Problem set 3

Phy-801

February 2026

1. **The Heat capacity of the degenerate 3D free electron gas:** Sommerfeld's refinement of Drude's theory incorporates the Pauli exclusion principle, replacing the Maxwell-Boltzmann distribution, with the Fermi-Dirac distribution.

   (a) Consider the fermi velocity v_F for a system with electron density $n = N/V$.

      i. Show that in 3D the Fermi velocity is
      $$v_\mathrm{F} = \frac{\hbar}{m^*}(3\pi^2 n)^{1/3}. \tag{1}$$

      ii. From Ohm's law $\boldsymbol{j} = \sigma \boldsymbol{E}$, show that the drift velocity v_d of an electron (the average speed of an electron) in a uniform electric field $\boldsymbol{E}$ is $v_\mathrm{d} = |\sigma E/(ne)|$, where σ is the electrical conductivity.

      iii. Assuming the free-electron model applies to copper: calculate v_d and v_F at $T = 300\,\mathrm{K}$ in an electric field of $0.1\,\mathrm{V\,m^{-1}}$ ($\approx$ max field strength in copper wiring under domestic conditions), and comment on their relative sizes.

      iv. Using the Drude form for the conductivity σ, and the definition of the mean free path λ
      $$\sigma = \frac{ne^2\tau}{m^*}, \quad \lambda = v_\mathrm{F}\tau \tag{2}$$
      estimate λ at $T = 300\,\mathrm{K}$ and compare it to the mean spacing between copper atoms.

      v. Consider an electron travelling at v_F, a crude estimate[1] for the scattering cross section with a single isolated copper ion yields $s_\mathrm{ion} \approx 20\text{Å}^2$, this implies a mean free path of
      $$\lambda = \frac{1}{n_\mathrm{ion} s_\mathrm{ion}} \tag{3}$$
      where n_ion is the ion density. Calculate this value of λ and compare with the value calculated in the previous part. Discuss the implications of this comparison for the Drude assumption that scattering was due to electrons scattering off of ions.

   You may use: copper is monovalent (one conduction electron per atom), with molar mass $63.55\,\mathrm{g\,mol^{-1}}$, and at $300\,\mathrm{K}$ has density $\rho = 8.96\,\mathrm{g\,cm^{-3}}$, and conductivity $\sigma = 5.9\times10^7\,\Omega^{-1}\mathrm{m^{-1}}$, and an effective electron mass $m^* = m_\mathrm{e}$.

   (b) For N free electrons in 3D, calculate the Fermi energy ε_F, and hence show that the density of states at the Fermi surface is
   $$g(\varepsilon_\mathrm{F}) = \frac{dn}{d\varepsilon_\mathrm{F}} = \frac{3n}{2\varepsilon_\mathrm{F}}. \tag{4}$$

   (c) Consider the heat capacity of the electron gas (the note provided on the Sommerfeld expansion may be useful). Obtain an explicit expression for the electronic heat capacity of a 3D metal at low temperature. Express the ratio of your result to the Drude (Maxwell–Boltzmann) prediction in terms of T/T_F.

[1] This is the scattering cross section for a screened Coulomb potential

(d) Show that for $T \gg T_\mathrm{F}$ the heat capacity approaches the Drude (Maxwell–Boltzmann) value, and sketch the heat capacity as a function of T/T_F

(e) Using your results for copper (data in question (1a)):

i. Compute the Fermi temperature $T_\mathrm{F} = \varepsilon_\mathrm{F}/k_\mathrm{B}$ and hence the electronic heat capacity at room temperature.

ii. At room temperature the phononic contribution to the heat capacity [2] of copper is within 2% of the Dulong–Petit value. Compare this with your electronic contribution.

iii. Calculate the temperature below which the electronic contribution to the heat capacity dominates the phononic contribution.

You may use: Debye's theory predicts low temperature scaling of the molar heat capacity given by $c_{\mathrm{ph,mol}}(T) \sim \frac{12\pi^4}{5} R(T/T_D)^3$ and copper has a Debye temperature $T_D = 343\,\mathrm{K}$.

(f) Let $f_{\boldsymbol{k},\sigma} = f_\mathrm{FD}(\beta(\varepsilon_{\boldsymbol{k},\sigma} - \mu))$ denote the occupancy of the state $|\boldsymbol{k},\sigma\rangle$.

i. Sketch $\delta f_{\boldsymbol{k},\sigma} = f_{\boldsymbol{k},\sigma} - f_{\boldsymbol{k},\sigma}|_{T=0}$ as a function of $\varepsilon_{\boldsymbol{k},\sigma}$. Show on your diagram that the typical excitation energy of a thermally excited electron is $\Delta\varepsilon_\mathrm{exc} \approx k_\mathrm{B}T$.

ii. Calculate the leading correction to the internal energy $\Delta U = U(T) - U(0)$ (you may use the leading order expansion of the heat capacity calculated in 1c) and estimate the fraction of thermally excited electrons

$$f_\mathrm{exc} = \frac{N_\mathrm{exc}}{N}, \qquad N_\mathrm{exc} = \frac{\Delta U}{\Delta\varepsilon_\mathrm{exc}} \tag{5}$$

Estimate f_exc for copper at 300K. Compare this value with the Drude-Lorentz expectation, that every electron carries $\frac{3}{2}k_\mathrm{B}T$ of thermal energy.

2. **Thermodynamics of the 3D free electron gas**: Recall Mayer's relation, which you derived in the first problem sheet

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{6}$$

where α is the coefficient of thermal expansion, and κ_T is the compressibility

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_{P,N}, \qquad \kappa_T \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{T,N}. \tag{7}$$

(a) Express the internal energy of a free electron gas in its ground state as $U = U(N,V)$. At $T = 0$ we have the entropy $S = 0$, and hence we may work at fixed entropy, and hence the pressure is given by

$$P = -\left.\frac{\partial U}{\partial V}\right|_{S,N}. \tag{8}$$

Using this relation, show that the $T = 0$ free electron gas satisfies

$$PV = \tfrac{2}{3}U \tag{9}$$

Further, give a form for the pressure P exerted by a free electron gas in its ground state in terms of the electron density n, and the Fermi energy ε_F.

(b) Using your previous result hence find a form for κ_T in terms of the electron density n and the Fermi energy ε_F.

(c) At $T = 0$ one finds that $\alpha(T = 0) = 0$. To calculate the leading order in T behaviour, we make use of the virial theorem, which states that (9) holds for any gas of particles with energy $\sum_n p_n^2/(2m)$, including the electron gas at finite temperature. Using (9), and the Sommerfeld expansion, obtain the leading order in T correction to P. Write your answer as a function of T/T_F [You may quote the Sommerfeld expansion without re-deriving it]

[2] i.e. from the vibrations of atoms

(d) Working at fixed V, show that

$$\alpha = -\frac{1}{n}\left(\frac{\partial n}{\partial T}\right)_P = \frac{1}{n}\frac{\left(\frac{\partial P}{\partial T}\right)_n}{\left(\frac{\partial P}{\partial n}\right)_T} \tag{10}$$

and hence obtain a leading order in T form for α in terms of T and T_{F}. [You may use the relation (4), and as before, quote the Sommerfeld expansion without re-deriving it]

(e) Using your previous results, and Mayer's Relation (6), calculate $C_P - C_V$ per mole of electrons, to leading order in T, give your answer in terms of T/T_{F} and R. Hence conclude that at room temperature free electron gas has $C_P - C_V \ll C_P, C_V$ due to small coefficient of thermal expansion α, as we previously saw was the case for crystalline solids.

3. **The 2D free electron gas:** The 2D free electron gas is the simplest model for electrons confined to a plane. It provides a basic reference point for understanding 2D electronic systems studied in GaAs quantum wells, metal-oxide-semiconductor field-effect transistor (MOSFET) inversion layers, and metal surface states. Moreover, when generalized to include realistic band structure and interactions, it provides a minimal model for complex layered materials currently at the cutting edge of research, such as graphene, transition metal dichalcogenide (TMD) monolayers, and moiré heterostructures.

(a) What is the relation between n and k_F in two dimensions?

(b) What is the relation between k_F and r_s in two dimensions?

(c) Show that in two dimensions the free electron density of states $g(\varepsilon)$ is a constant independent of ε for $\varepsilon > 0$, and 0 for $\varepsilon < 0$. What is the constant?

(d) Show that because $g(\varepsilon)$ is constant, every term in the Sommerfeld expansion for n vanishes except the $T = 0$ term. Deduce that $\mu = \varepsilon_F$ at any temperature.

(e) Deduce that when $g(\varepsilon)$ is as in (c), then

$$\mu + k_B T \ln\left(1 + e^{-\mu/k_B T}\right) = \varepsilon_F. \tag{11}$$

(f) Estimate from (11) the amount by which μ differs from ε_F. Comment on the numerical significance of this "failure" of the Sommerfeld expansion, and on the mathematical reason for the "failure."