UNIVERSITETET I OSLO

Det matematisk-naturvitenskapelige fakultet

Final exam in FYS3130/FYS4130 Statistical mechanics

Date of exam: Tuesday, 14. June, 2005, **Time:** 9:00 - 12:00

The problem set contains: 2 pages

You are allowed to bring: Two sheets (size A4) of handwritten notes, approved mathematical formulae (Rottmann) and approved calculator.

Please make sure that the problem set is complete before you start solving the problems!

Problem 1. Virial expansion

The Equation of State of a real gas can be written in a form

$$\frac{Pv}{RT} = 1 + \frac{B_2}{v} + \frac{B_3}{v^2} + \frac{B_4}{v^3} + \dots \tag{1}$$

called the virial expansion, which is valid for dilute gases with molar density $1/v = n/V$. Find first virial coefficients B_2, B_3, B_4 for the van der Waals gas equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \tag{2}$$

Hint: Assume that $b/v \ll 1$.

Solution.

Van der Waals equation fo state can be written as

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv}$$

Expand the term $v/(v-b)$ into Taylor series with respect to $x = b/v$ around $x_0 = 0$:

$$\begin{aligned}
f(x) &= f(b/v) = \frac{v}{v-b} = \frac{1}{1-(b/v)} = \frac{1}{1-x} = && (3)\\
&= f(0) + f'(0)x + \frac{1}{2!}f''(0)x^2 + \frac{1}{3!}f'''(0)x^3 + \dots = && (4)\\
&= 1 + x + \frac{1}{2}2x^2 + \frac{1}{6}6x^3 + \dots = && (5)\\
&= 1 + \frac{b}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \dots && (6)
\end{aligned}$$

Collect together terms in r.h.s. of van der Waals equation of state with respect to $1/v$:

$$\frac{Pv}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \cdots$$

and compare it with (1) one can obtain:

$$B_2 = b - \frac{a}{RT}, \quad \mathrm{B}_3 = \mathrm{b}^2, \quad \mathrm{B}_4 = \mathrm{b}^3$$

Problem 2. Fluctuations in Grand Canonical Ensemble

a) Using the partition function for Grand Canonical Ensemble, prove that dispersion of number of particles N can be expressed as

$$\overline{(\Delta N)^2} = \overline{(N - \overline{N})^2} = \left(\frac{\partial \overline{N}}{\partial \alpha}\right)_\beta$$

where $\beta = 1/T$, $\alpha = \mu/T$ and $\overline{N}$ is the average number of particles.

b) Let $\overline{N_i}$ be the average occupancy of a single orbital of a boson system. Show that

$$\overline{(\Delta N_i)^2} = \overline{N_i}(1 + \overline{N_i}).$$

c) Show that for a single orbital of a fermion system

$$\overline{(\Delta N_i)^2} = \overline{N_i}(1 - \overline{N_i}).$$

d) Show that for a Maxwell-Boltzmann gas $\overline{(\Delta N_i)^2} = \overline{N_i}$.

Solution.

(a) For Grand canonical ensemble $(T - V - \mu)$ partition function Q can be written as

$$Q = \sum_{i,N} e^{-\beta(E_i - \mu N)} = \sum_{i,N} e^{\alpha N - \beta E_i}$$

where $\beta = 1/kT$, $\alpha = \mu\beta$.

Then average number of particles in the system is

$$\overline{N} = \frac{1}{Q}\sum_{i,N} N e^{\alpha N - \beta E_i} = \frac{1}{Q}\left(\frac{\partial Q}{\partial \alpha}_\beta\right)_\beta$$

$$\overline{N^2} = \frac{1}{Q}\sum_{i,N} N^2 e^{\alpha N - \beta E_i} = \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \alpha^2}\right)_\beta$$

Therefore,

$$\begin{aligned}
\overline{(\Delta N)^2} &= \overline{(N-\overline{N})^2} = \overline{N^2} - \left(\overline{N}\right)^2 = \\
&= \frac{1}{Q}\left(\frac{\partial^2 Q}{\partial \alpha^2}\right)_\beta - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \alpha}\right)_\beta^2 = \frac{Q\left(\frac{\partial^2 Q}{\partial \alpha^2}\right)_\beta - \left(\frac{\partial Q}{\partial \alpha}\right)_\beta^2}{Q^2} = \left(\frac{\partial \overline{N}}{\partial \alpha}\right)_\beta
\end{aligned}$$

q.e.d.

(b,c,d) Let us consider the system from the previous problem (1.a) to be the single-particle state concerned and suppose that this state has energy ϵ. For boson/fermion/MB system with single orbital

$$\overline{N_i} = \frac{1}{\exp(\beta\epsilon - \alpha) + \eta}$$

,

where $\eta = -1$ for bosons, $\eta = +1$ for fermions and $\eta = 0$ for MB classical system. Since the system is microscopic, N_i should be replaced by $\overline{N_i}$. So, using the folmula from (1a) we will get

$$\begin{aligned}
\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_\beta &= -\frac{1}{(\exp(\beta\epsilon - \alpha) + \eta)^2}(-1)e^{\beta\epsilon - \alpha} = \frac{\exp(\beta\epsilon - \alpha)}{(\exp(\beta\epsilon - \alpha) + \eta)^2} = \\
&= \frac{1}{(\exp(\beta\epsilon - \alpha) + \eta)}\left(1 - \eta\frac{1}{\exp(\beta\epsilon - \alpha) + \eta}\right) = \overline{N}(1 - \eta\overline{N})
\end{aligned}$$

Problem 3. Two-dimensional photon gas

Consider two-dimensional photon gas with degeneracy $g = 2$ at temperature T. Using the formula for the mean occupation number of the photon energy state ϵ,

$$< n_\epsilon >= \frac{1}{\exp(\epsilon/kT) - 1}$$

where $\epsilon = pc = h\nu$, p is momentum and ν is frequency of the photon,

a) find the number of photons dn_ϵ per unit volume in the energy interval $(\epsilon, \epsilon + d\epsilon)$ and derive two-dimensional Planck's formula for spectral radiation energy density

$$\rho(\nu, T) = A\frac{\nu^2}{e^{h\nu/kT} - 1}$$

as a function of frequency, ν, if $\rho(\epsilon, T)d\epsilon = \epsilon dn_\epsilon$.
Define the coefficient A;

b) Consider two limiting cases: $h\nu \gg kT$ and $h\nu \ll kT$, and get two-dimensional analogues of Wien and Rayleigh-Jeans radiation laws, respectively.

c) Derive the Stefan-Boltzmann law for spatial energy density $u(T) = U/V$, where U is the total radiation energy.
Hint:

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = \Gamma(3)\zeta(3), \quad \text{where} \quad \Gamma(3) = 2 \text{ and } \zeta(3) \approx 1.202.$$

d) Find
– heat capacity at constant two-dimensional volume, C_v,
– entropy, S,
– the Helmholtz free energy, F,
– pressure of the photon gas, P,
– the Gibbs energy, Φ.

e) Show that for two-dimensional gas

$$PV = \frac{1}{2}U.$$

Solution.

Photon gas at temperature T with energy $\epsilon = h\nu = pc$, with degeneracy $g = 2$ in the cavity of volume $V = V_2$

$$\begin{aligned}
< n_\epsilon > &= \frac{1}{\exp{(\epsilon/kT)} - 1} \\
d\Gamma_2 &= \frac{2\pi V_2 g p dp}{h^2} = \frac{2\pi V_2 g \epsilon d\epsilon}{h^2 c^2} = \frac{2\pi V_2 g h^2 \nu d\nu}{h^2 c^2} = \\
&= \frac{2\pi V_2 g \nu d\nu}{c^2} \\
dN_2 &= V_2 \frac{2\pi g \nu d\nu}{c^2} \frac{1}{\exp{(h\nu/kT)} - 1} \\
dU_2 &= V_2 \frac{2\pi g h \nu^2 d\nu}{c^2} \frac{1}{\exp{(h\nu/kT)} - 1} \\
\rho(\nu, T) &= \frac{1}{V_2}\frac{dU_2}{d\nu} = \frac{2\pi g h}{c^2} \frac{\nu^2}{\exp{(h\nu/kT)} - 1}
\end{aligned}$$

$$\rho(\nu, T) = \frac{2\pi g h}{c^2} \frac{\nu^2}{\exp{(h\nu/kT)} - 1} \to \begin{cases} 4\pi h \nu^2 e^{-h\nu/kT}/c^2, & \text{if } h\nu \gg kT, \\ 4\pi \nu kT/c^2, & \text{if } h\nu \ll kT, \end{cases}$$

$$
\begin{aligned}
u = \frac{U_2}{V_2} &= \frac{4\pi h}{c^2}\int_0^\infty \frac{\nu^2 d\nu}{\exp{(h\nu/kT)}-1} = \\
&= \frac{4\pi h}{c^2}\left(\frac{kT}{h}\right)^3 \int_0^\infty \frac{x^2 dx}{\exp{(x)}-1} = \\
&= \frac{8\pi k^3 \zeta(3)}{c^2 h^2} T^3 \simeq \frac{9.6\pi k^3}{c^2 h^2} T^3 = \sigma_1 T^3
\end{aligned}
$$

The total energy emitted from the volume $V_2 = V$ is equal:

$$
\begin{aligned}
U &= \sigma_1 V T^3 \\
C_V &= \left(\frac{\partial U}{\partial T}\right)_V = 3\sigma_1 V T^2 \\
S &= V\int \frac{C_V}{T} dT + f(V) = \frac{3}{2}\sigma_1 V T^2 + f(V) \\
f(V) &= 0, \text{ because } S(T=0) = 0 \\
F &= U - TS = \sigma_1 (1 - \frac{3}{2}) T^3 V = -\frac{\sigma_1 T^3}{2} V \\
P &= -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\sigma_1 T^3}{2} = \frac{1}{2}\frac{U}{V} \\
\Phi &= U - TS + PV = -\frac{\sigma_1 T^3}{2} V + \frac{\sigma_1 T^3}{2} V = 0
\end{aligned}
$$