How to Model Quantum Plasmas

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Outline of the talk

- Introduction/Motivations
- When are quantum effects important?
- Mathematical models for quantum plasmas
  - Wigner-Poisson
  - Hartree (Multi-Schrödinger, TDLDA)
  - Quantum Hydrodynamics
- Examples and applications
  - Linear waves in infinite medium
  - Two-stream instability
  - Finite systems: Nanoparticles and thin metal films
- Conclusions and future developments

Introduction/Motivations

Fundamental questions

- How are kinetic equations modified by quantum effects?
- What happens to typical plasma effects : Debye screening, Landau damping, plasma and sound waves . . . ?

Applications

- **Semiconductors**
  - Miniaturisation of electronic devices
  - De Broglie wavelength comparable to size of the device
- **Nanosized objects**
  - E.g.: Metal clusters, thin metal films
  - Clusters composed of small (10−1000) number of metallic atoms
  - Valence electrons behave as an electron plasma, neutralized by ionic background
  - Large particle densities: $n \sim 10^{28}$ m^{-3}
  - But no crystalline structure: no Block waves etc . . . ("amorphous metals")

When are quantum effects important?

- Define the thermal de Broglie wavelength ("size" of a quantum particle):

$$\lambda_B = \frac{\hbar}{m v_{\rm th}}$$

- Quantum effects are important when λ_B exceeds the inter-particle distance $d = n^{-1/3}$, i.e.:

$$n\lambda_B^3 > 1$$

- This condition corresponds to $T < T_F$, where T_F is the Fermi temperature:

$$\kappa T_F = E_F = m\frac{v_F^2}{2} = \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} n^{2/3}$$

and E_F and v_F are the Fermi energy and Fermi speed.

- We have obtained our first dimensionless parameter :

$$\chi \equiv \left(\frac{T_F}{T}\right)^{3/2} = n\lambda_B^3$$

Collisionless (mean-field) regimes

Classical plasmas ($T \gg T_F$):

- The coupling parameter is defined as the ratio of the interaction energy to the kinetic energy

$$g_C \equiv \frac{E_{\rm int}}{E_{\rm kin}}$$

- For a classical plasma, the interaction and kinetic energies are given respectively by the electrostatic and the thermal energy:

$$E_{\rm int} = \frac{e^2 n^{1/3}}{\varepsilon_0} \; ; \qquad E_{\rm kin} = \kappa T$$

- The **classical coupling parameter** can be expressed as

$$g_c = \left(\frac{1}{n\lambda_D^3}\right)^{2/3} = \frac{e^2 n^{1/3}}{\varepsilon_0 \kappa T}$$

  where $\lambda_D = (\varepsilon_0 \kappa T / n e^2)^{1/2}$ is the Debye length.

- $g_C \ll 1 \Rightarrow$ collective effects dominate (mean-field)
  $g_C \simeq 1 \Rightarrow$ two-body correlations (collisions) are important.

- Classical plasmas are collisionless at high temperatures and low densities.

Quantum plasmas ($T \ll T_F$):

- Typical time, velocity, and length scales in a quantum plasma:
  - **Plasma frequency:**

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

  - **Fermi velocity** (replaces the classical thermal velocity; measures velocity dispersion):

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

  - **Fermi length** (length scale for electrostatic screening in a quantum plasma):

$$\lambda_F = \frac{v_F}{\omega_p}$$

- The kinetic energy is given by the Fermi energy $E_{\rm kin} = E_F$
- The **quantum coupling parameter** becomes

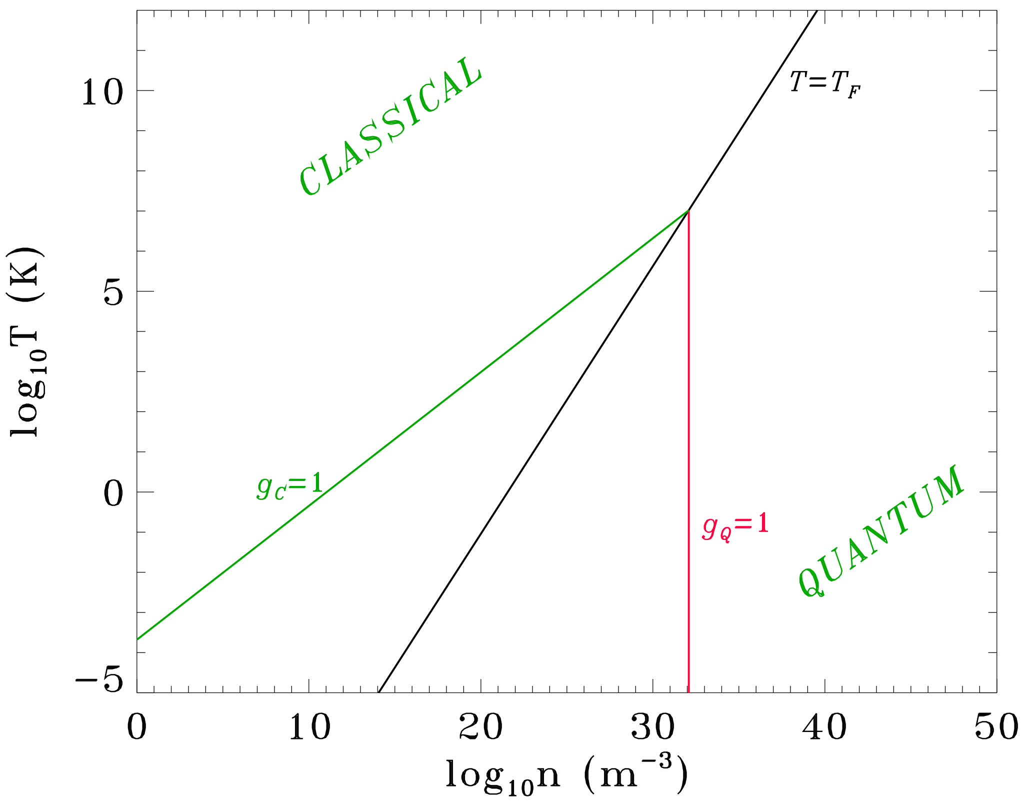
$$g_Q = \frac{E_{\rm int}}{E_F} = \left(\frac{1}{n\lambda_F^3}\right)^{2/3} = \left(\frac{\hbar\omega_p}{E_F}\right)^2 = \frac{e^2 m}{\hbar^2\varepsilon_0}\,n^{-1/3}$$

- Note: a quantum plasma is "more collisionless" at higher densities.

log T – log n diagram (for electrons)

- We plot the three curves corresponding to

$$T = T_F, \quad g_C = 1, \quad g_Q = 1$$



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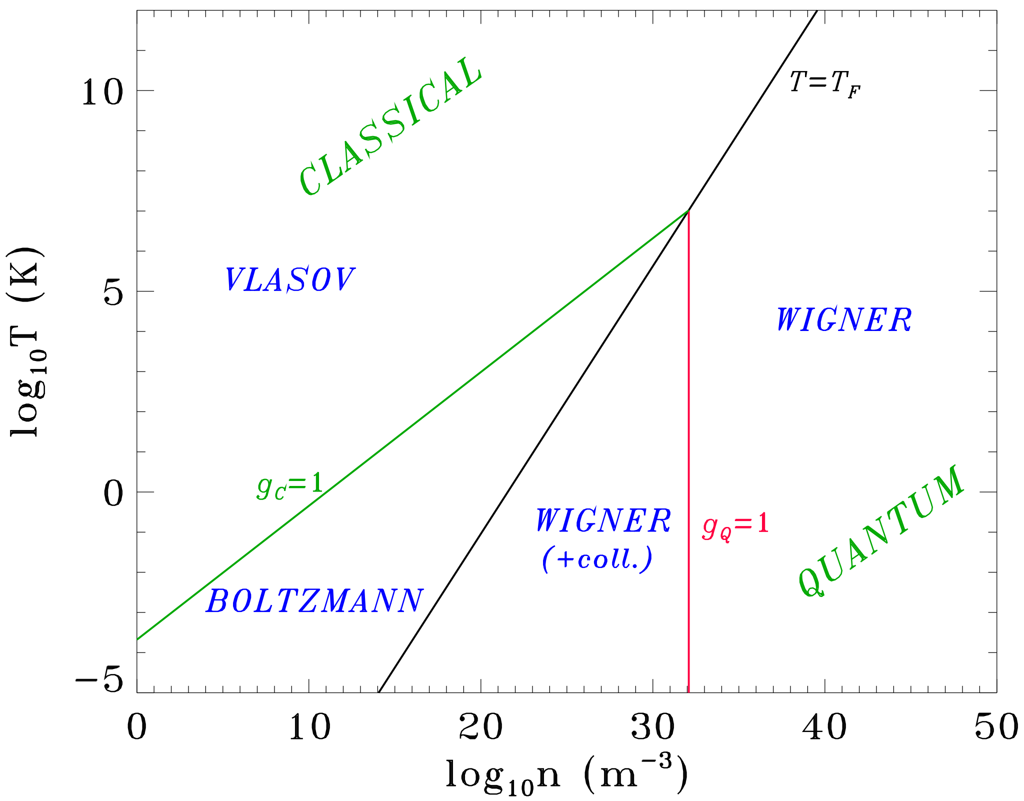

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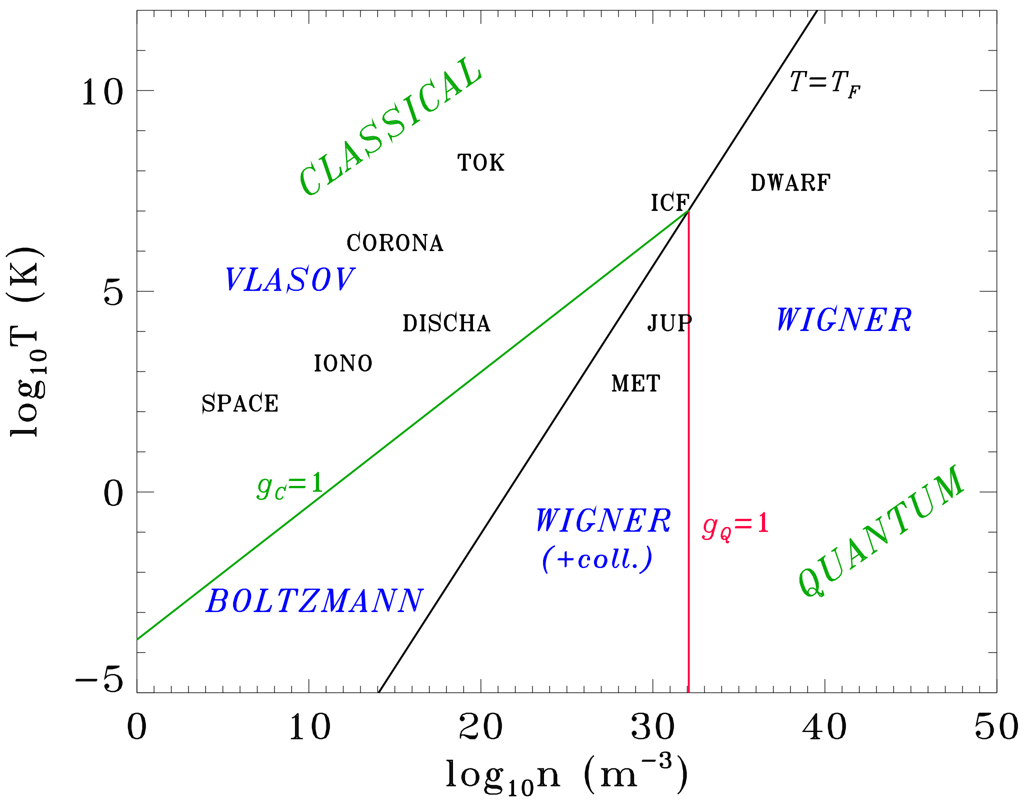
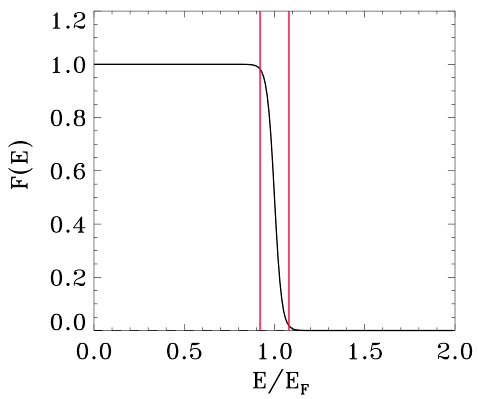


NB: Metals (and metallic nanoparticles) fall in the strongly-coupled quantum region ($T < T_F$, $g_Q > 1$): is the Wigner equation appropriate there?

Pauli blocking

- The Pauli exclusion principle inhibits electron-electron collisions at low temperatures (collision rate: $\nu_{ee} = 1/\tau_{ee}$).
- For $T = 0$, we have that: $\nu_{ee} \to 0$
- For $T < T_F$, only electrons with $E_F - \kappa T < E < E_F + \kappa T$ can undergo collisions.
- Their collision rate is: $\nu'_{ee} \simeq \kappa T/\hbar$ (Energy $\times$ lifetime $\sim \hbar$).



- The *average* e-e collision rate is obtained by multiplying ν'_{ee} by the fraction of electrons that can collide ($\sim T/T_F$):

$$\nu_{ee} = \nu'_{ee} \times \frac{T}{T_F} = \frac{\kappa T^2}{\hbar T_F}$$

- In normalized units, this expression reads as:

$$\frac{\nu_{ee}}{\omega_p} = \frac{E_F}{\hbar\omega_p} \left(\frac{T}{T_F}\right)^2 = \frac{1}{g_Q^{1/2}} \left(\frac{T}{T_F}\right)^2$$

- Thus $\nu_{ee} < \omega_p$ in the region where $T < T_F$, $g_Q > 1$.

Example with typical metallic parameters

n	5×10^{28} m^{-3}
T	300 K
ω_{pe}	1.3×10^{16} s^{-1}
τ_{pe}	0.5 fs
ν_{ee}	10^{11} s^{-1}
T_F	5.7×10^4 K
v_F	0.9×10^6 ms^{-1}
λ_F	0.9×10^{-10} m
g_Q	13.5

- $\tau_{pe} = 2\pi/\omega_{pe}$ is of the order of the femtosecond
- λ_F is of the order of the Ångstrom
- The e-e collision frequency is small: $\nu_{ee} \ll \omega_{pe}$

Remark

Far from thermodynamic equilibrium, Pauli blocking is less important, and the collision frequency can be considerably larger.

Wigner-Poisson model

- Representation of quantum mechanics in the classical phase space. Wigner function:

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

  with the probabilities p_α satisfying $\Sigma_{\alpha=1}^{N} p_\alpha = 1$.

- The Wigner function is not a true probability density, as it can be negative

- Can be used to compute averages :

$$\langle A \rangle = \int\int f_e(x,v) A(x,v) dx dv$$

- The Wigner function obeys the following evolution equation:

$$\frac{\partial f_e}{\partial t} + v \frac{\partial f_e}{\partial x} +$$

$$\frac{em}{2i\pi\hbar^2} \int\int d\lambda\, dv' e^{im(v-v')\lambda/\hbar} \left[\phi\left(x + \frac{\lambda}{2}\right) - \phi\left(x - \frac{\lambda}{2}\right)\right] f_e(x, v', t) = 0$$

  coupled to Poisson's equation for ϕ.

- Developing to order $O(\hbar^2)$

$$\frac{\partial f_e}{\partial t} + v \frac{\partial f_e}{\partial x} - \frac{e}{m} \frac{\partial \phi}{\partial x} \frac{\partial f_e}{\partial v} = \frac{e\hbar^2}{24m^3} \frac{\partial^3 \phi}{\partial x^3} \frac{\partial^3 f_e}{\partial v^3} + O(\hbar^4)$$

- The Vlasov equation is recovered for $\hbar \longrightarrow 0$.

Wigner-Poisson: linear approximation

- Dielectric constant:

$$\varepsilon(\omega, k) = 1 + \frac{m\omega_p^2}{k} \int_{-\infty}^{+\infty} \frac{f_0(v + \hbar k/2m) - f_0(v - \hbar k/2m)}{\hbar k(\omega - kv)} \, dv$$

- NB: recovers Vlasov-Poisson in the limit $\hbar \to 0$.

- For a homogeneous equilibrium $f_0(v)$ given by a 1D Fermi-Dirac at $T = 0$, the dispersion relation can be computed *exactly* :

$$\frac{\omega^2}{\omega_p^2} = \frac{\Omega^2}{\omega_p^2} \coth\left(\frac{\Omega^2}{\omega_p^2}\right) + k^2\lambda_F^2 + \frac{k^4\lambda_F^4}{4} \, g_Q$$

where

$$\frac{\Omega^2}{\omega_p^2} = \frac{\hbar\, k^3 v_F}{m\omega_p^2} = k^3\lambda_F^3 \, g_Q^{1/2}$$

- In the long wavelength limit, $k\lambda_F \ll 1$ (i.e. $\Omega \ll \omega_p$) the dispersion relation becomes:

$$\frac{\omega^2}{\omega_p^2} = 1 + k^2\lambda_F^2 + \left(\frac{k^4\lambda_F^4}{4} + \frac{k^6\lambda_F^6}{3}\right) g_Q - \frac{1}{45} k^{12}\lambda_F^{12} \, g_Q^2 + \ldots$$

- Double expansion in g_Q and $k\lambda_F$.

- NB : for $g_Q \to 0$, one obtains the (exact) Vlasov-Poisson dispersion relation: $\omega^2 = \omega_p^2 + k^2 v_F^2$

Multi-stream Schrödinger

(Hartree, TDLDA)

- N independent Schrödinger equations
- Coupled by Poisson's equation
- Describes a quantum-mechanical mixture

$$i\hbar\frac{\partial\psi_\alpha}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi_\alpha}{\partial x^2} - e\phi\psi_\alpha \ , \quad \alpha = 1, ..., N \qquad (1)$$

$$\frac{\partial^2\phi}{\partial x^2} = \frac{e}{\varepsilon_0}\left(\sum_{\alpha=1}^{N} p_\alpha|\psi_\alpha|^2 - n_0\right) \qquad (2)$$

- Each ψ_α can be though of as representing a "stream" (plane wave) with velocity u_α:

$$\psi_\alpha(x,t) = \sqrt{n_0}\ \exp\left(i\frac{mu_\alpha}{\hbar}\,(x - u_\alpha t/2)\right) \ ; \qquad |\psi_\alpha|^2 = n_0$$

- Linearizing around the above homogeneous equilibrium, we obtain the dielectric constant:

$$\varepsilon(\omega,k) = 1 - \sum_{\alpha=1}^{N}\frac{\omega_p^2}{(\omega - ku_\alpha)^2 - \hbar^2k^4/4m^2}$$

- Similar to the Dawson's classical multistream model. Indeed, the Wigner transform of ψ_α is $f_\alpha(x,v) = n_0\ \delta(v - u_\alpha)$.
- The Wigner-Poisson dielectric function is recovered for an infinite number of streams, $N \to \infty$.

Reduced collisionless quantum models

The Wigner-Poisson model includes both **quantum** and **kinetic** effects

Reduced models

- **Quantum + Fluid** $\Longrightarrow$ Quantum fluid equations
  - Obtained by taking moments of the Wigner equations in velocity space
  - Valid for long wavelengths: $k\lambda_F < 1$
- **Semiclassical + Kinetic** $\Longrightarrow$ Vlasov-Poisson
  - Classical dynamics (Vlasov)
  - Quantum ground state (Fermi-Dirac distribution)
  - Valid for relatively large excitation energies: $E^* \sim E_F$

Quantum fluid model – 1

- Take moments of the Wigner equation in velocity space
- Obtain continuity equation

$$\frac{\partial n}{\partial t} + \nabla \cdot (nu) = 0$$

and momentum balance equation with "exotic" pressure terms

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = \frac{e}{m}\nabla\phi + \frac{\hbar^2}{2m^2}\,\nabla \sum_{\alpha=1}^{N} p_\alpha \left(\frac{\nabla^2|\psi_\alpha|}{|\psi_\alpha|}\right) - \frac{1}{mn}\nabla P$$

- We want to obtain a closed system for the global quantities: density n and average velocity u.
- **First assumption:** $P = P(n)$ (equation of state).

For example, polytropic:

$$P(n) = C\ n^\gamma$$

- **Second assumption**

Replace:

$$\sum_{\alpha=1}^{N} p_\alpha \left(\frac{\nabla^2|\psi_\alpha|}{|\psi_\alpha|}\right) \implies \frac{\nabla^2\sqrt{n}}{\sqrt{n}}$$

It can be shown that this is correct for long wavelengths

$$\lambda \gg \lambda_F \equiv \frac{v_F}{\omega_p}$$

Quantum fluid model – 2

- With these assumptions, we obtain the following reduced system of fluid equations

$$\frac{\partial n}{\partial t} + \nabla \cdot (nu) = 0$$

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = \frac{e}{m}\nabla\phi + \frac{\hbar^2}{2m^2}\,\nabla\left(\frac{\nabla^2\sqrt{n}}{\sqrt{n}}\right) - \frac{1}{mn}\nabla P\ ,$$

where ϕ is given by Poisson's equation.

- By using the transformation

$$\Psi(x,t) = \sqrt{n(x,t)}\,\exp\left(iS(x,t)/\hbar\right)$$

(where $mu = \nabla S$ and $n = |\Psi|^2$), we show that the above system is equivalent to the following **nonlinear Schrödinger equation**

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\,\Psi - e\phi\Psi + W_{\text{eff}}(|\Psi|^2)\,\Psi$$

- $W_{\text{eff}}(n)$ is an effective potential related to the pressure $P(n)$. For instance, for a polytropic:

$$P = C\,n^\gamma \quad\Longrightarrow\quad W_{\text{eff}} = \frac{C\gamma}{\gamma-1}\,n^{\gamma-1}$$

Zero-temperature 1D electron gas

- For a 1D degenerate fermion gas ($T \ll T_F$) the pressure is given by

$$P(n) = \frac{mv_F^2}{3n_0^2}\, n^3$$

and the effective potential becomes

$$W_{\text{eff}} = \frac{mv_F^2}{2n_0^2}|\Psi|^4$$

- Note that here W_{eff} is a **repulsive** potential (manifestation of the Fermi pressure).

- We linearize our fluid model around the homogeneous equilibrium: $n = n_0$, $e\phi = E_F = \text{const}$.

- The reduced fluid system (or equivalently the NLSE) yields the **dispersion relation**

$$\omega^2 = \omega_p^2 + v_F^2 k^2 + \frac{\hbar^2 k^4}{4m^2}$$

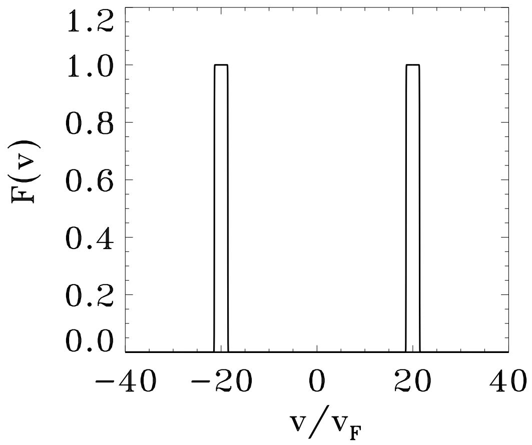
- Dispersion relation of the **full** Wigner-Poisson system for a FD equilibrium at $T = 0$:

$$\omega^2 = \omega_p^2 + v_F^2 k^2 + \frac{\hbar^2 k^4}{4m^2} + \frac{\hbar^2 \lambda_F^2}{3m^2}\, k^6 + \ldots$$

- The quantum fluid model is a good approximation of the linearized Wigner-Poisson system when: $k\lambda_F \ll 1$, i.e. for **long wavelengths**.

Quantum two-stream instability

- Consider two counterstreaming electron populations, each with $T \ll T_F$, and average velocities $\pm u_0$



- 1D, fixed neutralizing ionic background
- Modelled by two sets of fluid equations (one for each electron population)
- Suppose $u_0 \gg v_F$: then the Fermi pressure

$$P(n) = \frac{m v_F^2}{3 n_0^2}\, n^3$$

can be neglected

- We obtain a system of two Schrödinger equations coupled by Poisson's equation $\Longrightarrow$ **Multi-stream Schrödinger model with $N = 2$.**
- Equivalent to Wigner approach with equilibrium distribution:

$$f_e(v, t = 0) = \frac{n_0}{2}\left(\delta(v - u_0) + \delta(v + u_0)\right)$$

Two-stream instability: linear theory

- Linearize around the spatially homogeneous equilibrium

$$n_1 = n_2 = n_0/2 \;, \qquad u_1 = -u_2 = u_0 \;, \qquad \phi = 0$$

- We obtain the dispersion relation

$$\Omega^4 - \left(1 + 2K^2 + \frac{H^2K^4}{2}\right)\Omega^2 - K^2\left(1 - \frac{H^2K^2}{4}\right)\left(1 - K^2 + \frac{H^2K^4}{4}\right) = 0$$

where $\Omega = \omega/\omega_p \;, \quad K = u_0 k/\omega_p \;, \quad H = \hbar\omega_p/m u_0^2.$

- The instability condition ($\Omega^2 < 0$) is

$$(H^2K^2 - 4)(H^2K^4 - 4K^2 + 4) < 0$$

- This yields the following **instability diagram**

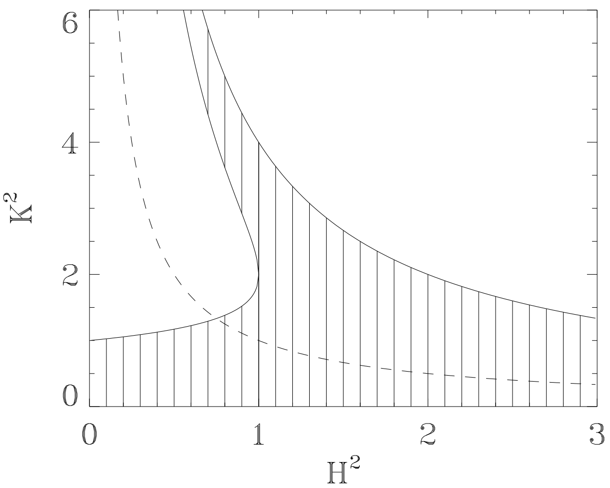
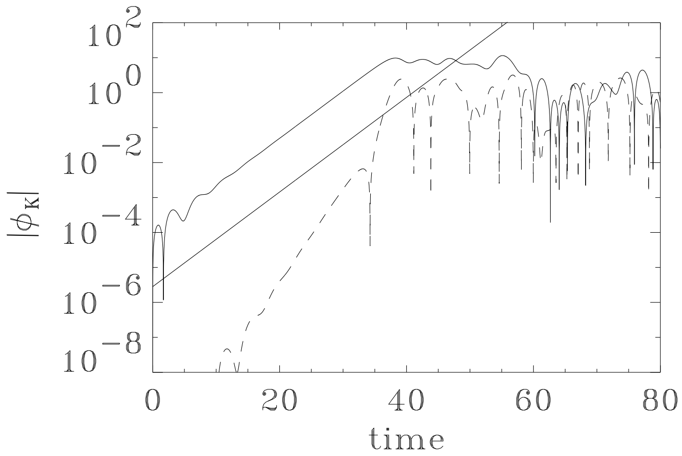


Figure 1, Phys. Rev. E, Haas

Simulations of the two-stream instability

- Time evolution of the fundamental mode $K_0 = 0.8$, and first harmonic $2K_0$ $(H = 0.25)$:



- Velocity distribution at $t = 0$ (dotted line) and $\omega_p t = 80$:

Figure 5, Phys. Rev. E, Haas

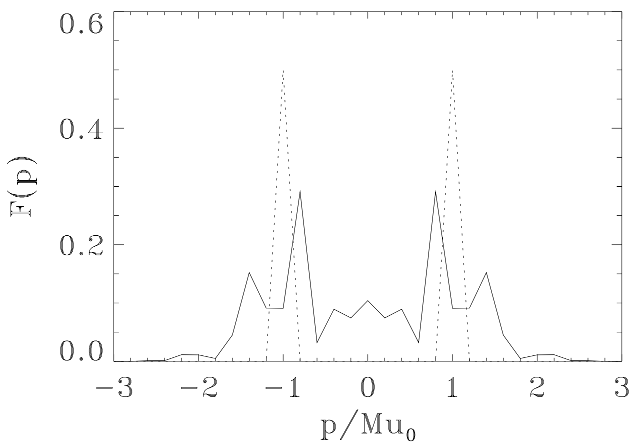
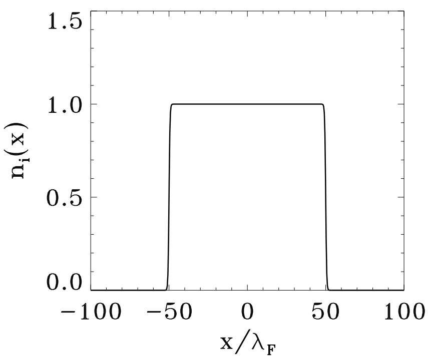


Figure 6, Phys. Rev. E, Haas

Application: thin metal films

- **Sodium films with realistic parameters:**
  - Thickness, $L = 100\ \lambda_F = 118$ Å
  - Initial temperature, $T = 300$ K $= 0.008\ T_F$
  - Electron plasma period, $2\pi/\omega_{pe} = 0.67$ fs
  - Fermi energy, $E_F = 3$ eV
  - Excitation energy, $E^* = 2$ eV
  - Mass ratio, $m_i/m_e = 42\ 228$
- We employ a **semiclassical model** (Vlasov-Poisson)
- The film is modelled by an infinite plane foil of thickness L
- 1D dynamics normal to the film
- **Fixed or mobile ions** with initial density profile:



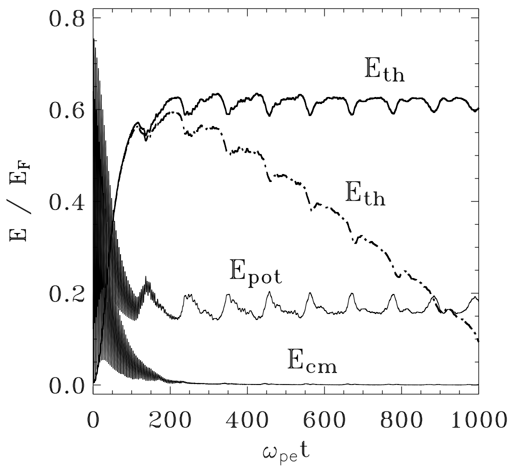
- **Ground state** given by a self-consistent FD distribution
- Electrons are excited by shifting their entire distribution in velocity space of $\delta v = 0.08 v_F$

Main results

1. **Damped electron oscillations** at the plasma frequency. Center-of-mass energy is converted into thermal energy (i.e. kinetic energy around the Fermi surface).

2. **Slow oscillations** persist over long times. Their period is $\sim L/v_F \sim 100$ (time-of-flight).

3. With **mobile ions**, energy exchanges between ions and electrons occur rather early



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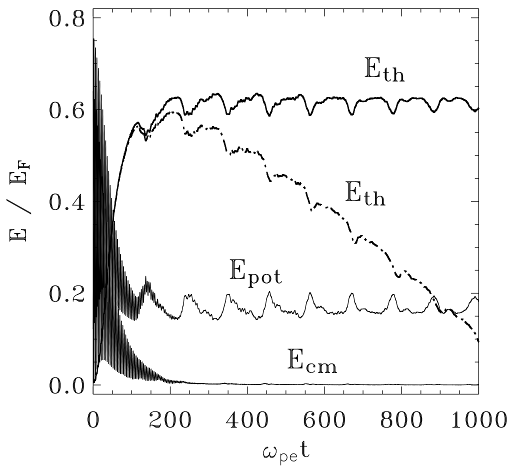
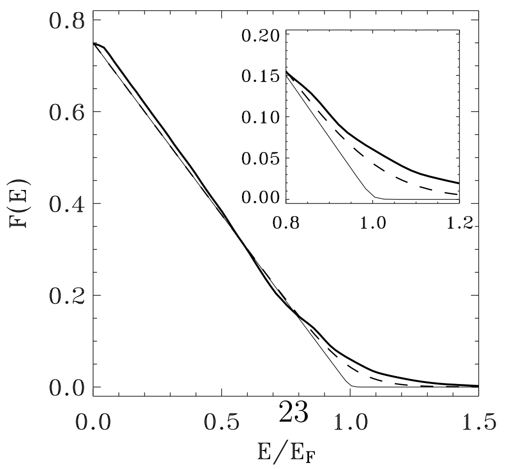


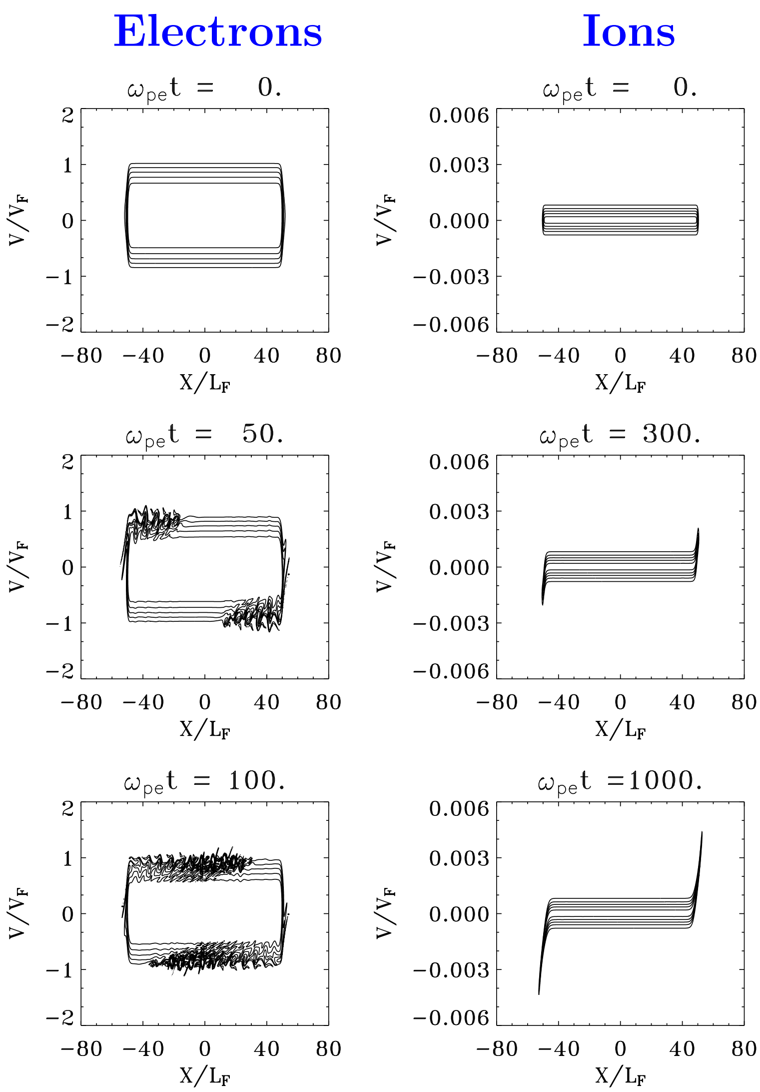
4. **Final electron distribution** is close to Fermi-Dirac with higher temperature $T_e^{\mathrm{final}} \simeq 0.084\ T_F$.



Phase space portraits

5. The electronic perturbation **propagates ballistically** at velocity v_F

6. Electron-ion exchanges occur at film **surfaces**.



- **Numerical results are consistent with experimental measurements on thin metal films**

Conclusions

- Physical systems at high density (metal clusters, thin metal films) display both **quantum** and **self-consistent** effects
- New field where plasma physics can play a useful role
- Typical plasma effects (collectives oscillations, collisionless damping, instabilities ...) occur on the **femtosecond** scale $\Rightarrow$ importance of ultrafast spectroscopy experiments.
- Can be described by mean-field (collisionless) models :
  - Wigner
  - Multi-stream Schrödinger (TDLDA, Hartree)
  - Quantum hydrodynamics
  - Vlasov
- Nice example of influence of quantum effects on nonlinear physics

Future developments

1. Explore Wigner and quantum fluid approaches for thin metal films

2. **Electron-electron collisions**: beyond mean-field.

   - **Ühling-Uhlenbeck** collision operator (analog of Boltzmann collision operator, but respects exclusion principle)

   - **Phenomenological models :**

     – Relaxation (BGK)

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}} = -\nu_{ee}\,(f - f_0)$$

     – Quantum Fokker-Planck