Nonlinear electron dynamics in metallic nanostructures

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Plan of the lectures

1. Introductory remarks on metallic nanostructures
   - Relevant quantities and typical physical parameters
   - Applications
2. Linear electron response: Mie theory and generalizations
3. Nonlinear response
   - Survey of various models from N-body to macroscopic
   - Mean-field approximation (Hartree and Vlasov equations)
4. Beyond the mean-field approximation
   - Hartree-Fock equations
   - Time-dependent density functional theory (DFT) and local-density approximation (LDA)
5. Macroscopic models: quantum hydrodynamics

   Linear theory and comparison of various models
6. Spin dynamics: experimental results and recent theoretical advances
7. Illustration: the nonlinear electron dynamics in thin metal films

Suggested reading

master-mc.u-strasbg.fr → 2eme année → Support des cours → Manfredi

- F. Calvayrac et al. *Nonlinear electron dynamics in metal clusters, Physics Reports* **337**, 493-578 (2000).
- U. Kreibig and M. Vollmer, *Optical properties of metal clusters*, Springer series in materials science (1995).
- E.K.U. Gross, J.F. Dobson, M. Petersilka, *Density functional theory of time-dependent phenomena*, in Topics in Current Chemistry n° 181 (Springer, 1996).
- K. Burke, *The ABC of DFT*, http://dft.uci.edu/
- G. Manfredi, *How to model quantum plasmas*, Fields Institute Communication Series (2005), quant-ph/0505004**.**
- G. Manfredi, P.-A. Hervieux, Y. Yin, and N. Crouseilles, *Collective Electron Dynamics in Metallic and Semiconductor Nanostructures,* Lecture Notes in Physics (Springer, 2009).

Lycurgus cup

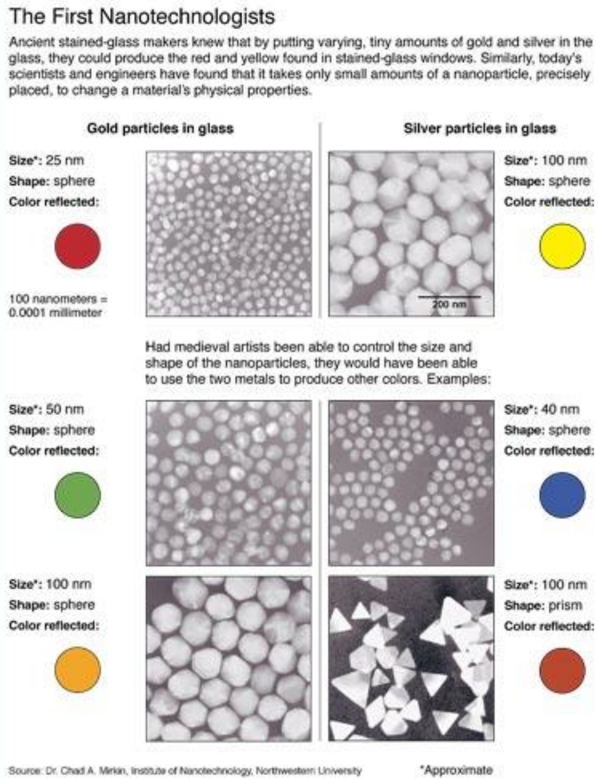
Late Roman, 4th century AD, British Museum, London

Green in scattered light

… and red in transmitted light

Silver-gold nanoparticles (50-100 nm) embedded in the glass

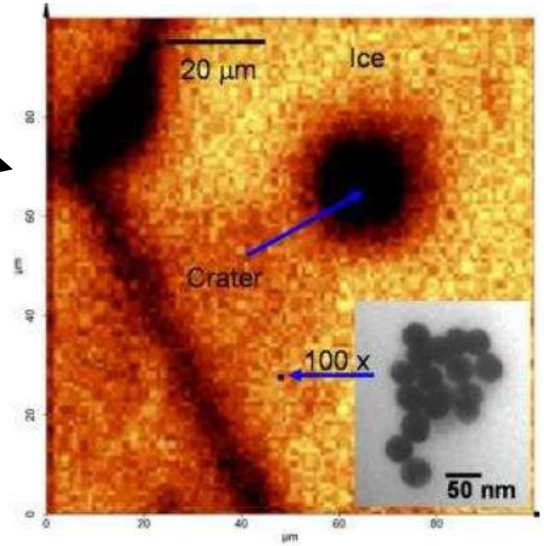
Stained-glass windows



Applications to biology

- A cluster of gold nanoparticles (d ≈ 50nm) can create a much larger crater (≈ 20µm) in an ice sample.

- Gold nanoparticles can act as powerful localized heat sources: possible biomedical applications .



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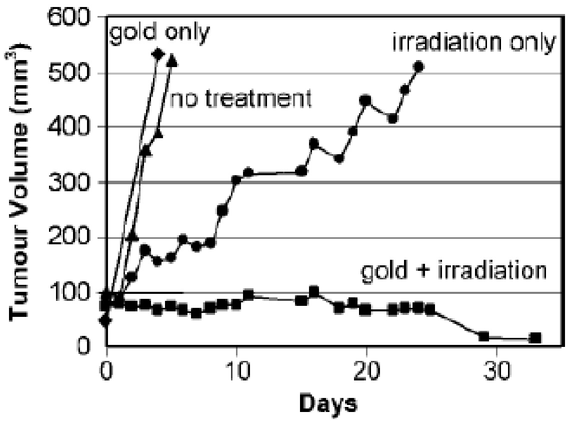
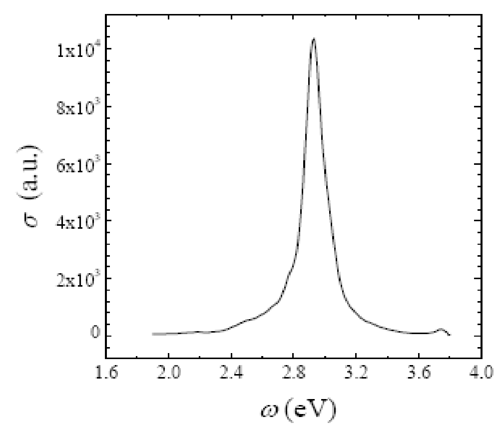
NOTE

The use of gold nanoparticles to enhance radiotherapy in mice

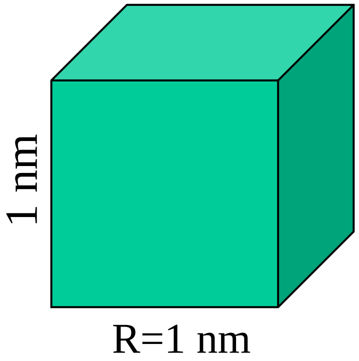
James F Hainfeld[1], Daniel N Slatkin[1] and Henry M Smilowitz[2]



Resonant absorption at the surface plasmon (Mie) frequency



Physics at the nano-scale



- Average distance between atoms $d_A \approx 0.15$ nm (order of magnitude of Bohr's radius $a_0 = 0.0529$ nm)
- $N \approx 300$ atoms
- $N \sim R^3$

- Average distance between electrons: **Wigner-Seitz radius r_s**

$$\boxed{\frac{4}{3}\pi\, r_s^{\,3} \times n = 1}$$ *Average "volume" occupied by one electron*

- Metallic densities $n \approx 10^{28}$ m^{-3}
- **For gold (Au): $r_s = 0.159$ nm**

Quantum or classical?

- De Broglie “thermal” wavelength: $\lambda_B = \dfrac{\hbar}{m_e V_{th}} = \dfrac{\hbar}{\sqrt{m_e k_B T_e}}$

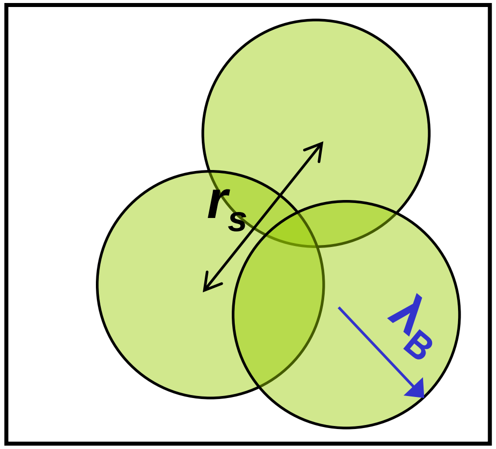
- Thermal speed: mean-square velocity from thermal random motion in a classical gas with a Maxwell-Boltzmann distribution

$$V_{th} = \sqrt{k_B T_e / m_e}$$

- At Te = 300K, λ_B = 1.7 nm ;   at Te = 10K, λ_B = 9.4 nm
- Quantum effects become important when

$$\boxed{\lambda_B > r_s \sim n^{-1/3}}$$

$$n\,\lambda_B^3 > 1$$



- **For gold: r_s = 0.159 nm**
- **Electrons in metals are in the quantum regime even at room temperature**

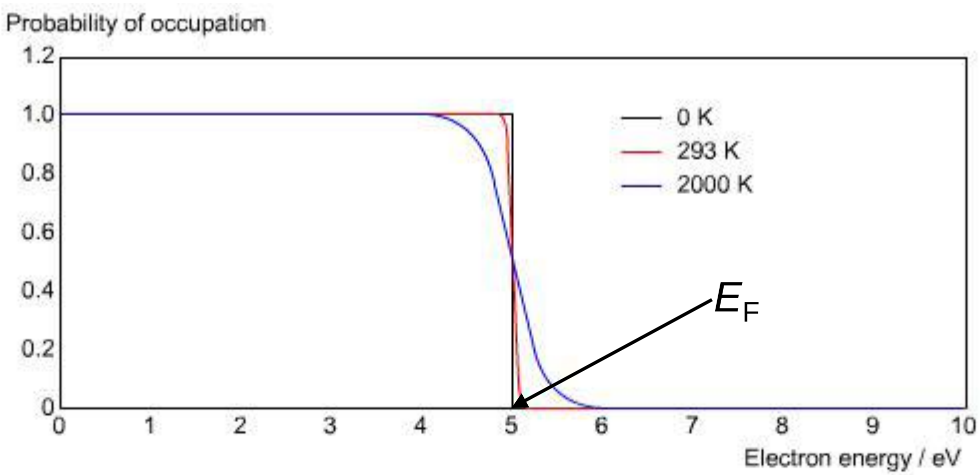
Quantum or classical? Fermi statistics

- **Quantum effects become important as: $T_e < T_F$**
  - **Fermi temperature**: $k_B T_F = E_F = m\frac{v_F^2}{2} = \frac{\hbar^2}{2m}\,(3\pi^2)^{2/3}\,n^{2/3}$
  - $T_e / T_F \sim (n\,\lambda_B^3)^{-2/3}$ where λ_B is the thermal de Broglie wavelength
  - $\boldsymbol{T_e < T_F \rightarrow \lambda_B > n^{-1/3} \sim r_s}$ = average distance between electrons

For gold:

- T_F **= 64200 K**
- E_F **= 5.53 eV**

Fermi-Dirac distribution



Fermi-Dirac distribution for several temperatures

Electron dynamics: some dimensional analysis

- Hypotheses:
  - Electrostatic (Coulomb interactions) between the electrons
  - Fixed ions
  - Zero temperature ($T_e << T_F$)
- The relevant quantities are: **m_e, e, ε_0, n**
- Combine these parameters to obtain a quantity with the dimensions of an **inverse time** (frequency):

$$\boxed{\omega_p = \left(\frac{e^2 n}{m\varepsilon_0}\right)^{1/2}}$$

"plasma frequency"

- **The plasma frequency represents the typical timescale for the electron dynamics in a metallic nanostructure**
- **For gold: $\tau_p = 2\pi\, \omega_p^{-1} \approx 0.5$ fs**

Dimensional analysis – the plasma frequency

$$\boxed{e,\ \varepsilon_0,\ m,\ n}$$

$$K = \frac{e^2}{\varepsilon_0} \quad ; \qquad F = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$[K] = \text{Force} \times (\text{Length})^2 = M L T^{-2} L^2 = M L^3 T^{-2}$$

$$[m] = M \quad ; \qquad [n] = L^{-3}$$

$$K^\alpha m^\beta n^\gamma = M^\alpha L^{3\alpha} T^{-2\alpha} M^\beta L^{-3\gamma} = M^{\alpha+\beta} L^{3\alpha-3\gamma} T^{-2\alpha} = T$$

Look for a quantity with the dimensions of a time

$$\begin{cases} \alpha+\beta = 0 \\ 3\alpha - 3\gamma = 0 \\ -2\alpha = 1 \end{cases} \qquad \begin{aligned} \alpha &= -\frac{1}{2} \\ \beta &= \frac{1}{2} \\ \gamma &= -\frac{1}{2} \end{aligned}$$

$$K^{-1/2} m^{1/2} n^{-1/2} = \left(\frac{m\,\varepsilon_0}{e^2\, n}\right)^{1/2} \equiv \omega_p^{-1}$$

Typical velocity and length scales

Classical

- **Thermal speed**

$$V_{th} = \sqrt{k_B T_e / m}$$

- **Debye length** (classical screening length)

$$\lambda_D = \frac{V_{th}}{\omega_p}$$

Quantum

- **Fermi speed**

$$v_F = \hbar \, (3\pi^2 n)^{1/3} / m$$

$$v_F = \sqrt{2 k_B T_F / m}$$

- **Thomas-Fermi screening length**

$$\lambda_{TF} = \frac{V_F}{\omega_p}$$

For gold at T = 300 K:

- $v_F = 1.4 \times 10^6$ **m/s** (<< c)
- λ_{TF} **= 0.1 nm** (NB: same order as r_s)

Plasma frequency

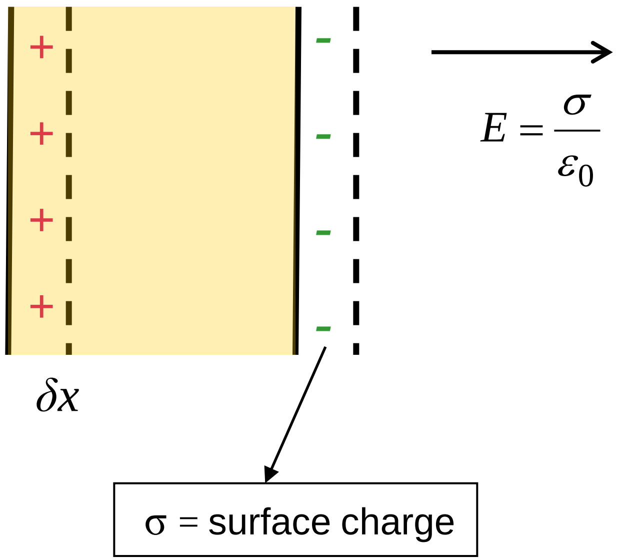
- Typical frequency of electrostatic oscillations in an electron gas.

$$\rho = -en = \text{charge density}$$

$$\sigma = -\rho\ \delta x = en\ \delta x$$

$$\ddot{\delta x} = -\frac{e}{m}E = -\underbrace{\frac{e^2 n}{m\epsilon_0}}_{\omega_p^2}\ \delta x$$

Slab with ne = ni



- Harmonic oscillator with frequency ω_p

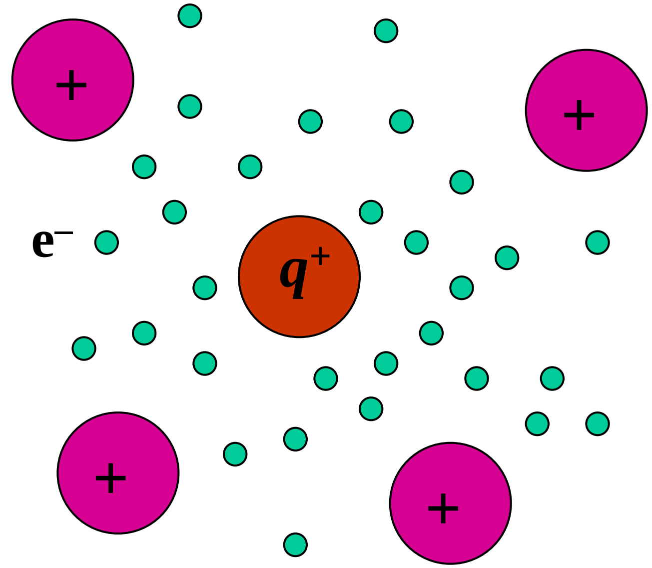
$$\delta x(t) = \delta x(0)\cos(\omega_p t)$$

$$E = \frac{\sigma}{\varepsilon_0} = \text{electric field created by a plane capacitor}$$

- NB: in this simple approximation there is *no damping of the oscillations*.

Screening length

- Positive charge is surrounded by negative electrons
- Screening of the electrostatic field



Poisson's equation

$$
\begin{aligned}
\Delta\phi &= -\frac{e}{\varepsilon_0}[n_i - n_e] - \frac{q}{\varepsilon_0}\delta(\mathbf{r}) \\
n_e &= n_0 \exp(e\phi/k_B T_e) \simeq n_0(1 + e\phi/k_B T_e) \\
\Delta\phi &= \boxed{\frac{e^2 n_0}{\varepsilon_0 k_B T_e}}\,\phi - \frac{q}{\varepsilon_0}\delta(\mathbf{r}) \\
\phi &\sim \frac{q}{4\pi\varepsilon_0}\frac{\exp(-r/\lambda_D)}{r}
\end{aligned}
$$

$n_i \approx n_0$

$\boxed{1/\lambda_D^2}$

$\lambda_D = V_{th}/\omega_p =$ Debye length

Quantum case: Fermi-Dirac distribution: $\lambda_{TF} = V_F/\omega_p =$ Thomas - Fermi screening length

Coupling parameter

- **<u>Dimensionless parameters</u>**: important to determine the physical regimes
- Using the quantities: **e, m, n, k_BT, ε_0** one can construct only one (classical) dimensionless parameter
- **Classical coupling parameter** :

$$\boxed{g_C = \frac{e^2 n^{1/3}}{\varepsilon_0 k_B T}}$$

- Can be written as the ratio of the kinetic energy over the potential (Coulomb) energy

$$g_C = E_{\rm pot}/E_{\rm kin} \qquad E_{\rm pot} \sim e^2 n^{1/3}/\varepsilon_0 \;; \qquad E_{\rm kin} \sim k_B T$$

- **Quantum coupling parameter:**

$$g_Q = \frac{E_{\rm pot}}{E_F} \sim \frac{e^2 m}{\hbar^2 \varepsilon_0 \; n^{1/3}} \sim \left(\frac{\hbar \omega_p}{E_F}\right)^2 \sim \boxed{\frac{r_s}{a_0}}$$

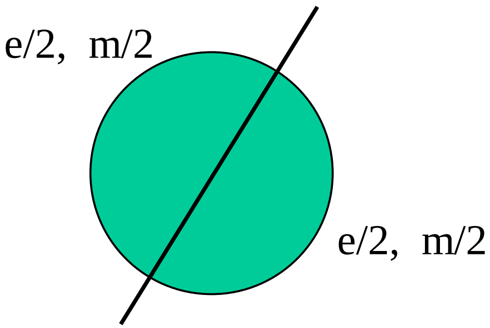
Bohr radius:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

- *g* << 1 : "collective" effects dominate → "mean field"
- *g* ≈ 1 : binary collisions become important

A (classical) thought experiment

- Let's imagine we can "cut" an electron in two
- Various quantities then transform as follows
  - $e \to e/2$; $m \to m/2$
  - $v \to v$
  - $n \to 2n$, but: $\rho = en \to \rho$
  - $T \to T/2$, but: $p = nT \to p$



- What happens to the classical time, space, and velocity scales :

$$\left.\begin{array}{l} \omega_p \to \omega_p \\ \lambda_D \to \lambda_D \\ v_{th} \to v_{th} \end{array}\right\} \text{They remain invariant!}$$

- Classical coupling parameter: $g_C \to g_C / 2$
- After N>>1 "cuttings", we end up with a continuous distribution of mass and charge
- Only the **mean field** remains, which is thus characterized by:
  - **Classical time, space, and velocity scales : ω_{p}, v_{th}, λ_D**
  - **Coupling parameter: $g_C \to 0$**

Typical metallic parameters

Gold

n	$5.90 \times 10^{28}\ \mathrm{m}^{-3}$
$\hbar\omega_p$	$9.02\ \ \mathrm{eV}$
τ_p	$0.5\ \mathrm{fs}$
T_F	$6.42 \times 10^{4}\ \mathrm{K}$
E_F	$5.53\ \mathrm{eV}$
v_F	$1.4 \times 10^{6}\ \mathrm{ms}^{-1}$
λ_{TF}	$0.09\ \mathrm{nm}$
r_s	$0.159\ \mathrm{nm}$
r_s/a_0	3.01

Same order of magnitude

Metal vs. semiconductor nanostructures

Metals

$$
\begin{aligned}
n_e &\simeq 10^{28}\ \mathrm{m}^{-3} \\
m &= m_e \\
\varepsilon &= \varepsilon_0 \\
a_0 &\simeq 0.0529\ \mathrm{nm} \\
L_{\mathrm{screen}} &\simeq 0.1\ \mathrm{nm} \\
\omega_p^{-1} &\simeq 1\ \mathrm{fs} \\
E_F &\simeq 5\ \mathrm{eV} \approx 60000\ \mathrm{K} \\
r_s/a_0 &\simeq 1
\end{aligned}
$$

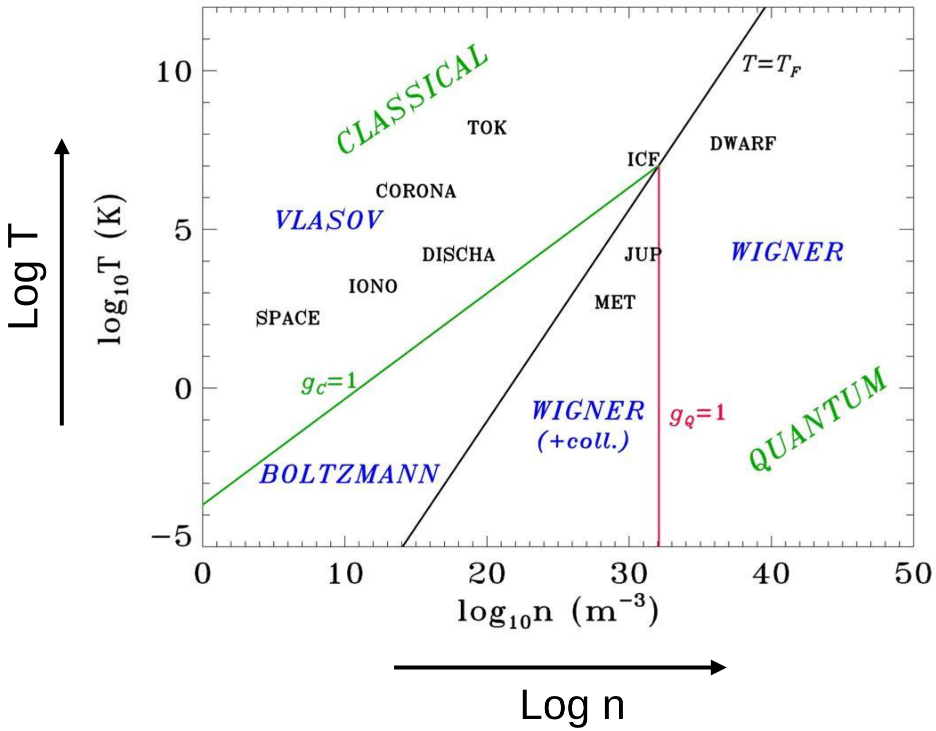
Semiconductors

$$
\begin{aligned}
n_e &\simeq 10^{22}\ \mathrm{m}^{-3} \\
m_* &\simeq 0.067\ m_e \\
\varepsilon &\simeq 12\ \varepsilon_0 \\
a_0^* &\simeq 10\ \mathrm{nm} \\
L_{\mathrm{screen}} &\simeq 10\ \mathrm{nm} \\
\omega_p^{-1} &\simeq 1\ \mathrm{ps} \\
E_F &\simeq 5\ \mathrm{meV} \approx 60\ \mathrm{K} \\
r_s/a_0^* &\simeq 1
\end{aligned}
$$

$$
a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}
$$

Log n – log T diagram

- We have found three dimensionless parameters (which depend on n and T):
  - T/T_F : classical vs. quantum
  - g_C : collective vs. collisional (classical)
  - $g_Q \sim r_s/a_0$: collective vs. collisional (quantum)



$$T/T_F = 1$$

$$T_F = K \times n^{2/3}$$

$$\log(T/T_F) = \log T - \frac{2}{3}\log n - \log K$$

$$\boxed{\log T = \frac{2}{3}\log n + \log K}$$

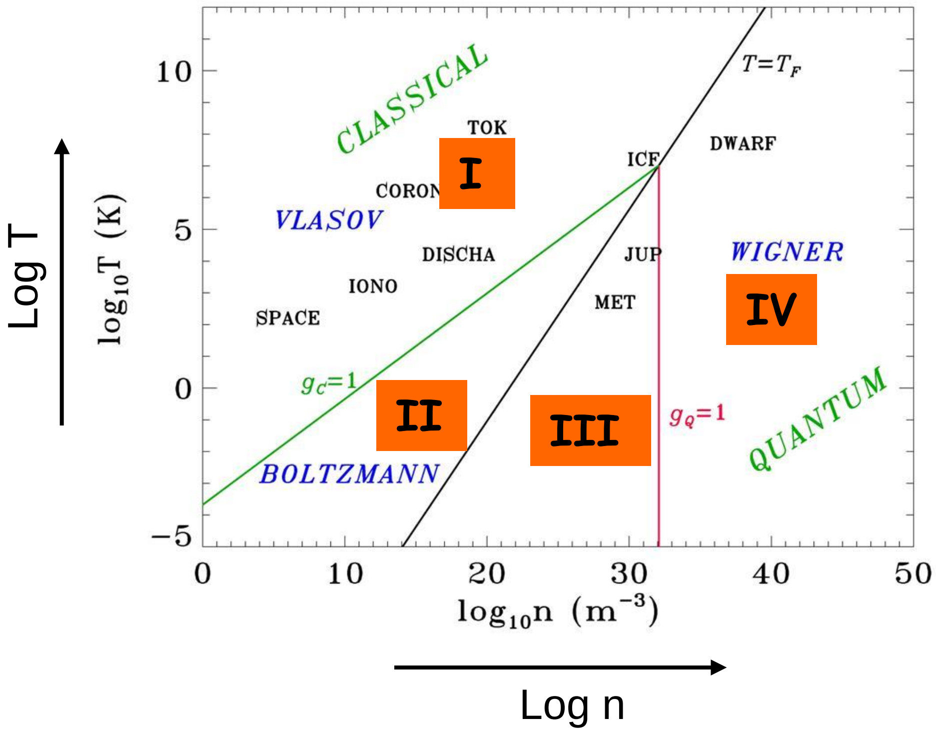
Log n – log T diagram

I. Mean-field classical

II. Non-mean-field classical

III. Non-mean-field quantum

IV. Mean-field quantum



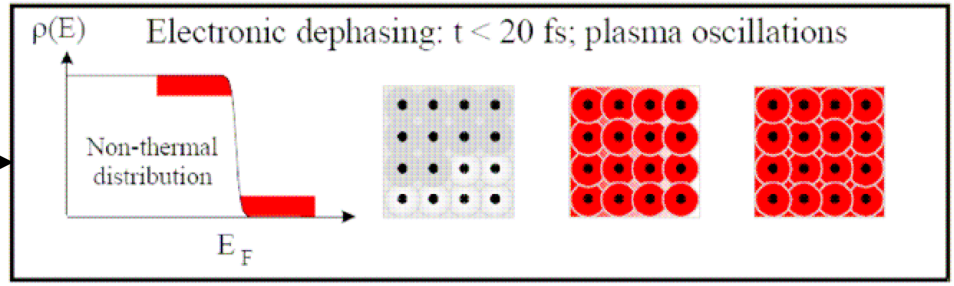
- TOK: tokamak experiment (magnetic confinement fusion)
- CORONA: solar corona
- IONO: ionosphere
- DISCHA: electric discharge
- SPACE: interstellar space
- ICF: inertial confinement fusion
- DWARF: white dwarf star
- JUP: Jupiter's core
- MET: metals

Timescales beyond the plasma period (τ_p~1 fs)

Initial equilibrium: Te = Ti ≈ 300K

The laser pulse deposits some energy in the electron gas → nonequilibrium distribution.

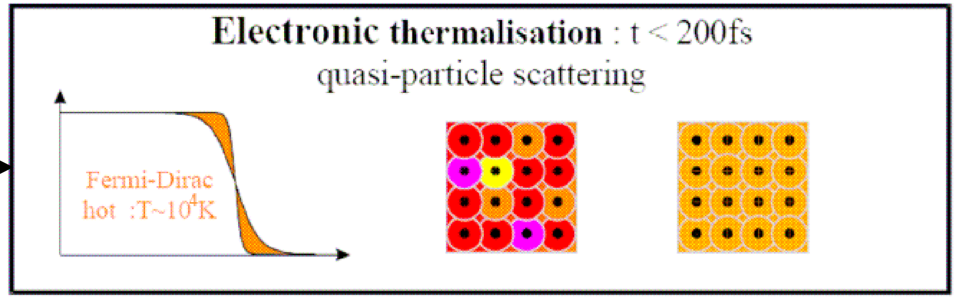
Mean field



τ_p

The electron gas thermalizes via **e-e collisions**: Te >> 300K

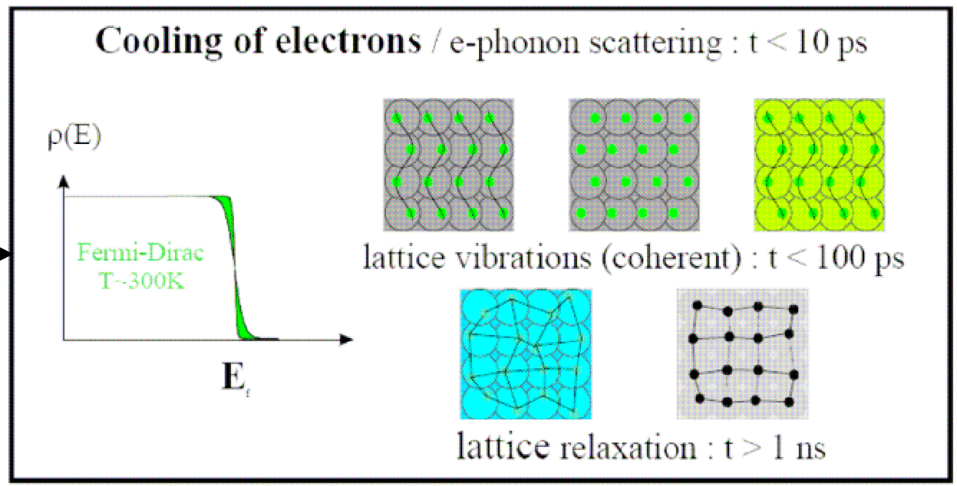
Beyond mean field



$\tau_{e\text{-}e}$

Coupling to the ion lattice (**phonons**) : the electron gas returns to its initial temperature.

Beyond mean field



$\tau_{e\text{-}ph}$

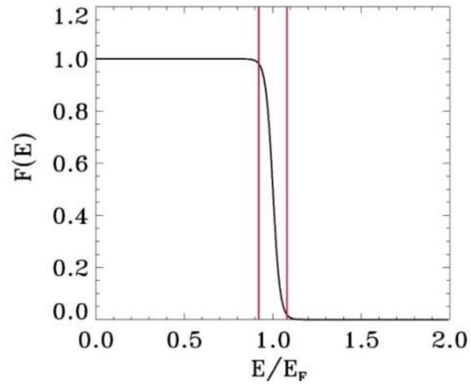
Collisional timescales — electron-electron collisions

- Pauli principle reduces the e-e collision frequency
- For T=0: no collisions, as all quantum states are occupied ("**Pauli blocking**").
- For T>0: only electrons with energy comprised in a range of $k_B T$ around the Fermi surface (E_F) can undergo collisions. Their collision rate is (inverse of lifetime τ):

$$\nu'_{ee} \sim k_B T/\hbar \qquad\qquad (\tau = \hbar / \Delta E)$$

- The *average* collision rate is obtained by multiplying ν'_{ee} by the number of electrons available for collisions, which is of the order T/T_F :

$$\nu_{ee} \sim \frac{k_B T^2}{\hbar\, T_F}$$



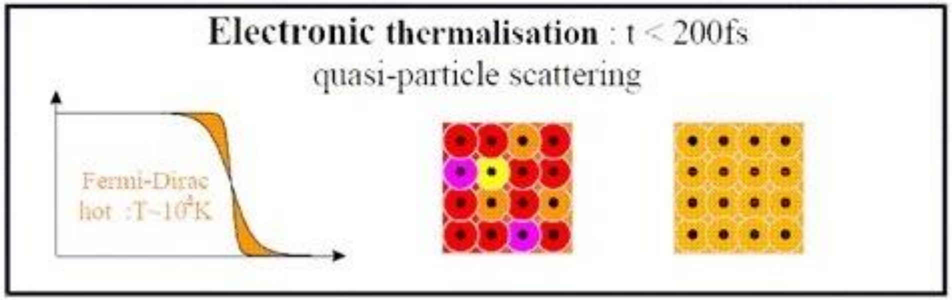
- Using dimensionless quantities:

$$\frac{\nu_{ee}}{\omega_p} = \frac{E_F}{\hbar\omega_p}\left(\frac{T}{T_F}\right)^2 \sim 10^{-5}$$

which would yield (at T=300K): **$\tau_{ee} = 1/\nu_{ee} \approx 8\,\mathrm{ps}$ → far too long!**

Electron-electron collisions

- But the previous reasoning is correct only at thermal equilibrium
- Recall that the laser pulse brings the electrons strongly out of equilibrium
- The kinetic energy acquired by the electrons in this early transient corresponds to an effective temperature T ≈ 3000 K
- Using this value we obtain, for gold
  - $\tau_{e\text{-}e} \approx$ **80 fs**
  - Consistent with observations



Electron-phonon collisions: two-temperature model

$$U = \text{ internal energy}$$

$$\frac{dU}{dt} = -(\text{heat diffusion}) - (\text{heat transfer to ions}) + (\text{power injected})$$

$$dU = C(T)\, dT \ : \ C = \text{heat capacity}$$

$$\boxed{\begin{aligned} C_e(T_e)\frac{dT_e}{dt} &= \kappa\nabla^2 T_e - G(T_e - T_i) + P(t) \\ C_i \frac{dT_i}{dt} &= G(T_e - T_i) \end{aligned}}$$

$C_{e,i}$: heat capacities

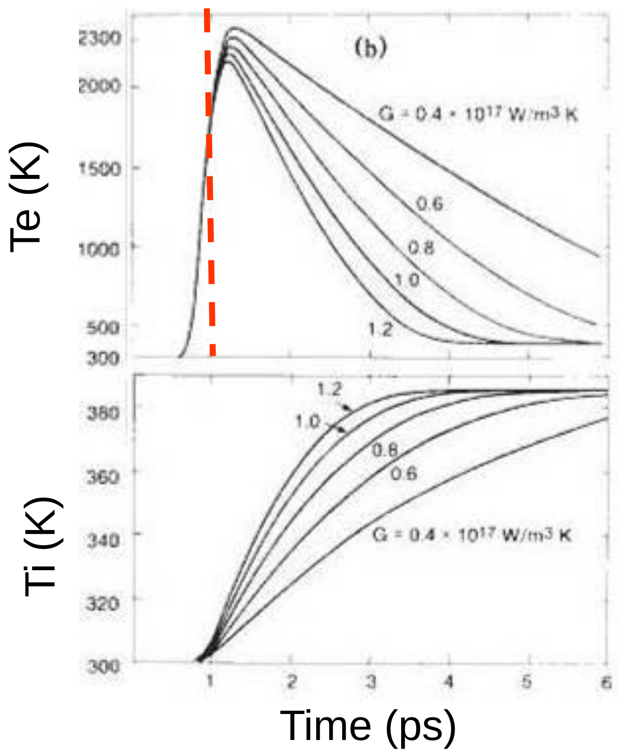
G : coupling constant

κ : heat conductivity

Electron-phonon collisions: two-temperature model

$$C_e(T_e)\frac{dT_e}{dt} = \kappa\nabla^2 T_e - G(T_e - T_i) + P(t)$$

$$C_i \frac{dT_i}{dt} = G(T_e - T_i)$$



Sodium

$$C_e(T_e) = \frac{\pi^2}{2} n_e k_B \frac{T_e}{T_F} \approx 96.6\, T_e \quad \left[\mathrm{J\,m^{-3}K^{-1}}\right]$$

$$C_i = 3.5\times 10^6 \left[\mathrm{J\,m^{-3}K^{-1}}\right] >> C_e$$

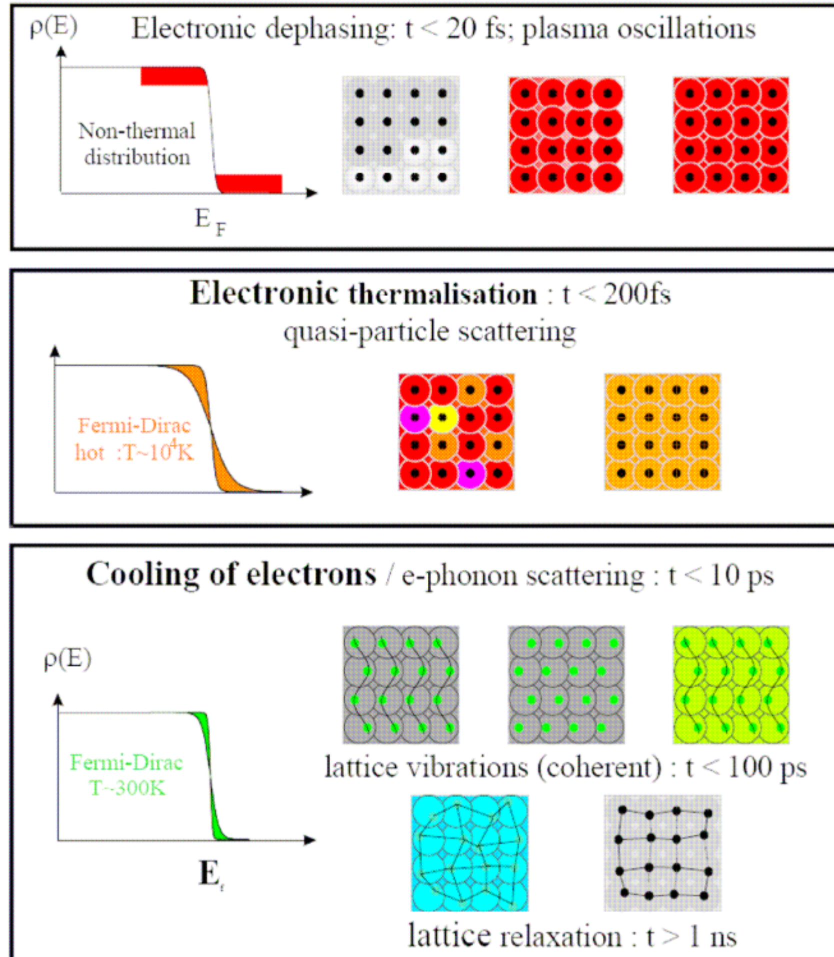
$$G = 0.4\times 10^{17} \left[\mathrm{W\,m^{-3}K^{-1}}\right]$$

$\boxed{\tau_{e\text{-}ph} = 1 - 5\ \mathrm{ps}}$

Summary of time scales

$$\tau_p \ll \tau_{e\text{-}e} \leq \tau_{e\text{-}ph}$$

τ_p	$\tau_{e\text{-}e}$	$\tau_{e\text{-}ph}$
0 – 50 fs	50 – 500 fs	1 ps – 5 ps



What we (might) have learnt from lecture #1…

- Transition from classical to quantum at the nanometer scale
  - $\lambda_B > r_s \sim n^{-1/3}$
  - $T_e < T_F$
- Typical time, velocity, and length scales
  - Plasma frequency
  - Thermal speed / Fermi speed
  - Debye length / Thomas-Fermi screening length
- Dimensionless coupling parameter (classical and quantum)
  - Defines the “mean field” approximation
- Various regimes in the log n – log T plane
- Timescales beyond the plasma period
  - Electron-electron collision time
  - Electron-phonon collision time