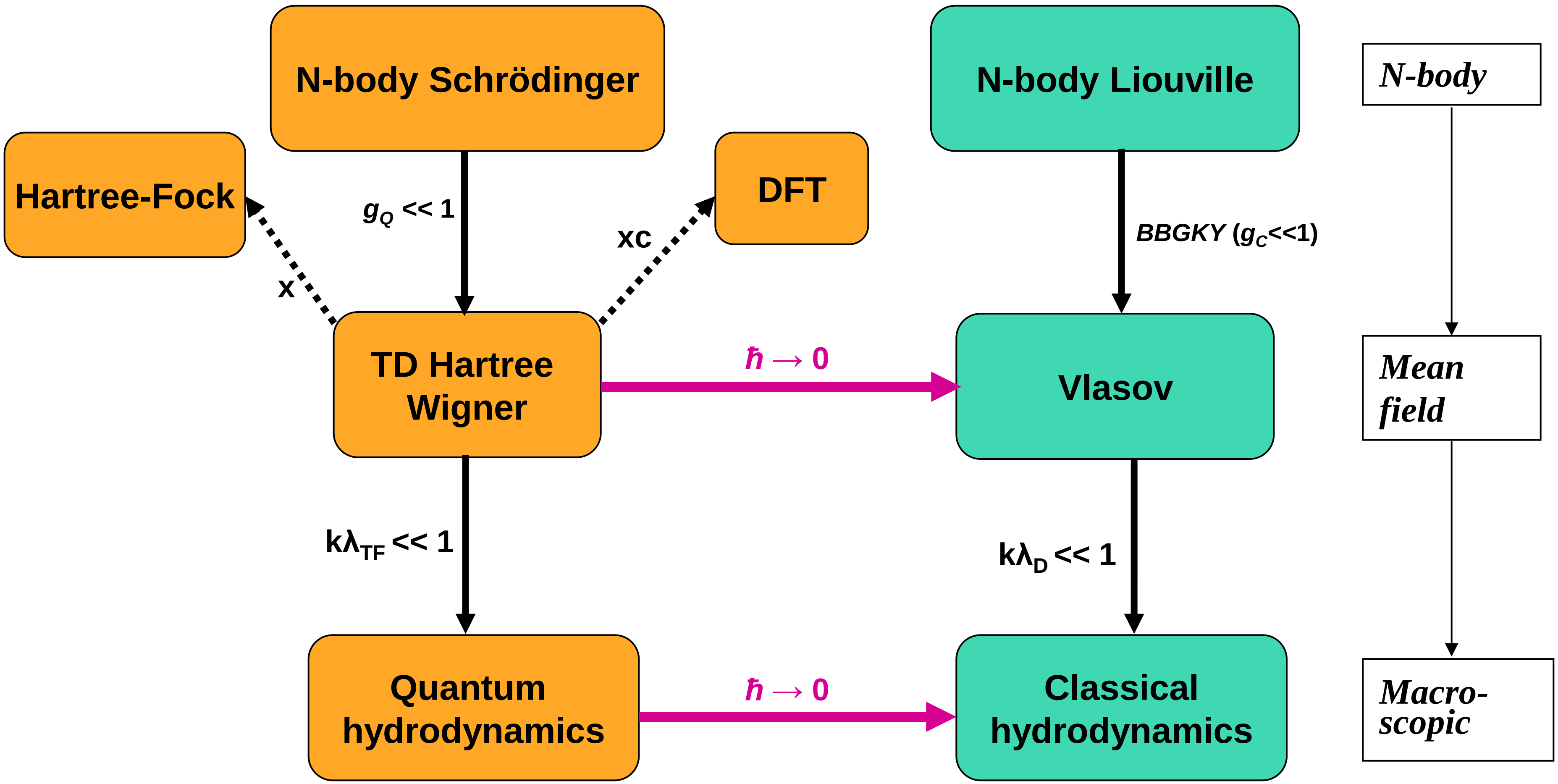
Plan of the lectures

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**
6. Linear theory and comparison of various models
7. Illustration: the nonlinear electron dynamics in thin metal films

Synopsis of classical and quantum models



Why do we need macroscopic models?

- Even mean-field model are sometimes too complex
  - **Classical**: 6D Vlasov equation in phase space
  - **Quantum**: Hartree or DFT equations: N three-dimensional Schrödinger-like equations (N >> 1)

Classical fluid (hydrodynamic) models – I.

Vlasov eq.

$$\boxed{\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + \frac{eE}{m}\frac{\partial f}{\partial v} = 0}$$

$f = f(x, v, t)$; $E(x,t) = -\frac{\partial \phi}{\partial x}$

Take velocity "moments" of the left-hand side:

$$\int (\mathrm{LHS}) \cdot v^\alpha \, dv = 0 \quad , \qquad \alpha = 0, 1, 2, \ldots$$

- $\underline{\alpha = 0}$

$$\boxed{\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(n u) = 0 \quad ; \ \text{continuity equation}}$$

- $n(x,t) \equiv \int f \, dv$: density
- $u(x,t) \equiv \frac{\int f v \, dv}{n}$: average velocity
- $J(x,t) \equiv n u$: current

in 3D : $\boxed{\frac{\partial n}{\partial t} + \nabla \cdot (n \vec{u}) = 0}$

Classical fluid models II.

- $\underline{d = 1}$

♦ $\frac{\partial}{\partial t} \int v f \, dv = \frac{\partial}{\partial t}(nu)$

♦ $\int dv \, v^2 \frac{\partial f}{\partial x} = \frac{\partial}{\partial x} \int v^2 f \, dv$

♦ $\int v \frac{\partial f}{\partial v} \, dv = - \int f \, dv = -n$

$$\boxed{\frac{\partial}{\partial t}(nu) + \frac{\partial}{\partial x} \int v^2 f \, dv - \frac{e}{m} E n = 0}$$

Let us write : $v = u + w$: $\begin{cases} u = \text{average} = \langle v \rangle \\ w = \text{fluctuations}, \ \langle w \rangle = 0 \end{cases}$

$$\int v^2 f \, dv = \int u^2 f \, dv + \int w^2 f \, dw + 2 \int u w f \, dw =$$

$$= n u^2 + \int w^2 f \, dw + 0$$

We define the pressure : $P(x,t) \equiv m \int w^2 f \, dw = m \int (v-u)^2 f \, dv$

Then : $\int v^2 f \, dv = n u^2 + \frac{P}{m}$

Classical fluid models III.

$$\frac{\partial}{\partial t}(nu) = n\frac{\partial u}{\partial t} + u\frac{\partial n}{\partial t} = n\frac{\partial u}{\partial t} - u\frac{\partial}{\partial x}(nu) = n\frac{\partial u}{\partial t} - \frac{\partial}{\partial x}(nu^2) + nu\frac{\partial u}{\partial x}$$

Finally :

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = \frac{e}{m}E - \frac{1}{mn}\frac{\partial P}{\partial x}$$

In 3D :

$$\boxed{\frac{\partial \vec{u}}{\partial t} + \vec{u}\cdot\nabla\vec{u} = \frac{e}{m}\vec{E} - \frac{1}{mn}\partial_j P_{ij}}$$

Pressure can be a tensor : $P_{ij} = m\iiint w_i w_j f \, d\vec{w}$

Classical fluid models IV.

Closure : adiabatic hypothesis : $q=0$

$$\underbrace{\frac{\partial P}{\partial t} + u\frac{\partial P}{\partial x}}_{\frac{DP}{Dt}} + 3P\frac{\partial u}{\partial x} = 0$$

$$\boxed{\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + u\frac{\partial}{\partial x} \quad : \text{ convective derivative}}$$

Using the continuity equation:

$$\frac{\partial u}{\partial x} = -\frac{1}{n}\left(\frac{\partial n}{\partial t} + u\frac{\partial n}{\partial x}\right) = -\frac{1}{n}\frac{Dn}{Dt}$$

$$\Rightarrow \quad \frac{1}{P}\frac{DP}{Dt} - \frac{3}{n}\frac{Dn}{Dt} = 0$$

$$\frac{D}{Dt}\left(\log P - 3\log n\right) = 0 \quad \Longrightarrow \quad \boxed{P = \text{const.} \times n^3}$$

in N dimensions, the exponent is : $\boxed{\gamma = \frac{N+2}{N}}$

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

Classical fluid models V.

$$\begin{cases} \dfrac{\partial n}{\partial t} + \nabla\cdot(n\vec{u}) = 0 & \text{Continuity} \\ \dfrac{\partial \vec{u}}{\partial t} + \vec{u}\cdot\nabla\vec{u} = \dfrac{e}{m}\vec{E} - \dfrac{1}{m}\dfrac{\nabla P}{n} & \text{"Euler" eq.} \\ P = P(n) & \text{Closure} \end{cases}$$

$$P(n) = \text{const.} \times n^{\gamma}$$

- $\gamma = \dfrac{N+2}{N}$: adiabatic closure $(q=0)$
- $\gamma = 1$: isothermal closure : $P = k_B T\, n$

- We have obtained a set of just 2 evolution equations in real space (3D)
  - Electric field comes from Poisson's equation + external fields
- They replace the more complex Vlasov equation in phase space (6D)

Quantum hydrodynamics I.

- Hydrodynamic ("fluid") equations are obtained by taking moments of the relevant kinetic equation (Vlasov or Wigner):

$$n(x,t) = \int f\, dv\,, \quad u(x,t) = \frac{1}{n}\int f v\, dv\,, \quad P(x,t) = m\left(\int f v^2 dv - n u^2\right)$$

density (0) average velocity (1) pressure (2)

- Starting with either the Vlasov or Wigner equations, we obtain the **same fluid equations:**

$$\frac{\partial n}{\partial t} + \frac{\partial (nu)}{\partial x} = 0\,,$$

Continuity equation

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = \frac{e}{m}\frac{\partial \phi}{\partial x} - \frac{1}{mn}\frac{\partial P}{\partial x}\,.$$

Euler equation

- What happened to quantum effects? They're hidden in the pressure term…

Quantum hydrodynamics II.

- We rewrite the pressure $P(x,t) = m\left(\int f v^2 dv - nu^2\right)$ using the expression of the Wigner function in terms of *N* wave functions ψ_α :

$$f(x,v,t) = \sum_{\alpha=1}^{N_{\rm orb}} \frac{m}{2\pi\hbar}\, p_\alpha \int_{-\infty}^{+\infty} \psi_\alpha^*\left(x+\frac{\lambda}{2},t\right)\psi_\alpha\left(x-\frac{\lambda}{2},t\right) e^{imv\lambda/\hbar}\, d\lambda$$

- We obtain:

$$P = \frac{\hbar^2}{4m}\sum_\alpha p_\alpha\left(2\left|\frac{\partial\psi_\alpha}{\partial x}\right|^2 - \psi_\alpha^*\frac{\partial^2\psi_\alpha}{\partial x^2} - \psi_\alpha\frac{\partial^2\psi_\alpha^*}{\partial x^2}\right)$$

$$+\frac{\hbar^2}{4mn}\left[\sum_\alpha p_\alpha\left(\psi_\alpha^*\frac{\partial\psi_\alpha}{\partial x} - \psi_\alpha\frac{\partial\psi_\alpha^*}{\partial x}\right)\right]^2 .$$

Mean velocity for each ψ_α

- We express the wave functions in terms of their amplitude A and phase S

$$\psi_\alpha(x,t) = A_\alpha(x,t)\exp\left(iS_\alpha(x,t)/\hbar\right) \qquad mu_\alpha = \partial S_\alpha/\partial x$$

- We can split the pressure into a "classical" and a "quantum" part:

$$P = P^{\rm C} + P^{\rm Q}$$

Quantum hydrodynamics III.

$$P^C = mn\left[\frac{\sum_\alpha p_\alpha A_\alpha^2 u_\alpha^2}{n} - \left(\frac{\sum_\alpha p_\alpha A_\alpha^2 u_\alpha}{n}\right)^2\right] = mn(\langle u_\alpha^2\rangle - \langle u_\alpha\rangle^2)$$

Uncertainty due to standard velocity dispersion

$$P^Q = \frac{\hbar^2}{2m}\sum_\alpha p_\alpha\left[\left(\frac{\partial A_\alpha}{\partial x}\right)^2 - A_\alpha\frac{\partial^2 A_\alpha}{\partial x^2}\right]$$

Uncertainty due to quantum effects

- In order to close the system, we need a relation between the pressure and the density:
  - $\boxed{P^C = P^C(n)}$: classical equation of state
  - $A_\alpha \rightarrow \sqrt{n} \Rightarrow \boxed{P^Q = \frac{\hbar^2}{2m}\left[\left(\frac{\partial}{\partial x}\sqrt{n}\right)^2 - \sqrt{n}\frac{\partial^2}{\partial x^2}\sqrt{n}\right]}$ valid for $\lambda >> \lambda_{TF}$ (long wavelengths)
- We finally obtain the conservation equation for u

$$\boxed{\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = \frac{e}{m}\frac{\partial \phi}{\partial x} - \frac{1}{mn}\frac{\partial P^C}{\partial x} - \frac{1}{mn}\frac{\partial P^Q}{\partial x}.}$$

coupled to the continuity and Poisson's equations

Quantum hydrodynamics: summary

$$\begin{cases} \dfrac{\partial n}{\partial t} + \dfrac{\partial (nu)}{\partial x} = 0, \\ \dfrac{\partial u}{\partial t} + u\dfrac{\partial u}{\partial x} = \dfrac{e}{m}\dfrac{\partial \phi}{\partial x} - \dfrac{1}{mn}\dfrac{\partial P^C}{\partial x} - \dfrac{1}{mn}\dfrac{\partial P^Q}{\partial x}. \end{cases}$$

$P^C = P^C(n)$: "equation of state"

$$P^Q = \frac{\hbar^2}{2m}\left[\left(\frac{\partial}{\partial x}\sqrt{n}\right)^2 - \sqrt{n}\frac{\partial^2}{\partial x^2}\sqrt{n}\right]$$

QHD: steady state solutions

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = \frac{e}{m}\frac{\partial \phi}{\partial x} - \frac{1}{mn}\frac{\partial P^C}{\partial x} - \frac{1}{mn}\frac{\partial P^Q}{\partial x} . = 0$$

- For a perfect Fermi gas at T=0

  $$P_C = \frac{2}{5} n E_F \qquad E_F = \text{const} \times n^{2/3}$$

- Then it follows: $\frac{1}{n}\frac{\partial P_C}{\partial x} = \frac{\partial E_F}{\partial x}$

- Also assume: $P_Q = 0$

- Then: $e\frac{\partial \phi}{\partial x} - \frac{\partial E_F}{\partial x} = 0 \qquad -e\,\phi = V_H + V_{ext}$

- Finally: $V_{ext} + V_H + E_F = \mu$ Thomas-Fermi equation

- *QHD can be viewed as a time-dependent generalization of Thomas-Fermi theory*

Equations of state

- Zero-temperature 3D electron gas. “Classical” pressure **at equilibrium**, computed from the Fermi-Dirac distribution

$$P_0 = \frac{2}{5} n_0 E_F \sim n_0^{5/3}$$

- What happens in a dynamical situation?

  The density n(x,t) will differ from the equilibrium value n_0(x).

  We write for the pressure

$$\frac{P}{P_0} = \left(\frac{n}{n_0}\right)^{\gamma}$$

- Adiabatic closure: $\gamma = (N+2)/N = 5/3$
- Not appropriate for wave propagation, which is essentially a 1D phenomenon
- In that case, one has to take the 1D value ($\gamma = 3$) even for a 3D situation.

Schrödinger equation in hydrodynamic form – I.

- What is the origin of P^{Q}?
- Schrödinger equation: $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi$
- Separate amplitude and phase of the wave function ("Madelung transformation")

$$\psi(x,t) = A(x,t)e^{iS(x,t)/\hbar}$$

- By using:

$$\psi_t = (A_t + iS_t A/\hbar)\, e^{iS/\hbar}$$
$$\psi_{xx} = \left\{A_{xx} - (S_{xx})^2 A/\hbar^2 + i(S_{xx}A + 2A_x S_x)\right\} e^{iS/\hbar}$$

- The equations for the imaginary part yields the continuity equation:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(nu) = 0 \qquad \begin{cases} n = A^2 \\ u = \dfrac{\partial_x S}{m} \end{cases}$$

Schrödinger equation in hydrodynamic form – II.

- The real part of the Schrödinger equation yields:

$$\frac{\partial S}{\partial t} = -\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 - V(x,t) + \underbrace{\frac{\hbar^2}{2m}\left(\frac{\partial^2_{xx} A}{A}\right)}_{\text{Bohm potential}}$$

Hamilton-Jacobi equation

- It can be written as an Euler hydrodynamic equation

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} = -\frac{1}{m}\frac{\partial V}{\partial x} + \frac{\hbar^2}{2m^2}\frac{\partial}{\partial x}\left(\frac{\partial^2_{xx}\sqrt{n}}{\sqrt{n}}\right)$$

$$\begin{cases} n = A^2 \\ u = \dfrac{S_x}{m} \end{cases}$$

- The Bohm potential is related to the "quantum pressure"

$$\frac{1}{n}\frac{\partial P^Q}{\partial x} = \frac{\partial V_{Bohm}}{\partial x}$$

- Remember also:

$$\frac{1}{n}\frac{\partial P^C}{\partial x} = \frac{\partial E_F}{\partial x}$$

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