

Problem 1

(9)

a) With microstate a complete microscopic description of a system is meant, e.g. the position and momentum of all molecules/atoms in a gas. It is very difficult to describe, since 1 mole of a gas has $\sim 10^{23}$ atoms.

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With a macrostate a description of a system at the macroscopic scale is meant, e.g. P, T, V , etc. A macrostate may comprise many microstates.

b) * postulate of equal a priori probabilities: the microstates comprising a macrostate of an isolated system occur with equal probability.

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* equilibrium postulate: equilibrium corresponds to the macrostate with the maximum number of microstates.

c) The microcanonical, canonical and grand canonical ensemble methods apply to an isolated system, a heat bath and a heat bath/particle reservoir respectively.

As treated in this course, the microcanonical ensemble method was the application of the 2 postulates and $S = k \ln \Omega$ to an isolated system. But this method was insufficient with respect to a heat bath. Therefore the canonical ensemble method with the Boltzmann distribution was developed. Also, the canonical ensemble method could be applied to systems with more than 2 states. In the canonical ensemble the microstates have the weight $\sim e^{-\beta \epsilon_i}$.

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For the treatment of the quantum gasses we had the limiting condition $N = \sum_i n_i$, which made it hard to use the canonical ensemble. Therefore the grand canonical ensemble method was developed for a system in a heat bath/particle reservoir, so that we didn't have to count $N = \sum_i n_i$. In the grand canonical ensemble method the microstates are weighted with $\sim e^{-\beta(\epsilon_i - \mu)n_i}$.

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Problem 2

$$a) Z = e^x + e^{-x} = 2 \cosh x \quad x \equiv \beta \varepsilon = \frac{1}{kT} \left(\mu_0 \mu H + \frac{k\theta M}{\mu N} \right)$$

$$\bar{\mu} = (+\mu) \frac{e^x}{2 \cosh x} + (-\mu) \frac{e^{-x}}{2 \cosh x} = \mu \tanh x$$

$$M = \bar{\mu} N \rightarrow \frac{M}{\mu N} = \tanh x = \tanh \left[\frac{1}{kT} \left(\mu_0 \mu H + \frac{k\theta M}{\mu N} \right) \right]$$

b) For $x \ll 1$: $\tanh x \approx x$

$$M \approx \frac{\mu N}{kT} \left(\mu_0 \mu H + \frac{k\theta}{\mu} \cdot \frac{M}{N} \right) = \frac{N}{kT} \left(\mu_0 \mu^2 H + k\theta \cdot \frac{M}{N} \right)$$

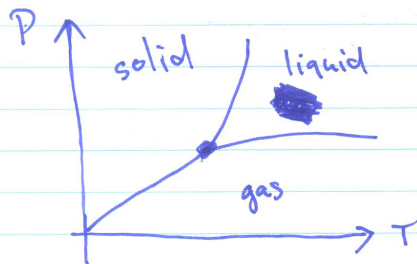
$$\chi = \frac{M}{HN} = \frac{1}{kT} \left(\mu_0 \mu^2 + k\theta \cdot \chi \right) = \frac{\mu_0 \mu^2}{kT} + \frac{\theta}{T} \chi$$

$$\left(1 - \frac{\theta}{T} \right) \chi = \frac{\mu_0 \mu^2}{kT} \rightarrow \chi = \frac{\mu_0 \mu^2}{kT} \frac{T}{T - \theta} = \frac{\mu_0 \mu^2}{k(T - \theta)}$$

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Problem 3

a) Using an arbitrary phase diagram for explanation:



$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

P - pressure
 T - temperature
 S - entropy
 V - volume

3 The Clausius-Clapeyron equation relates the slope $\frac{dP}{dT}$ of a substance in thermal equilibrium to the difference in entropy between 2 phases divided by the difference in volume of the 2 phases. It is applied to pure substances rather than mixtures of substances.

$$b) \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V} \approx \frac{\Delta H}{T V} = P \frac{\Delta H}{RT^2}$$

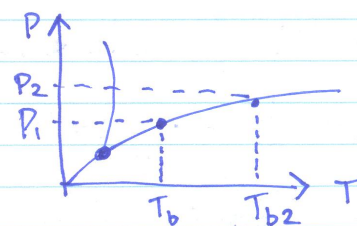
$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_b}^{T_{b2}} \frac{\Delta H}{RT^2} dT$$

$$\ln \frac{P_2}{P_1} = - \frac{\Delta H}{R} \left(\frac{1}{T_{b2}} - \frac{1}{T_b} \right)$$

$$T_{b2} = \left(\frac{1}{T_b} - \frac{R}{\Delta H} \ln \frac{P_2}{P_1} \right)^{-1}$$

$$6 \quad \approx 393.8 \text{ K} = 394 \text{ K}$$

$$\Delta T \approx 20.8 \text{ K} = 21 \text{ K}$$



$P_1 = 1 \text{ bar}$
$P_2 = 2 \text{ bar}$
$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H = 40.6 \cdot 10^3 \text{ J mol}^{-1}$
$T_b = 373 \text{ K}$

Problem 4

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a) The partition function of photon gas can be written as:

$$Z_{ph} = \sum_{n_1} \sum_{n_2} \dots e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} = \prod_{r=1}^{\infty} \sum_{n_r} e^{-\beta \epsilon_r n_r}$$

3 since $\sum_{nr} e^{-\beta \epsilon_r n_r} = \frac{1}{1 - e^{-\beta \epsilon_r}}$ (geometric series)

$$\text{9 } Z_{ph} = \prod_{r=1}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_r}}$$

$$b) F = -kT \ln Z_{ph} = -kT \ln \left[\prod_{r=1}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_r}} \right]$$

$$= +kT \sum_{r=1}^{\infty} \ln(1 - e^{-\beta \epsilon_r})$$

$$f(k) dk = 2 \cdot \frac{\frac{1}{2} \cdot 4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} = \frac{V k^2 dk}{\pi^2} \quad (2 \text{ polarizations})$$

$$\epsilon = pc = \hbar ck \rightarrow k = \frac{\epsilon}{\hbar c} \rightarrow dk = \frac{d\epsilon}{\hbar c}$$

$$4 f(\epsilon) d\epsilon = \frac{V}{\pi^2 c^3 \hbar^3} \epsilon^2 d\epsilon$$

$$F = kT \int_0^{\infty} f(\epsilon) d\epsilon \ln(1 - e^{-\beta \epsilon}) = \frac{kTV}{\pi^2 c^3 \hbar^3} \int_0^{\infty} \epsilon^2 \ln(1 - e^{-\beta \epsilon}) d\epsilon$$

$$x = \frac{\epsilon}{kT} \rightarrow \epsilon = kT x \rightarrow d\epsilon = kT dx$$

$$\text{9 } F = \frac{k^4 T^4 V}{\pi^2 c^3 \hbar^3} \int_0^{\infty} x^2 \ln(1 - e^{-x}) dx = -\frac{\pi^2 k^4 T^4 V}{45 c^3 \hbar^3}$$

$$c) dE = TdS - PdV$$

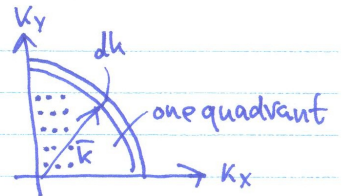
$$F = E - TS \rightarrow dF = dE - TdS - SdT = -SdT - PdV$$

$$2 \Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\pi^2 k^4 T^4}{45 c^3 \hbar^3}$$

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Problem 5 2 states for electrons $\uparrow\downarrow$



a) Using the Pauli principle, we have:

$$f(k) dk = 2 \cdot \frac{1}{4} \cdot 2\pi k \cdot dk = \frac{A k dk}{\pi} \quad \text{where } A = L^2$$

2 1/2

$$p = \hbar k \rightarrow k = \frac{p}{\hbar} = \frac{2\pi}{h} p \rightarrow dk = \frac{2\pi}{h} dp$$

$$f(p) dp = \frac{A \cdot \frac{2\pi}{h} p \cdot \frac{2\pi}{h} dp}{\pi} = \frac{4\pi A p dp}{h^2}$$

b) The mean occupation number for the FD distribution is:

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$$

$$\epsilon = \frac{p^2}{2m} \rightarrow p = (2m\epsilon)^{1/2} \rightarrow dp = \frac{1}{2} (2m)^{1/2} \epsilon^{-1/2} d\epsilon$$

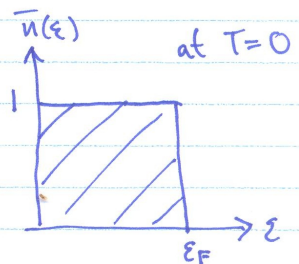
$$f(\epsilon) d\epsilon = \frac{4\pi A \cdot (2m)^{1/2} \epsilon^{1/2} \cdot \frac{1}{2} (2m)^{1/2} \epsilon^{-1/2} d\epsilon}{h^2} = \frac{A 4\pi m}{h^2} d\epsilon$$

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$$N = \int_0^{\infty} \bar{n}(\epsilon) f(\epsilon) d\epsilon = \frac{A 4\pi m}{h^2} \int_0^{\infty} \frac{d\epsilon}{e^{\beta(\epsilon - \mu)} + 1}$$

c) The Fermi energy is defined as the chemical potential at zero temperature: $\epsilon_F \equiv \mu(0)$.

$$\bar{n}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \epsilon_F \\ 0 & \text{for } \epsilon > \epsilon_F \end{cases}$$



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$$N = \frac{A 4\pi m}{h^2} \int_0^{\epsilon_F} d\epsilon = \frac{A 4\pi m}{h^2} \epsilon_F$$

$$\Rightarrow \epsilon_F = \frac{h^2 N}{4\pi m A}$$

d) At $T=0$: $\bar{\epsilon} = \int_0^{\infty} \epsilon \bar{n}(\epsilon) f(\epsilon) d\epsilon = \frac{A 4\pi m}{h^2} \int_0^{\epsilon_F} \epsilon d\epsilon$

1 1/2

$$= \left[\frac{A 4\pi m}{h^2} \right] \frac{1}{2} \epsilon_F^2 = \frac{1}{2} N \epsilon_F$$

\downarrow
1/2 ϵ_F for one electron