangle_\alpha = \frac{\rho_\alpha(\boldsymbol{r},t)}{2}\int d^3\boldsymbol{v}\,(\boldsymbol{u}_\alpha(\boldsymbol{r},t)+\boldsymbol{c}_\alpha)^2 f_\alpha(\boldsymbol{r},\boldsymbol{v},t)$$

$$= \frac{\rho_\alpha(\boldsymbol{r},t)}{2}\boldsymbol{u}_\alpha^2(\boldsymbol{r},t) + \frac{\rho_\alpha(\boldsymbol{r},t)}{2}\int d^3\boldsymbol{v}\,\boldsymbol{c}_\alpha^2 f_\alpha(\boldsymbol{r},\boldsymbol{v},t)$$

$$W_\alpha = \frac{\rho_\alpha(\boldsymbol{r},t)}{2}\boldsymbol{u}_\alpha^2(\boldsymbol{r},t) + \frac{1}{2}\mathrm{Tr}\{\boldsymbol{P}_\alpha\}$$

Energy flow

- The microscopic velocity, $\boldsymbol{v}$, does not have a fixed values (stochastic variable).
- The macroscopic velocity field, $\boldsymbol{u}_\alpha(\boldsymbol{r},t)$, is well-defined (average).
- Both contribute to the kinetic energy (classical).

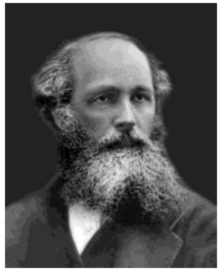


$$n_\alpha(\boldsymbol{r},t)\left\langle\frac{m_\alpha}{2}\boldsymbol{v}_\alpha\boldsymbol{v}_\alpha^2\right\rangle_\alpha = W_\alpha(\boldsymbol{r},t)\boldsymbol{u}_\alpha(\boldsymbol{r},t) + \boldsymbol{u}_\alpha(\boldsymbol{r},t)\cdot\boldsymbol{P}_\alpha(\boldsymbol{r},t) + \boldsymbol{q}_\alpha(\boldsymbol{r},t)$$

$$\boldsymbol{q}_\alpha(\boldsymbol{r},t) = n_\alpha(\boldsymbol{r},t)\left\langle\frac{m_\alpha}{2}\boldsymbol{c}_\alpha\boldsymbol{c}_\alpha^2\right\rangle_\alpha = \frac{\rho_\alpha(\boldsymbol{r},t)}{2}\langle\boldsymbol{c}_\alpha\boldsymbol{c}_\alpha^2\rangle_\alpha$$

Check point 1

Macroscopic transport equations


Source: Wikipedia

- Velocity moments of the distribution function, $f_\alpha(\boldsymbol{r}, \boldsymbol{v}, t)$, of species α.
- The <u>microscopic</u> velocity, $\boldsymbol{v}$, does <u>not</u> have a fixed value (stochastic variable).

$$\frac{\partial f_\alpha}{\partial t} + \boldsymbol{v}\cdot\nabla f_\alpha + \boldsymbol{a}\cdot\nabla_v f_\alpha = \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

$$\int d^3\boldsymbol{v}\,\chi(\boldsymbol{v})\frac{\partial f_\alpha}{\partial t} + \int d^3\boldsymbol{v}\,\chi(\boldsymbol{v})(\boldsymbol{v}\cdot\nabla f_\alpha) + \int d^3\boldsymbol{v}\,\chi(\boldsymbol{v})(\boldsymbol{a}\cdot\nabla_v f_\alpha) = \int d^3\boldsymbol{v}\,\chi(\boldsymbol{v})\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

$$\frac{\partial}{\partial t}(n_\alpha\langle\chi\rangle_\alpha) + \nabla\cdot(n_\alpha\langle\chi\boldsymbol{v}\rangle_\alpha) - n_\alpha(\boldsymbol{a}\cdot\nabla_v\boldsymbol{\chi}) = \int d^3\boldsymbol{v}\,\chi(\boldsymbol{v})\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

$\chi(\boldsymbol{v}) = m_\alpha$ $\qquad$ $\chi(\boldsymbol{v}) = m_\alpha\boldsymbol{v}$ $\qquad$ $\chi(\boldsymbol{v}) = \frac{m_\alpha}{2}\boldsymbol{v}^2$

Macroscopic transport equations

Mass balance (continuity)

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha \boldsymbol{u}_\alpha) = m_\alpha \int d^3\boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

$$\chi(\boldsymbol{v}) = m_\alpha$$

Momentum balance

$$\rho_\alpha \left[\frac{\partial \boldsymbol{u}_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\boldsymbol{u}_\alpha\right] + \nabla \cdot \boldsymbol{P}_\alpha - \rho_\alpha \langle \boldsymbol{a} \rangle_\alpha = m_\alpha \int d^3\boldsymbol{v}\, \boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} - m_\alpha \boldsymbol{u}_\alpha \int d^3\boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

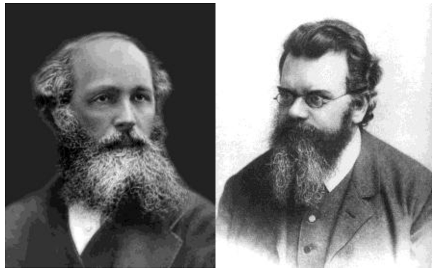
$$\chi(\boldsymbol{v}) = m_\alpha \boldsymbol{v}$$

(kinetic) energy balance

$$\frac{1}{2}\left[\frac{\partial \mathrm{Tr}\{\boldsymbol{P}_\alpha\}}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\mathrm{Tr}\{\boldsymbol{P}_\alpha\}\right] + \frac{\mathrm{Tr}\{\boldsymbol{P}_\alpha\}}{2} \nabla \cdot \boldsymbol{u}_\alpha + (\boldsymbol{P}_\alpha \cdot \nabla) \cdot \boldsymbol{u}_\alpha + \nabla \cdot \boldsymbol{q}_\alpha$$
$$= \frac{m_\alpha}{2} \int d^3\boldsymbol{v}\, \boldsymbol{v}^2 \chi(\boldsymbol{v}) \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} - m_\alpha \boldsymbol{u}_\alpha \cdot \int d^3\boldsymbol{v}\, \boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} + \frac{m_\alpha}{2} \boldsymbol{u}_\alpha^2 \int d^3\boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.}$$

$$\chi(\boldsymbol{v}) = \frac{m_\alpha}{2} \boldsymbol{v}^2$$

Local Maxwell-Boltzmann distribution



Source: Wikipedia

- Velocity moments of the distribution function, $f_\alpha(\boldsymbol{r},\boldsymbol{v},t)$, of species α.
- Local equilibrium for species α

$$f_\alpha^0(\boldsymbol{r},\boldsymbol{v},t) = n_\alpha(\boldsymbol{r},t)\left(\frac{m_\alpha}{2\pi k_B T_\alpha(\boldsymbol{r},t)}\right)^{\frac{3}{2}} e^{-\frac{m_\alpha(\boldsymbol{v}-\boldsymbol{u}_\alpha(\boldsymbol{r},t))^2}{2k_B T_\alpha(\boldsymbol{r},t)}}$$

$$\int d^3\boldsymbol{v}\, f_\alpha^0(\boldsymbol{r},\boldsymbol{v},t) = \frac{N_\alpha}{V} = n_\alpha(\boldsymbol{r},t)$$

Normalisation

$$\langle v_i\rangle_\alpha^0 = \frac{\int d^3\boldsymbol{v}\, v_i f_\alpha^0(\boldsymbol{r},\boldsymbol{v},t)}{n_\alpha(\boldsymbol{r},t)} = u_{\alpha,i}(\boldsymbol{r},t)$$

Average velocity

$$\langle v_i v_j\rangle_\alpha^0 = \frac{\int d^3\boldsymbol{v}\, v_i v_j f_\alpha^0(\boldsymbol{r},\boldsymbol{v},t)}{n_\alpha(\boldsymbol{r},t)} = \frac{k_B T_\alpha(\boldsymbol{r},t)}{m_\alpha}\delta_{ij} - u_{\alpha,i}(\boldsymbol{r},t)u_{\alpha,j}(\boldsymbol{r},t)$$

Kinetic temperature

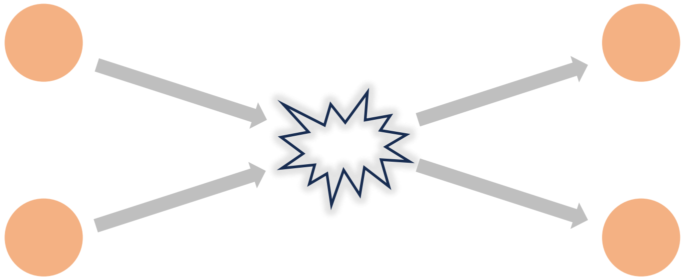
$$\langle v_i v^2\rangle_\alpha^0 = \frac{\int d^3\boldsymbol{v}\, v_i v^2 f_\alpha^0(\boldsymbol{r},\boldsymbol{v},t)}{n_\alpha(\boldsymbol{r},t)} = 0$$

Heat flux

Bittencourt, *Fundamentals of Plasma*, 3rd edition, 2004 --- Chapter 7

Conservation laws & collisions

- Mass, momentum and energy conserved in homogeneous (*i.e.*, same species) collisions.
- Ideal fluid behaviour.



$$\int d^3\boldsymbol{v}\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0$$

$$m_\alpha \int d^3\boldsymbol{v}\,\boldsymbol{v}\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0$$

$$\frac{m_\alpha}{2}\int d^3\boldsymbol{v}\,\boldsymbol{v}^2\chi(\boldsymbol{v})\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0$$

Euler's hydrodynamics

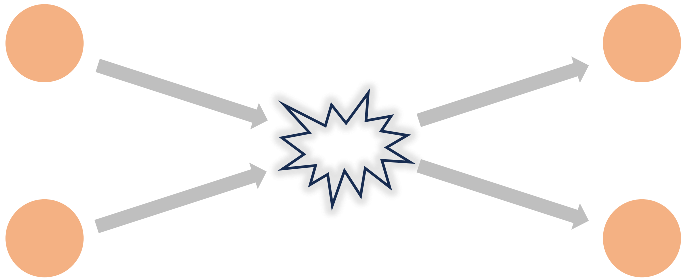
Source: Wikipedia

- No viscosity: $\boldsymbol{P}_{\alpha,ij} = p_\alpha \delta_{ij} = n_\alpha(\boldsymbol{r},t) k_B T_\alpha(\boldsymbol{r},t)\delta_{ij}$.
- No irreversible heat transfer: $\boldsymbol{q}_{\alpha,i} = 0$.
- <u>Compressible</u> ideal fluid.

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha \boldsymbol{u}_\alpha) = 0$$

$$\rho_\alpha \left[\frac{\partial \boldsymbol{u}_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\boldsymbol{u}_\alpha\right] + \nabla p_\alpha - \rho_\alpha \langle \boldsymbol{a} \rangle_\alpha = 0$$

$$\frac{3}{2}\left[\frac{\partial p_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla) p_\alpha\right] + \frac{5}{2} p_\alpha (\nabla \cdot \boldsymbol{u}_\alpha) = 0$$



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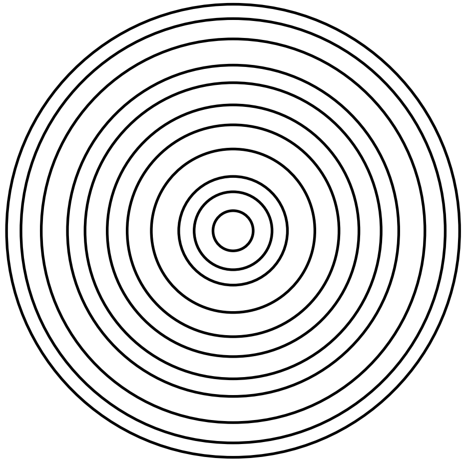
Adiabaticity

- No viscosity: $\boldsymbol{P}_{\alpha,ij} = p_\alpha \delta_{ij} = n_\alpha(\boldsymbol{r},t) k_B T_\alpha(\boldsymbol{r},t)\delta_{ij}$.
- No irreversible heat transfer: $\boldsymbol{q}_{\alpha,i} = 0$.
- Compressible ideal fluid.



$$\left[\frac{\partial \rho_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\rho_\alpha\right] + \rho_\alpha(\nabla \cdot \boldsymbol{u}_\alpha) = 0$$

$$\rho_\alpha \left[\frac{\partial \boldsymbol{u}_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\boldsymbol{u}_\alpha\right] + \nabla p_\alpha - \rho_\alpha \langle \boldsymbol{a} \rangle_\alpha = 0$$

Speed of "sound" $c_{s,\alpha} = \sqrt{\gamma \frac{p_\alpha^0}{\rho_\alpha^0}} = \sqrt{\frac{\gamma k_B T_\alpha^0}{m_\alpha}}$

$$\left[\frac{\partial p_\alpha}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)p_\alpha\right] + \frac{5}{3} p_\alpha(\nabla \cdot \boldsymbol{u}_\alpha) = 0 \implies \left[\frac{\partial}{\partial t} + (\boldsymbol{u}_\alpha \cdot \nabla)\right] \ln\left(p_\alpha \rho_\alpha^{-\gamma}\right) = 0$$

$$\gamma = \frac{5}{3}$$

Adiabatic index

Bernoulli's law

Source: Wikipedia

- Potential flow, $\boldsymbol{u}_\alpha = -\nabla\Psi_\alpha$ if $\nabla \times \boldsymbol{u}_\alpha = 0$ (irrotational).
- From the Euler's equation (inviscid flow).
- Barotropic fluid, $\rho(p)$. *E.g.*, adiabatic ideal gas, $\rho \propto p^{\frac{1}{\gamma}}$ (polytropic).

$$(\boldsymbol{u}_\alpha \cdot \nabla)\boldsymbol{u}_\alpha = \nabla\left(\frac{\boldsymbol{u}_\alpha^2}{2}\right) - \boldsymbol{u}_\alpha \times (\nabla \times \boldsymbol{u}_\alpha)$$

$$\nabla\left(\frac{\partial\Psi_\alpha}{\partial t} - \frac{|\nabla\Psi_\alpha|^2}{2} - w(p_\alpha) - \frac{q_\alpha V}{m_\alpha}\right) = 0$$

$$w(p) = \int_0^p \frac{\mathrm{d}p'}{\rho(p')} = \left(\frac{\gamma}{\gamma - 1}\right)\frac{p}{\rho}$$

Pressure potential

- Hydrodynamic formulation of the Schrödinger eq. F. Bloch, *Z. Phys.*, 1933 (also see S. Lundqvist, 1983)

Lautrup, *Physics of Continuous Matter*, 2nd edition, 2011 --- Chapter 14

Check point 2

Drude-Lorentz model

Source: Wikipedia

- Provisionally assume neither generation nor recombination: $\int d^3\boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0.$

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \boldsymbol{u}_e) = 0$$

$$n_e \left[\frac{\partial \boldsymbol{u}_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)\boldsymbol{u}_e\right] + \frac{\nabla p_e}{m_e} + \frac{e n_e \boldsymbol{E}}{m_e} = \int d^3\boldsymbol{v}\, \boldsymbol{v} \left(\frac{\delta f_e}{\delta t}\right)_{coll.}$$

$$\int d^3\boldsymbol{v}\, \boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = -\frac{n_e \boldsymbol{u}_e}{\tau_{p,e}} = \frac{\boldsymbol{J}_e}{e\tau_{p,e}}$$

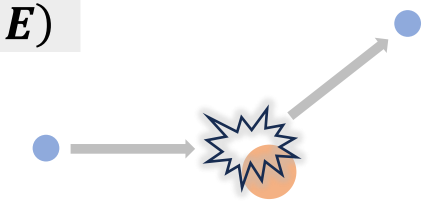
- Stationary (Lagrange frame): $\frac{D\boldsymbol{u}_e}{Dt} = \frac{\partial \boldsymbol{u}_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)\boldsymbol{u}_e = 0.$

$$\boldsymbol{J}_e = -e n_e \boldsymbol{u}_e$$

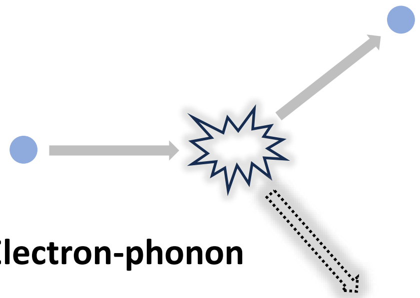
$$\boldsymbol{J}_e = \mu_e(\nabla p_e + e n_e \boldsymbol{E}) = \mu_e(k_B \nabla(n_e T_e) + e n_e \boldsymbol{E})$$

$$\mu_e = \frac{e\tau_{p,e}}{m_e} > 0$$

Electron mobility



Electron-impurity



Electron-phonon

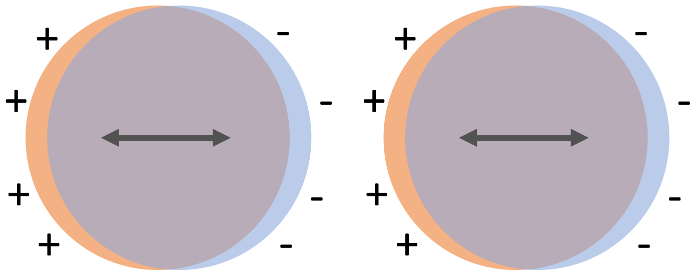
Electronic pressure

Source: Wikipedia

- ❑ Electrons can be treated as a fluid.
- ❑ Pressure given by *e.g.*, Thomas-Fermi approximation: $P_e = \frac{\hbar^2 (3\pi^2)^{\frac{2}{3}}}{5m_e} n_e^{\frac{5}{3}}$.
- ❑ Barotropic fluid, $\rho \propto p^{\frac{1}{\gamma}}$ with $\gamma = \frac{5}{3}$.

$$n_e \left[\frac{\partial \boldsymbol{u}_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)\boldsymbol{u}_e \right] + v_s^2 \nabla n_e + \frac{e n_e}{m_e} \boldsymbol{E} = -\frac{n_e \boldsymbol{u}_e}{\tau_{p,e}}$$

$$v_s^2 = \gamma \frac{P_e}{n_e} = \frac{\hbar^2 (3\pi^2)^{\frac{2}{3}}}{3m_e^2} n_e^{\frac{2}{3}} = \frac{v_F^2}{3}$$



Plasmonic modes

- ❑ Generalised to arbitrary functional (DFT): $w(p) = \frac{1}{m_e} \frac{\delta G}{\delta n}$. N.A. Mortensen, *Nanophotonics*, 2021

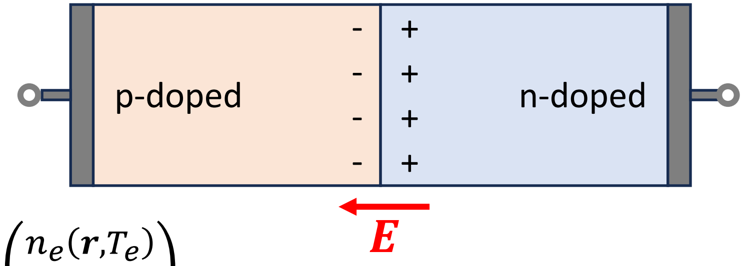
Thermal equilibrium

- Provisionally assume neither generation nor recombination: $\int d^3\boldsymbol{v}\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0.$
- Constant electronic temperature, T_e.
- No electric current.

$$\boldsymbol{J}_e = \mu_e(k_B\nabla(n_e T_e) + e n_e \boldsymbol{E}) = \mu_e n_e\left(k_B T_e \frac{\nabla n_e}{n_e} - e\nabla V\right) = 0 \Longrightarrow n_e(\boldsymbol{r}, T_e) \propto \exp\left(\frac{eV}{k_B T_e}\right)$$

Boltzmann factor

- At constant T_e, same as drift-diffusion model for semiconductors.
- Einstein relation: $eD_e = k_B T_e \mu_e$.



- Electro-chemical potential: $\xi_e(\boldsymbol{r}, T_e) = E_c(\boldsymbol{r}) - \frac{E_g}{2} - \frac{3}{4}k_B T_e \ln\left(\frac{m_e}{m_h}\right) + k_B T_e \ln\left(\frac{n_e(\boldsymbol{r},T_e)}{n_i(T_e)}\right)$

$$\boldsymbol{J}_e = -e n_e \mu_e \nabla\left(\frac{\xi_e}{e}\right) \qquad \boldsymbol{E} = -\nabla V = \frac{\nabla E_c}{e}$$

Energy equation

- Provisionally assume neither generation nor recombination: $\int d^3\boldsymbol{v} \left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0.$

$$\frac{3}{2}\left[\frac{\partial p_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)p_e\right] + \frac{5}{2}p_e(\nabla \cdot \boldsymbol{u}_e) + \nabla \cdot \boldsymbol{q}_e = \frac{m_e}{2}\int d^3\boldsymbol{v}\,\boldsymbol{v}^2\chi(\boldsymbol{v})\left(\frac{\delta f_e}{\delta t}\right)_{coll.} - m_e\boldsymbol{u}_e \cdot \int d^3\boldsymbol{v}\,\boldsymbol{v}\left(\frac{\delta f_e}{\delta t}\right)_{coll.}$$

Momentum relaxation

$$\int d^3\boldsymbol{v}\,\boldsymbol{v}\left(\frac{\delta f_e}{\delta t}\right)_{coll.} = \frac{\boldsymbol{J}_e}{m_e\mu_e}$$

- <u>Thermal equilibrium</u> between electrons and lattice, $T_e = T_L$

(Kinetic) energy relaxation

$$\frac{m_\alpha}{2}\int d^3\boldsymbol{v}\,\boldsymbol{v}^2\chi(\boldsymbol{v})\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = -\frac{n_e(W - W_0)}{\tau_{W,e}} = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}}$$

Energy equation

Source: Wikipedia

- Provisionally assume neither generation nor recombination: $\int d^3\boldsymbol{v}\left(\frac{\delta f_\alpha}{\delta t}\right)_{coll.} = 0.$
- Thermal equilibrium between electrons and lattice, $T_e = T_L$.
- Ideal gas EoS.

Internal energy $$\frac{3p_e}{2} = \frac{3k_B}{2} n_e T_e = c_{v,e} n_e T_e$$

Enthalpy $$\frac{5p_e}{2} = \frac{5k_B}{2} n_e T_e = c_{p,e} n_e T_e$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_e) + \nabla\cdot\left(\frac{5k_B}{2} n_e T_e \boldsymbol{u}_e + \boldsymbol{q}_e\right) = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \boldsymbol{E}\cdot\boldsymbol{J}_e$$

$$n_e\boldsymbol{S} = \frac{5k_B}{2} n_e T_e \boldsymbol{u}_e + \boldsymbol{q}_e = -\frac{5k_B T_e}{2e}\boldsymbol{J}_e - \kappa_e \nabla T_e$$

Irreversible heat flux $$\boldsymbol{q}_e = -\kappa_e \nabla T_e$$

Some criticisms

- No band structure effects ("parabolic bands"). *It can be fixed by using effective masses, multiple valleys.*
- Non-degenerate carriers. *It can be fixed by using Fermi-Dirac.*
- The moment equations are correct, the approximations comes from the closure(s). *Use more moments.*
- Inaccurate transport coefficients (*e.g.*, Peltier coefficient). *They can be computed from first principles, but…*
- We used a macroscopic relaxation time approximation (RTA). *The microscopic RTA is different!*

$$n_e\left[\frac{\partial \boldsymbol{u}_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)\boldsymbol{u}_e\right] + \frac{\nabla p_e}{m_e} + \frac{e n_e \boldsymbol{E}}{m_e} = \int d^3\boldsymbol{v}\, \boldsymbol{v} \left(\frac{\delta f_e}{\delta t}\right)_{coll.} = -\frac{n_e \boldsymbol{u}_e}{\tau_{p,e}}$$

- The microscopic RTA cannot be implemented directly. Perturbation theory is used.

$$\left(\frac{\delta f_e}{\delta t}\right)_{coll.} = -\frac{f_e - f_e^0}{\tau'_{p,e}} \Longrightarrow f_e(\boldsymbol{r},\boldsymbol{v},t) \approx f_e^0(\boldsymbol{r},\boldsymbol{v},t) - \tau'_{p,e}\left(\frac{\partial f_e^0}{\partial t} + \boldsymbol{v}\cdot\nabla f_e^0 + \boldsymbol{a}\cdot\nabla_v f_e^0\right) \qquad \tau'_{p,e}(E) = \tau'_0\left(\frac{E}{k_B T_L}\right)^r$$

T. Grasser *et al. Proceedings of the IEEE*, 2003
Huang, *Statistical Mechanics*, 2nd edition, 1987 --- Chapter 5

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Check point 3 + Pause

Hydrodynamic equations

- For electrons and holes.
- Provisionally assume neither generation nor recombination.

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \boldsymbol{u}_e) = 0$$

$$m_e n_e \left[\frac{\partial \boldsymbol{u}_e}{\partial t} + (\boldsymbol{u}_e \cdot \nabla)\boldsymbol{u}_e\right] + k_B \nabla(n_e T_e) + e n_e \boldsymbol{E} = \frac{\boldsymbol{J}_e}{\mu_e}$$

$$\boldsymbol{J}_e = -e n_e \boldsymbol{u}_e$$

$$\frac{\partial n_h}{\partial t} + \nabla \cdot (n_h \boldsymbol{u}_h) = 0$$

$$m_h n_h \left[\frac{\partial \boldsymbol{u}_h}{\partial t} + (\boldsymbol{u}_h \cdot \nabla)\boldsymbol{u}_h\right] + k_B \nabla(n_h T_h) - e n_h \boldsymbol{E} = -\frac{\boldsymbol{J}_h}{\mu_h}$$

$$\boldsymbol{J}_h = e n_h \boldsymbol{u}_h$$

$$\nabla \cdot \boldsymbol{E} = \frac{e(n_h - n_e)}{\varepsilon_0 \varepsilon_r}$$

$$\boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_e) + \nabla \cdot \left(\frac{5k_B}{2} n_e T_e \boldsymbol{u}_e + \boldsymbol{q}_e\right) = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \boldsymbol{E} \cdot \boldsymbol{J}_e$$

$$\boldsymbol{q}_h = -\kappa_h \nabla T_h$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_h T_h) + \nabla \cdot \left(\frac{5k_B}{2} n_h T_h \boldsymbol{u}_h + \boldsymbol{q}_h\right) = -\frac{3k_B}{2}\frac{n_h(T_h - T_L)}{\tau_{W,h}} + \boldsymbol{E} \cdot \boldsymbol{J}_h$$

Energy transfer equations

- For electrons *and* holes
- Provisionally assume neither generation nor recombination.

$$\frac{\partial n_e}{\partial t} - \nabla \cdot \left(\frac{\boldsymbol{J}_e}{e}\right) = 0$$

$$\boldsymbol{J}_e = k_B \mu_e \nabla(n_e T_e) + e n_e \mu_e \boldsymbol{E}$$

$$\frac{\partial n_h}{\partial t} + \nabla \cdot \left(\frac{\boldsymbol{J}_h}{e}\right) = 0$$

$$\boldsymbol{J}_h = -k_B \mu_h \nabla(n_h T_h) + e n_h \mu_h \boldsymbol{E}$$

$$\nabla \cdot \boldsymbol{E} = \frac{e(n_h - n_e)}{\varepsilon_0 \varepsilon_r}$$

$$\boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_e) + \nabla \cdot \left(-\frac{5k_B T_e}{2e}\boldsymbol{J}_e + \boldsymbol{q}_e\right) = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \boldsymbol{E} \cdot \boldsymbol{J}_e$$

$$\boldsymbol{q}_h = -\kappa_h \nabla T_h$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_h T_h) + \nabla \cdot \left(\frac{5k_B T_h}{2e}\boldsymbol{J}_h + \boldsymbol{q}_h\right) = -\frac{3k_B}{2}\frac{n_h(T_h - T_L)}{\tau_{W,h}} + \boldsymbol{E} \cdot \boldsymbol{J}_h$$

Lattice dynamics

- Neglect phonon mass & momentum transport.
- Energy balance.
- Thermal equilibrium between electrons and lattice, $T_e = T_h = T_L$.

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_e) + \nabla\cdot\left(-\frac{5k_B T_e}{2e}\boldsymbol{J}_e + \boldsymbol{q}_e\right) = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \boldsymbol{E}\cdot\boldsymbol{J}_e \qquad \boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_h T_h) + \nabla\cdot\left(\frac{5k_B T_h}{2e}\boldsymbol{J}_h + \boldsymbol{q}_h\right) = -\frac{3k_B}{2}\frac{n_h(T_h - T_L)}{\tau_{W,h}} + \boldsymbol{E}\cdot\boldsymbol{J}_h \qquad \boldsymbol{q}_h = -\kappa_h \nabla T_h$$

$$c_{v,L} n_L \frac{\partial T_L}{\partial t} + \nabla\cdot\boldsymbol{q}_L = \frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \frac{3k_B}{2}\frac{n_h(T_h - T_L)}{\tau_{W,h}} \qquad \boldsymbol{q}_L = -\kappa_L \nabla T_L$$

Two-temperature model

- Neglect phonon mass & momentum transport.
- Energy balance.
- Thermal equilibrium between electrons and lattice, $T_e = T_h = T_L$.
- No currents: $\boldsymbol{J}_e = 0$ and $\boldsymbol{J}_h = 0$. If no generation & recombination, n_e and n_h are constant.

$$\frac{3k_B}{2} n_e \frac{\partial T_e}{\partial t} + \nabla \cdot \boldsymbol{q}_e = -\frac{3k_B}{2} \frac{n_e (T_e - T_L)}{\tau_{W,e}} \qquad \boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$\frac{3k_B}{2} n_h \frac{\partial T_h}{\partial t} + \nabla \cdot \boldsymbol{q}_h = -\frac{3k_B}{2} \frac{n_h (T_h - T_L)}{\tau_{W,h}} \qquad \boldsymbol{q}_h = -\kappa_h \nabla T_h$$

$$c_{v,L} n_L \frac{\partial T_L}{\partial t} + \nabla \cdot \boldsymbol{q}_L = \frac{3k_B}{2} \frac{n_e (T_e - T_L)}{\tau_{W,e}} + \frac{3k_B}{2} \frac{n_h (T_h - T_L)}{\tau_{W,h}} \qquad \boldsymbol{q}_L = -\kappa_L \nabla T_L$$

Ambipolar diffusion

- Local neutrality, $n_h = n_e$, maintained if $\boldsymbol{J}_h = -\boldsymbol{J}_e$.
- Generation & recombination assumed to be local processes.

$$\boldsymbol{J}_e = k_B \mu_e \nabla(n_e T_e) + e n_e \mu_e \boldsymbol{E}$$

$$\boldsymbol{J}_h = -k_B \mu_h \nabla(n_h T_h) + e n_h \mu_h \boldsymbol{E}$$

$$\Longrightarrow \quad \boldsymbol{E} = -\frac{k_B\big(\mu_e \nabla(n_e T_e) - \mu_h \nabla(n_h T_h)\big)}{e n_e(\mu_e + \mu_h)}$$

- Remove dependence on $\boldsymbol{E}$

$$\boldsymbol{J}_e = k_B \left(\frac{1}{\mu_e} + \frac{1}{\mu_h}\right)^{-1} \big(\nabla(n_e T_e) + \nabla(n_e T_h)\big)$$

- Diffusion dictated by the species with the lowest mobility.
- Bipolar thermodiffusion effect. Peltier heat flow can occur also without net electric current.

Simplified energy transfer equations

- Local neutrality, $n_h = n_e$, maintained if $\boldsymbol{J}_h = -\boldsymbol{J}_e$.
- Provisionally assume neither generation nor recombination.

$$\frac{\partial n_e}{\partial t} - \nabla \cdot \left(\frac{\boldsymbol{J}_e}{e}\right) = 0$$

$$\boldsymbol{J}_e = k_B \left(\frac{1}{\mu_e} + \frac{1}{\mu_h}\right)^{-1} \left(\nabla(n_e T_e) + \nabla(n_e T_h)\right)$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_e) + \nabla \cdot \left(-\frac{5k_B T_e}{2e}\boldsymbol{J}_e + \boldsymbol{q}_e\right) = -\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}}$$

$$\boldsymbol{q}_e = -\kappa_e \nabla T_e$$

$$\frac{3k_B}{2}\frac{\partial}{\partial t}(n_e T_h) + \nabla \cdot \left(-\frac{5k_B T_h}{2e}\boldsymbol{J}_e + \boldsymbol{q}_h\right) = -\frac{3k_B}{2}\frac{n_e(T_h - T_L)}{\tau_{W,h}}$$

$$\boldsymbol{q}_h = -\kappa_h \nabla T_h$$

$$c_{v,L} n_L \frac{\partial T_L}{\partial t} + \nabla \cdot \boldsymbol{q}_L = \frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} + \frac{3k_B}{2}\frac{n_e(T_h - T_L)}{\tau_{W,h}}$$

$$\boldsymbol{q}_L = -\kappa_L \nabla T_L$$

Mobility models ("hot" carriers)

- Carrier velocity <u>saturates</u> to v_{sat} at large $\boldsymbol{E}$.
- The electronic temperature T_e scales as $\boldsymbol{E}^2$.
- Neglecting Peltier effect, $\boldsymbol{J}_e \propto e n_e \mu_e \boldsymbol{E}$
- Assume the joule heating is entirely dissipated to the lattice (R.H.S. of the energy equation).

$$\frac{3k_B}{2}\frac{n_e(T_e - T_L)}{\tau_{W,e}} = \boldsymbol{E}\cdot\boldsymbol{J}_e \propto e n_e \mu_e \boldsymbol{E}^2 \Longrightarrow T_e = T_L + \frac{2e\tau_{W,e}\mu_e}{3k_B}\boldsymbol{E}^2$$

"Hot" electrons

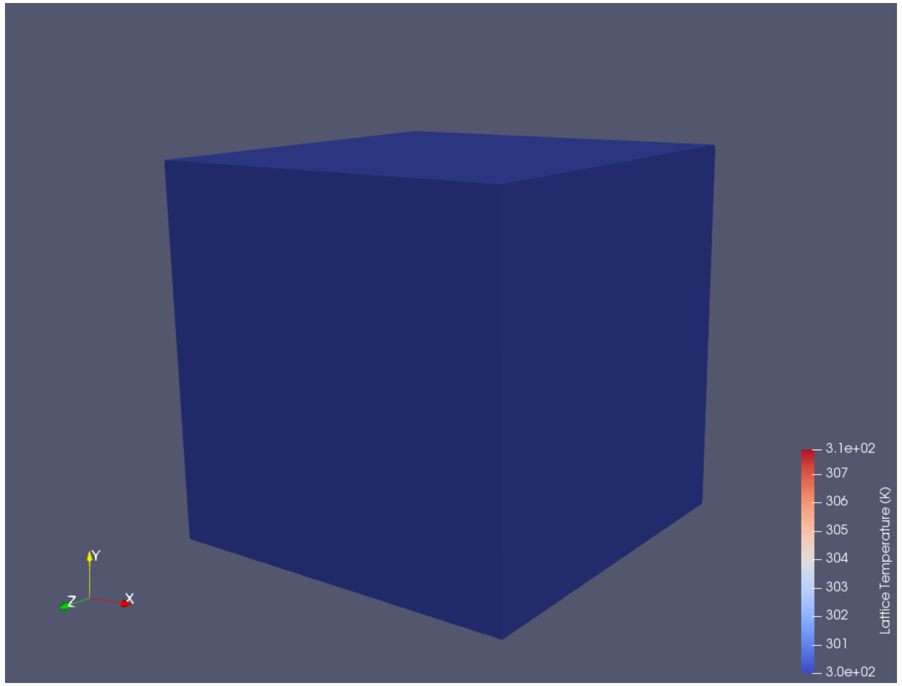
$$\mu_e(T_e) = \frac{\mu_e^0(T_L)}{\left(1 + \frac{3k_B}{2e}\frac{\mu_e^0(T_L)}{\tau_{W,e} v_{sat}^2}(T_e - T_L)\right)}$$

- In SiO_2 the hole mobility is <u>activated</u>, $\mu_e^0 \propto e^{-\frac{E_a}{k_B T_L}}$.

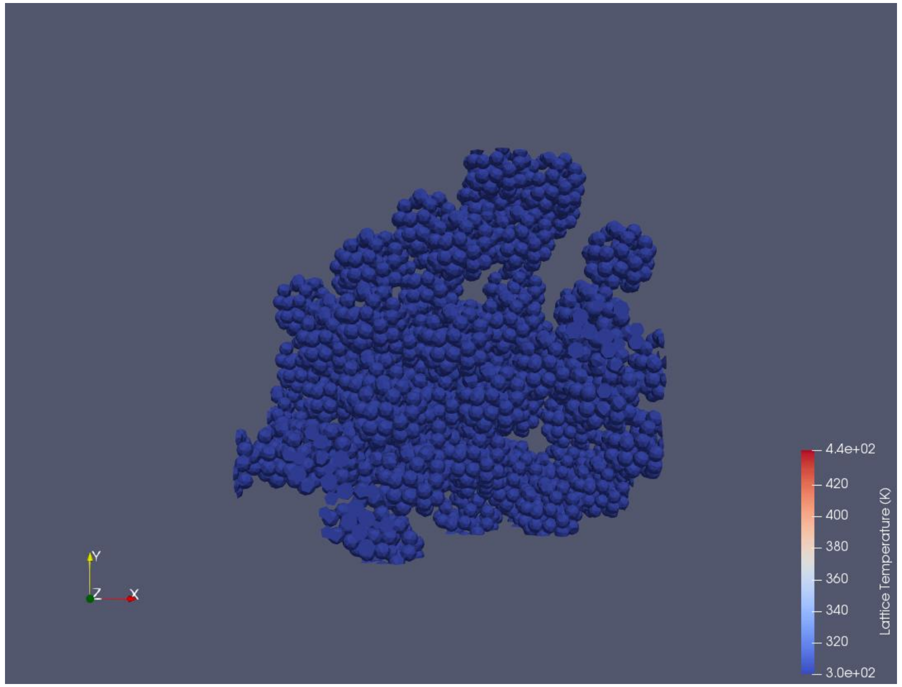
W. Hänsch & M. Miura-Mattausch, *J. Appl. Phys.* 1986

Results: a-SiO_2 vs aerogel

- Initial conditions for **one 10 eV proton**, Gaussian distribution of e-h density, $W = 3E_g$ per e-h pair.
- Lattice temperature, T_L, evolution.



Bulk, cube side 40 nm side



Aerogel, cube 110 nm side, **11%**

J. Smyth, PhD thesis (unpublished)

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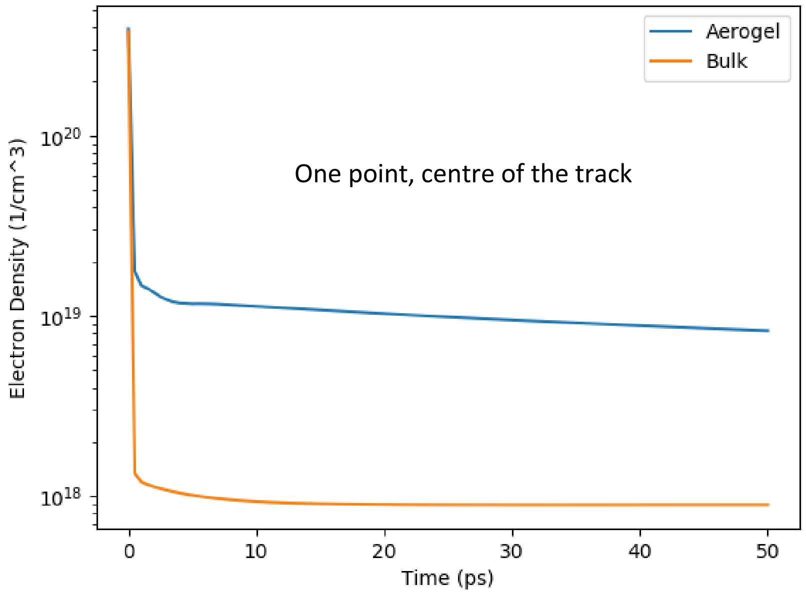
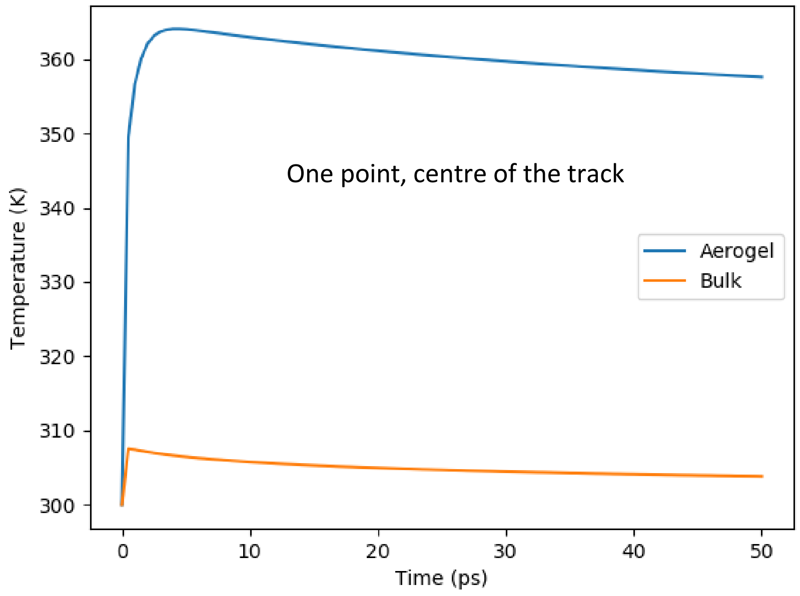
Results: a-SiO_2 vs aerogel

- Initial conditions for **one 10 eV proton**, Gaussian distribution of e-h density, $W = 3E_g$ per e-h pair.

Electron density, $n_e(t)$



Lattice temperature, $T_L(t)$



- CAVEAT: Very simple model, no e-h recombination.

J. Smyth, PhD thesis (unpublished)

Check point 4

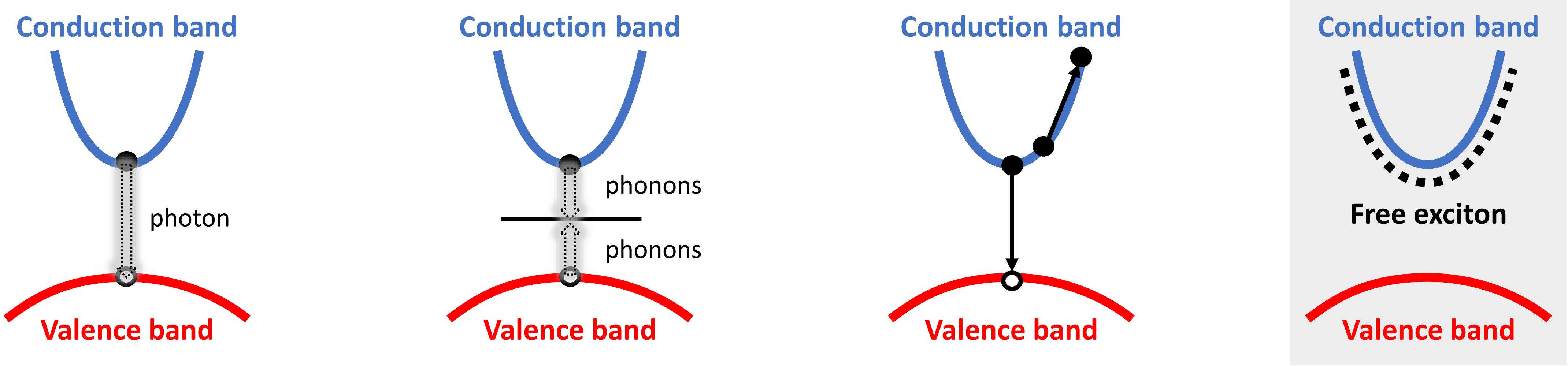
Generation & recombination rates

- Radiative processes are typically slow.
- Excitonic processes are typically fast.

$$\frac{\partial n_e}{\partial t} + \nabla \cdot (n_e \boldsymbol{u}_e) = -\left(R_{rad} + R_{srh} + R_{aug} + R_x + \cdots\right) + (\text{reverse processes})$$

- "ABC" model of recombination (Piprek, 2010)

$R_{rad} = -An_e$ $\qquad R_{srh} = -Bn_en_h$ $\qquad R_{aug} = -Cn_e^2n_h$



Band-to-band Auger processes

- Band-to-band Auger is an activated process.
- The reverse process is analogue to impact ionisation.
- Drive electron-hole equilibrium at large T_e.

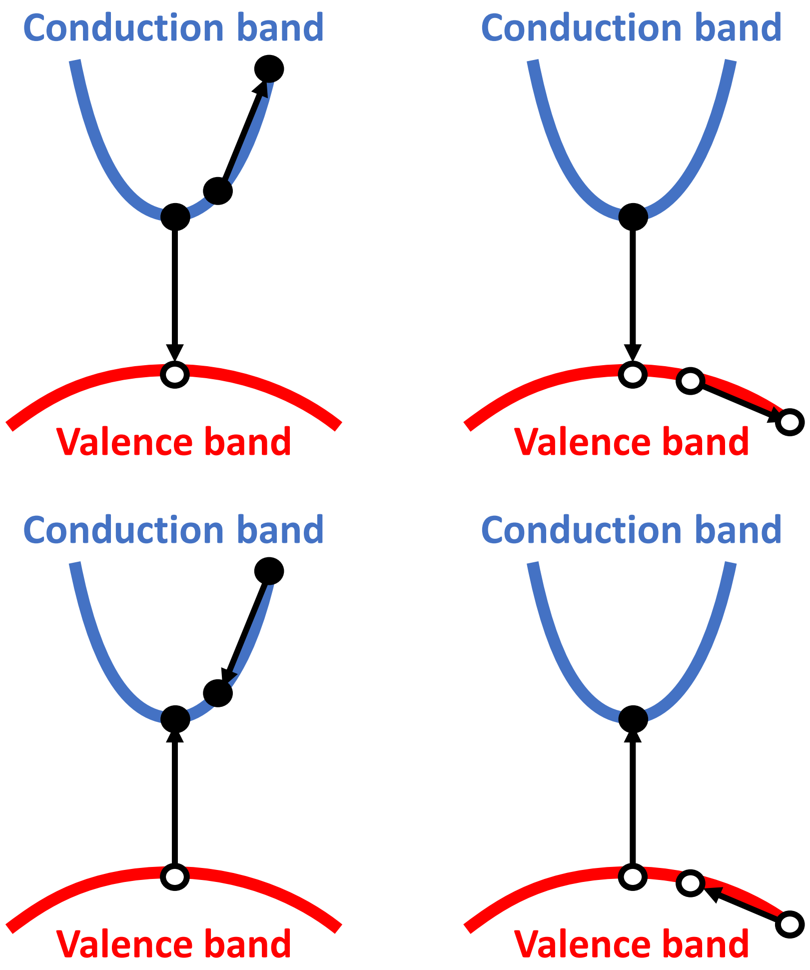
$$R_{aug} = -(C_e n_e + C_h n_h)(n_e n_h - n_i^2)$$

$$n_i^2 = n_e^{eq} n_h^{eq}$$

Law of mass action

- The activation energy is of the order of the band gap, E_g.

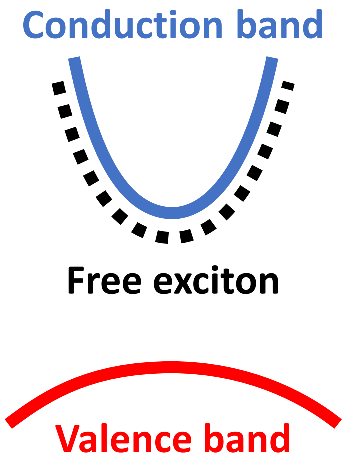
$$C_{e,h}(T_{e,h}) \propto \left(\frac{E_g}{k_B T_{e,h}}\right)^{-\frac{3}{2}} \exp\left(-\frac{sE_g}{k_B T_{e,h}}\right)$$

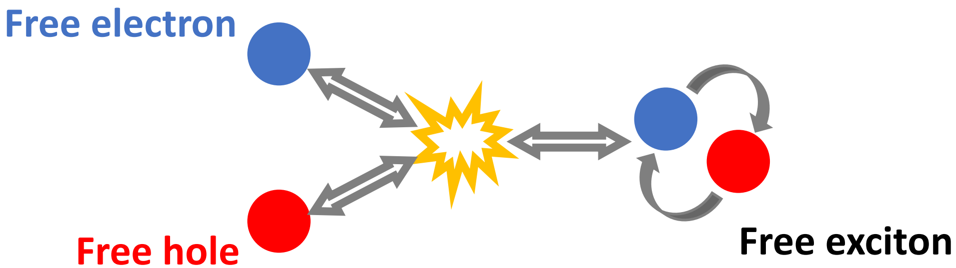


Blakemore, *Semiconductor Statistics*, 1987 --- Chapter 6

The "chemistry" of the excitons

- Electrons and holes can bind together to form a free exciton.
- The process can be modelled as a chemical reaction: $e + h \leftrightarrow x$



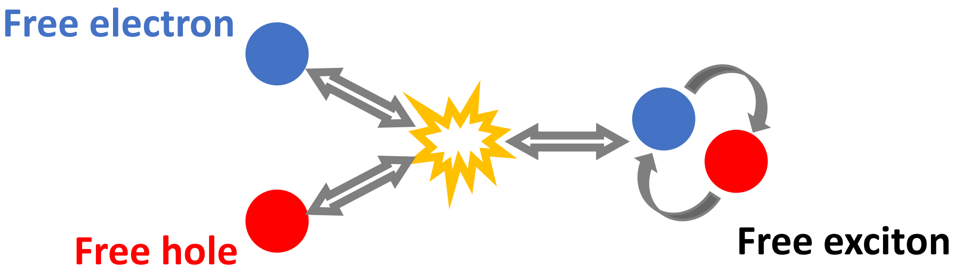


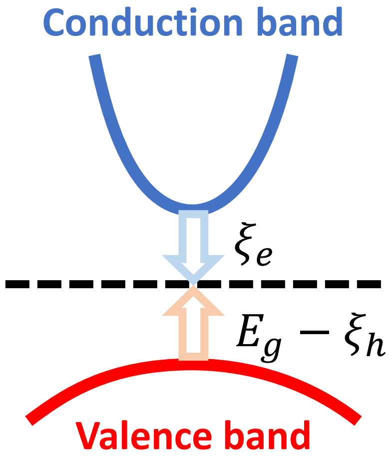
- The condition for chemical equilibrium is $\xi_e + \xi_h = \xi_x$.

P. Würfel, *The chemical potential of radiation*, 1982
F. Herrmann & P. Würfel, *Light with nonzero chemical potential*, 2005

"Chemical" equilibrium

- Electrons and holes can bind together to form a free exciton.
- The process can be modelled as a chemical reaction: $e + h \leftrightarrow x$.
- Local neutrality, $n_h = n_e$.
- At thermal and chemical equilibrium, $T_h = T_e$ and $\xi_e + \xi_h = \xi_x = 0$.





$$\xi_e(\boldsymbol{r}, T_e) = E_c(\boldsymbol{r}) - \frac{E_g}{2} - \frac{3}{4} k_B T_e \ln\left(\frac{m_e}{m_h}\right) + k_B T_e \ln\left(\frac{n_e(\boldsymbol{r}, T_e)}{n_i(T_e)}\right)$$

Chemical potential electrons

$$\xi_h(\boldsymbol{r}, T_e) = -E_v(\boldsymbol{r}) - \frac{E_g}{2} - \frac{3}{4} k_B T_e \ln\left(\frac{m_h}{m_e}\right) + k_B T_e \ln\left(\frac{n_e(\boldsymbol{r}, T_e)}{n_i(T_e)}\right)$$

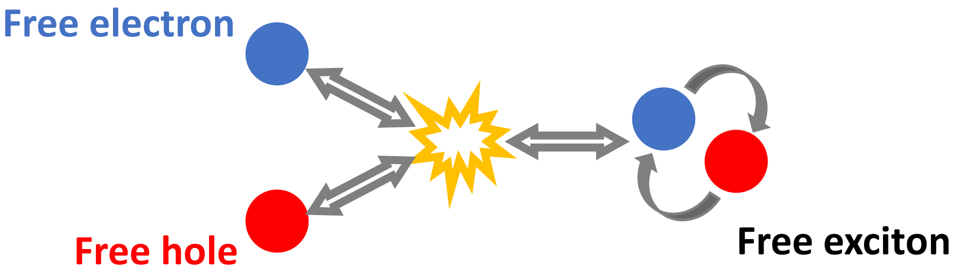
Chemical potential holes

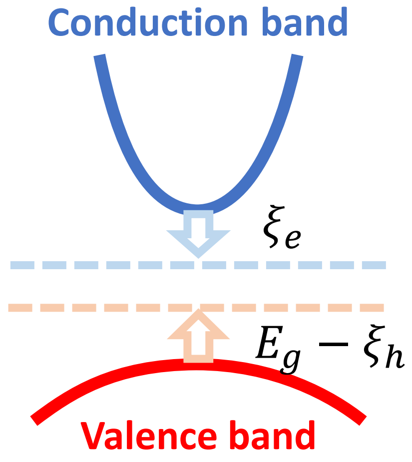
$$n_i(T_e) = \frac{2}{\sqrt{\Lambda_e^3 \Lambda_h^3}} \exp\left(-\frac{E_g}{2 k_B T_e}\right)$$

Intrinsic carrier concentration

"Chemical" equilibrium

- Electrons and holes can bind together to form a free exciton.
- The process can be modelled as a chemical reaction: $e + h \leftrightarrow x$.
- Local neutrality, $n_h = n_e$.
- At thermal equilibrium, $T_h = T_e$.





$$\xi_e(\boldsymbol{r}, T_e) = E_c(\boldsymbol{r}\,) - \frac{E_g}{2} - \frac{3}{4} k_B T_e \ln\left(\frac{m_e}{m_h}\right) + k_B T_e \ln\left(\frac{n_e(\boldsymbol{r}, T_e)}{n_i(T_e)}\right)$$

Chemical potential electrons

$$\xi_h(\boldsymbol{r}, T_e) = -E_v(\boldsymbol{r}\,) - \frac{E_g}{2} - \frac{3}{4} k_B T_e \ln\left(\frac{m_h}{m_e}\right) + k_B T_e \ln\left(\frac{n_e(\boldsymbol{r}, T_e)}{n_i(T_e)}\right)$$

Chemical potential holes

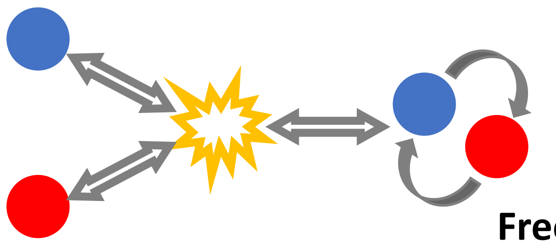
$$n_i(T_e) = \frac{2}{\sqrt{\Lambda_e^3 \Lambda_h^3}} \exp\left(-\frac{E_g}{2 k_B T_e}\right)$$

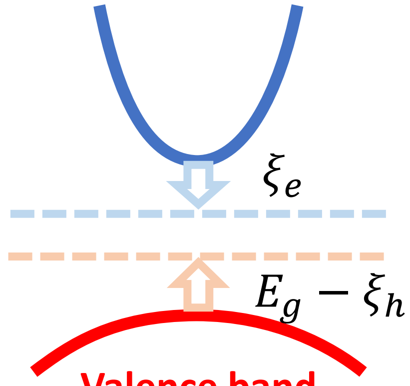
Intrinsic carrier concentration

- If electrons and holes are not in chemical equilibrium, $\xi_e + \xi_h = \xi_h \neq 0$

Saha equation

- Electrons and holes can bind together to form a free exciton.
- The process can be modelled as a chemical reaction: $e + h \leftrightarrow x$.
- Local neutrality, $n_h = n_e$.
- At thermal equilibrium, $T_h = T_e$.





$$\xi_x(\boldsymbol{r}, T_e) = k_B T_e \ln\left(\frac{n_x(\boldsymbol{r}, T_e)}{n_x^{eq}(T_e)}\right)$$ **Chemical potential excitons**

$$n_x^{eq}(T_e) = \frac{4}{\Lambda_x^3} \exp\left(-\frac{E_x}{k_B T_e}\right)$$ **Equilibrium exciton concentration**

$$\frac{n_x}{n_e^2} = \frac{\Lambda_e^3 \Lambda_h^3}{\Lambda_x^3} \exp\left(\frac{E_g - E_x}{k_B T_e}\right) = \left(\frac{2\pi\hbar^2}{m_x^\star k_B T_e}\right) \exp\left(\frac{E_b}{k_B T_e}\right)$$ **"Ionisation" equilibrium**

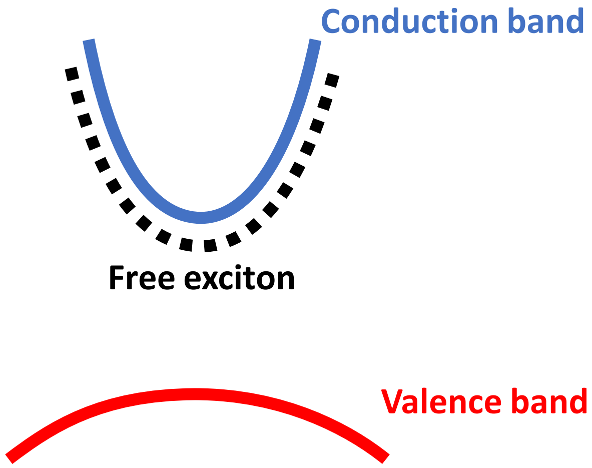
- If electrons and holes are not in chemical equilibrium, $\xi_e + \xi_h = \xi_h \neq 0$

Band gap renormalisation

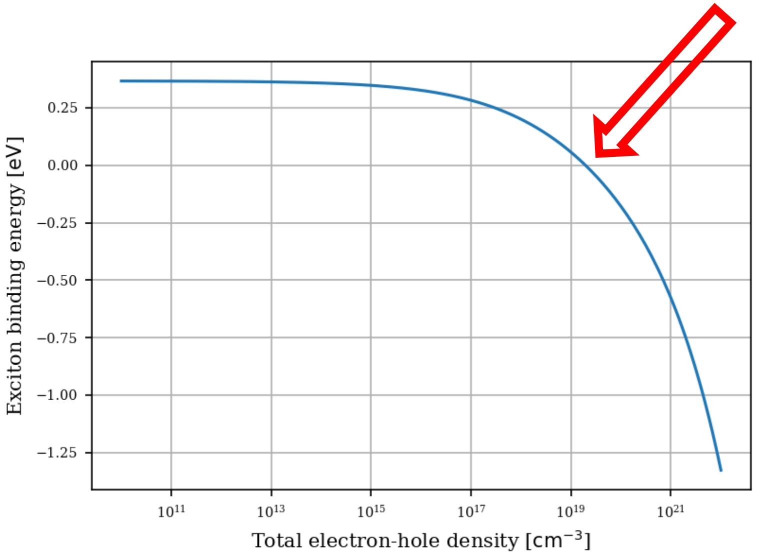
- “Universal” exchange-correlation energy for homogenous e-h liquid (Vashishta & Kalia, 1982)
- Dimensionless exciton Wigner-Seitz radius, $r_s = \left(\frac{4\pi n_e}{3}\right)^{-\frac{1}{3}} / a_x$

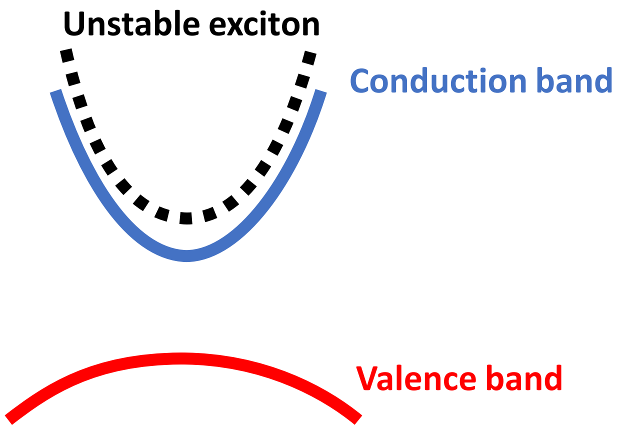
$$\varepsilon_{xc}(r_s) \propto \frac{a + b r_s}{d + d r_s + r_s^2} \quad \Longrightarrow \quad \Delta\mu_{eh} = \varepsilon_{xc}(r_s) + n_e \frac{d\varepsilon_{xc}}{dn_e}$$

Exciton Mott transition (EMT) @ $n_e(r_s) = 1.94 \cdot 10^{19}$ cm^{-3}



Low e-h density

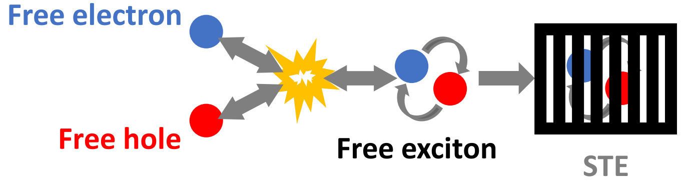




High e-h density

Simplified model, no transport

- Decay of electron-hole plasma in highly excited a-SiO_2
- Model includes Auger recombination and decay to both free and self-trapped excitons (STE).
- Band gap renormalisation (BGR) also included.
- Carrier and heat diffusion is neglected. Model only provides an upper limit.



$$E_g = 8.7\ eV$$

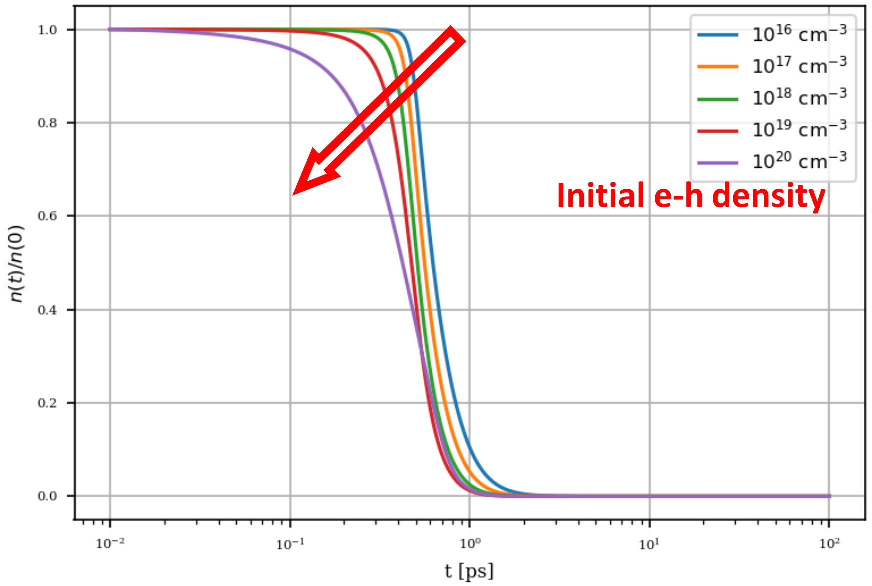
$$T_e(0) = 67{,}300\ K$$

$$E_{ste} = 3.1\ eV$$

$$m_x = 3.25\ m_e$$

$$a_x = 4.9\ A$$

$$\tau = 0.1\ ps$$



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Conclusions

- Energy transport models based on the moment equations to model relaxation of highly excited insulators.
- Composite and nanostructured material (*e.g.*, aerogels) can be modelled.
- Existing numerical implementations for semiconductor device modelling can be adapted.
- Energy transport in bulk and nanostructure materials looks qualitatively differently, although a quantitative explanation is still missing.

Thank You

Any question?