

University of Illinois at Chicago
Department of Physics

Thermodynamics & Statistical Mechanics
Qualifying Examination

January 8, 2010
9.00 am - 12.00 pm

Full credit can be achieved from completely correct answers to 4 questions. If the student attempts all 5 questions, all of the answers will be graded, and the top 4 scores will be counted towards the exam's total score.

Various equations, constants, etc. are provided on the last page of the exam.

1. Van der Waals Fluid

A mole of fluid obeys the van der Waals equation of state:

$$p = \frac{RT}{V-b} - \frac{a}{V^2},$$

where R , a and b are positive constants, and $V > b$.

(a) Show that the specific heat at constant volume (C_V) is a function of T only.

(b) Is the results still true if the fluid obeys the Dieterici equation of state

$$p = \frac{RT}{V-b} \exp\left[-\frac{1}{VRT}\right]?$$

Here, R , a and b are positive constants, and $V > b$.

(c) Find the entropy $S(T, V)$ of the van der Waals fluid in the case when C_V is independent of T .

2. Simple paramagnet

A simple paramagnet consists of N spin- $\frac{1}{2}$ particles immersed in an external magnetic field H_{ext} pointing in the z -direction. Each spin- $\frac{1}{2}$ particle can only be in either an “up” or “down” state, and the energy of a particle with spin pointing down is $+\mu B$, while the energy of particles with spin up is $-\mu B$.

(a) Show that the thermodynamic potential is

$$G(T, H_{ext}) = -aT \log \left[2 \cosh \left(b \frac{H_{ext}}{T} \right) \right],$$

where T is the temperature. Determine the constants a and b .

(b) Find the expression of the magnetization M and the magnetic enthalpy $H = G + TS$ in terms of H_{ext} and T . Verify that $H = -MH_{ext}$.

(c) Show that the expression for the entropy S obeys the Planck formulation of the third law (i.e. $C_V \rightarrow 0$ for $T \rightarrow 0$).

(d) Is the expression of the isothermal susceptibility χ_T in terms of H_{ext} and T consistent with the postulates of thermodynamics? [Hint: Show that $\chi_T \rightarrow 0$ for $T \rightarrow 0$.]

3. Degenerate Fermi Gas

The crystal structure of metallic copper (Cu) is face-center cubic (fcc) with a unit-cell length of $a = 3.615 \text{ \AA}$. This structure results in a density of atoms of $\rho_{Cu} = 8.46 \times 10^{28} \text{ m}^{-3}$. Each Cu atom in the crystal donates $1e^-$ to the conduction band, which leads to a density of states ($g(\varepsilon)$) for the 3-dimensional Fermi gas:

$$g(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}},$$

where m is the effective mass of the conduction electrons. For this problem, you can assume m to be the free electron mass m_e .

(a) In the low temperature limit (i.e. $T = 0 \text{ K}$), find the Fermi energy E_F and the total energy U_0 of all electrons in the conduction band (per unit volume). Express your answer in eV.

(b) Electrons that can participate in a current have energies that correspond to an occupancy $n(\varepsilon)$ which is neither too close to 1 (no empty final states available for the moving electrons) nor too small (no electrons left in the conduction band). Calculate the energy interval that is occupied by the electrons that participate in the current at room temperature (i.e. $T = 300 \text{ K}$), assuming that the occupancy for these electrons varies between $n_1(\varepsilon) = 0.1$ and $n_2(\varepsilon) = 0.9$.

(c) Using your answers to part (b), find the fraction of “current carrying” electrons N_1 to the total number of electrons in the conduction band N_{total} (i.e. $\frac{N_1}{N_{total}}$). Assume that within the range of allowed occupancies, the density of states is energy-independent, and the occupancy will vary linearly with energy. [Hint: Use the Taylor series expansion of the occupancy around the Fermi-energy ε_f up to the linear term.]

4. The Ideal Gas

One mole of ideal gas with a constant heat capacity C_V is placed at a constant pressure p_1 inside a cylinder, which is thermally insulated from the environment. The volume of the cylinder can be changed using a piston, which moves without friction along the vertical axis.

At the beginning of the experiment, the pressure of the gas is abruptly changed from p_1 to p_2 , resulting in a decrease in the volume from V_1 at pressure p_1 to V_2 at pressure p_2 . Similarly, the temperature T_1 at pressure p_1 will increase to T_2 at pressure p_2 after thermodynamic equilibrium has been reached.

(a) Determine the type of compression that took place here. Explain!

(b) Find the temperature T_2 and the volume V_2 in terms of V_1 , p_2 and T_1 after the thermodynamic equilibrium has been reached. [Hint: Use the equation of state for an ideal gas and the relationship between C_V and C_P].

After thermodynamic equilibrium has been established in part (a), the pressure is abruptly reset to its original value p_1 , resulting in V_f and T_f at pressure p_1 .

(c) Find the final values of the temperature T_f and volume V_f in terms of p_1 , V_2 , and T_2 after thermodynamic equilibrium is reached again. Use the first law of thermodynamics and the adiabatic equation to compute the difference in the temperatures ($T_f - T_1$).

Comment on both the sign and the relative magnitude of the temperature difference. What happens in the limit of very small changes in pressure?

5. Einstein Solid

Consider two interacting Einstein solids that are in a box with adiabatic walls. The number of oscillators in system A is $N_A = 4$ and the number in system B is $N_B = 6$. The total number of units of heat energy is $q = 20$.

(a) For the most probable macrostate, determine the number of units of heat energy in each of the two systems. Explain your approach.

(b) Determine the probability of finding the system in the most probable macrostate.

Equations and Constants

$$k_B = 1.381 \times 10^{-23} \frac{J}{K}; m_e = 9.109 \times 10^{-31} \text{ kg}; m_p = 1.673 \times 10^{-27} \text{ kg};$$
$$e = 1.602 \times 10^{-19} \text{ C}; h = 6.626 \times 10^{-34} \text{ J s}; c = 2.998 \times 10^8 \frac{m}{s};$$
$$N_A = 6.023 \times 10^{23}; R = 8.315 \frac{J}{\text{mol K}}$$

Hyperbolic Functions:

$$\sinh x = \frac{1}{2} (\exp[x] - \exp[-x]); \cosh x = \frac{1}{2} (\exp[x] + \exp[-x]);$$

$$\tanh x = \frac{\sinh x}{\cosh x}$$

Maxwell's relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V; \left(\frac{\partial T}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial S}\right)_T; \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P;$$
$$\left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\partial V}{\partial S}\right)_T$$

Ideal gas:

$$pV = Nk_B T; C_V + Nk_B T = C_p$$

Fermi-Dirac distribution:

$$\bar{n}_{FD} = \left(\exp\left[\frac{\varepsilon - \varepsilon_f}{k_B T}\right] + 1\right)^{-1}$$

Bose-Einstein distribution:

$$\bar{n}_{BE} = \left(\exp\left[\frac{\varepsilon - \varepsilon_f}{k_B T}\right] - 1\right)^{-1}$$

Boltzmann distribution:

$$\bar{n}_{Boltzmann} = \exp\left[-\frac{\varepsilon - \varepsilon_f}{k_B T}\right]$$