Solution

NAME: 1 March 2005

Physics 112

Spring 2005

Midterm 1

(80 minutes =80 points)

Time yourself and move to the next problem after a number of minutes equal to the number of points.

1. **Thermodynamic identity (20 points)**

We consider a system with only one species of particles and define with our usual notation the "Grand Potential"

$$\Omega = F - \mu N \equiv U - \tau\sigma - \mu N$$

a) (5 points) Write down the fundamental (differential) thermodynamic identity for Ω.

$$d\Omega = dU - d(\tau\sigma) - d(\mu N)$$
$$= dU - \tau d\sigma - \sigma d\tau - \mu dN - N d\mu$$
$$= (\tau d\sigma - p dV + \mu dN) - \tau d\sigma - \sigma d\tau - \mu dN - N d\mu$$
$$= \boxed{-p dV - \sigma d\tau - N d\mu}$$

What independent variables are the most natural to use for Ω?

V, τ, μ

b) (5 points) Show that when expressed as a function of temperature, volume and chemical potential, the pressure is independent of the volume

$$p(\tau, V, \mu) = p(\tau, \mu)$$

(Hint: divide the system into two unequal volumes in equilibrium)

p_1, τ_1, μ_1, V_1	p_2, τ_2, μ_2, V_2

equilibrium $\Rightarrow$ $p_1 = p_2$, $\tau_1 = \tau_2$, $\mu_1 = \mu_2$ $\Rightarrow$

$p(V_1, \tau, \mu) = p_1 = p_2 = p(V_2, \tau, \mu)$

so p is independent of volume when expressed as a function of μ, τ.

c) (5 points) Deduce from b) and the fact that Ω is zero at zero volume that

$$\Omega = -PV$$

(Since we have three variables, be careful in defining the path of integration)

$$\Omega(V, \mu, \tau) = \Omega(V, \mu, \tau) - \Omega(0, \mu, \tau)$$
$$= \int_0^V d\Omega \quad \text{along the path } \mu = \text{constant}, \ \tau = \text{constant}, \ V \text{ ranges from } 0 \text{ to its maximum value.}$$
$$= \int_0^V (-p dV - \sigma d\tau - N d\mu) = \int_0^V -p(\tau, \mu)\, dV$$
$$= -pV \quad \text{as desired.}$$

d) (2 points) Deduce from this result that the Gibbs Free Energy is equal to

$$G = F + PV = \mu N$$

(as we have directly derived in one of the homeworks)

$G = F + PV$ is the definition of G.

$$G = F + PV = F - (-PV) = F - \Omega = F - (F - \mu N) = \boxed{\mu N}$$

e) (3 points) Check this general result with the expression of U, σ and μ for a monoatomic ideal gas

$$U = \tfrac{3}{2} N\tau$$

$$\sigma = N\left(\tfrac{5}{2} + \log \frac{n_Q}{n}\right)$$

$$\mu = \tau \log n/n_Q$$

$$PV = N\tau$$

$$G = F + PV = U - \tau\sigma + PV$$

$$= \tfrac{3}{2} N\tau - \left(\tfrac{5}{2} N\tau + N\tau \log \frac{n_Q}{n}\right) + N\tau$$

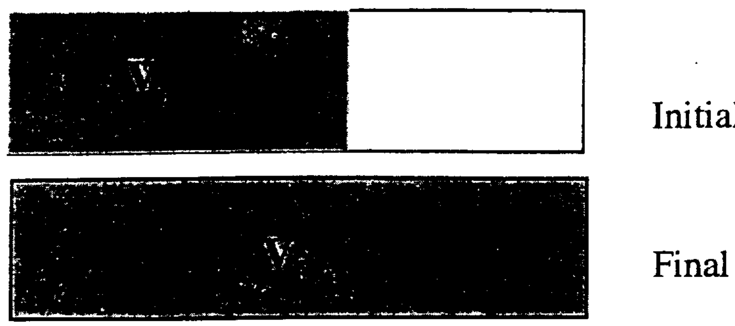
$$= -N\tau \log \frac{n_Q}{n}$$

$$= N\tau \log n/n_Q$$

$$= \boxed{\mu N}$$

2. **Expansion in vacuum** (15 pts).

Let us consider the sudden expansion in vacuum of a mono-atomic spinless gas *without exchange with the outside.* This is an ideal gas containing N molecules. The initial volume is V_i and the final volume V_f.



a) (5 points) What is the change of temperature?

$U = \frac{3}{2} N \tau$, U constant, N constant $\Rightarrow$

τ constant.

b) (5 points) Use what we know about the density of states in phase space, to determine what is the dependence of the number of states on the volume (at constant energy and number of particles).

$$g = \int \frac{d^{3N}x \, d^{3N}p}{h^{3N}} = V^N \int \frac{d^{3N}p}{h^{3N}}$$

$$\Rightarrow \boxed{g \propto V^N}$$

c) (3 points) Using the result under b) compute the change $\Delta\sigma$ of entropy.

$$\Delta\sigma = \log V_f^N - \log V_i^N = \log\left(\frac{V_f}{V_i}\right)^N = \boxed{N \log \frac{V_f}{V_i}}$$

d) (2 points) Check your result with the Sackur Tetrod formula

$$\Delta\sigma = N\left(\tfrac{5}{2} + \log \frac{n_Q}{n_f}\right) - N\left(\tfrac{5}{2} \log \frac{n_Q}{n_i}\right)$$

$$= N \log \frac{n_Q}{(N/V_f)} - N \log \frac{n_Q}{(N/V_i)} = N\big(\log n_Q - \log N + \log V - \log n_Q + \log N - \log V$$

$$= N(\log V_f - \log V_i) = N \log \frac{V_f}{V_i}$$

3. **Paramagnetism and adiabatic demagnetization (20 points)**

Let us consider a system of N_s distinguishable 1/2 spins in a magnetic field B at temperature τ. Each spin has magnetic moment m and its energy in the magnetic field is $\varepsilon_+ = -mB$ and $\varepsilon_- = mB$, depending whether it points along or opposite to the magnetic field.

a) (7points) Write down the partition function of each spin and probabilities of it pointing along or opposite to the magnetic field.

$$Z_1 = \underbrace{e^{-\frac{(-mB)}{\tau}}}_{\text{along}} + \underbrace{e^{-\frac{(+mB)}{\tau}}}_{\text{opposite}} = 2\cosh\left(\frac{mB}{\tau}\right)$$

$$\text{Prob(along)} = \frac{e^{+\frac{mB}{\tau}}}{Z_1} = \frac{e^{\frac{mB}{\tau}}}{e^{\frac{mB}{\tau}} + e^{-\frac{mB}{\tau}}} = \frac{1}{1+e^{-\frac{2mB}{\tau}}}$$

$$\text{Prob(opposite)} = \frac{e^{-\frac{mB}{\tau}}}{Z_1} = \frac{e^{-\frac{mB}{\tau}}}{e^{\frac{mB}{\tau}} + e^{-\frac{mB}{\tau}}} =$$

b) (8 points) From the partition function of a single spin, deduce that the total entropy of the system is (at small mB/τ)

$$\sigma_s = N_s(\log 2 - \frac{m^2B^2}{2\tau^2}).$$

Total entropy $\sigma_s = -\sum p_s \log p_s = \sum p_s \left(+\frac{\varepsilon_s}{\tau}\right) + \log Z_t = \tau \frac{\partial \log Z_t}{\partial \tau} + \log Z_t$

with $Z_t = 2^{N_s} \cosh^{N_s}\left(\frac{mB}{\tau}\right)$

$$\log Z_t = N \log 2 + N_s \log\left(\cosh\left(\frac{mB}{\tau}\right)\right)$$

$$\Rightarrow \sigma_s = N_s \tau \left(-\frac{mB}{\tau^2}\right)\frac{\sinh\left(\frac{mB}{\tau}\right)}{\cosh\left(\frac{mB}{\tau}\right)} + N_s \log 2 + N_s \log\left[\cosh\left(\frac{mB}{\tau}\right)\right]$$

for $\frac{mB}{\tau} \ll 1$ $\quad \tanh\left(\frac{mB}{\tau}\right) \sim \frac{mB}{\tau} + \ldots \quad \cosh\left(\frac{mB}{\tau}\right) \sim 1 + \frac{m^2B^2}{2\tau^2} + \ldots \Rightarrow \boxed{\sigma_s = N_s\left(\log 2 - \frac{m^2B^2}{2\tau^2}\right)}$

c) (5 points) The spin system is part of a larger system (e.g., the solid containing the spins) that we suppose isolated from the outside. We decrease reversibly the magnetic field to zero. Explain qualitatively what happens? (Hint: the total entropy remains constant).

Because we have an isolated system undergoing a reversible transformation, the total entropy remains constant. But when $B \downarrow$, $\sigma_s \nearrow$ (the spins become more and more random). Therefore entropy (and therefore heat) is extracted from the rest of the system: it cools down!

4. Fermi-Dirac Particles (25 points)

We will see later in the course that two half-integer spin particles cannot be in the same quantum state (Pauli exclusion principle). Therefore in one state s of energy ε_s per particle, we can have either zero or one particle. Let consider such a state in equilibrium with a much larger system at temperature τ, with which it can exchange energy and particles.

a) (5 points) Write down the grand partition function of this state as a function of ε_s, τ and the chemical potential μ.

$$\mathcal{Z} = 1 + e^{-\frac{(\varepsilon-\mu)}{\tau}}$$

b) (5 points) What is the general expression of the mean number of particles in a state in term of a partial derivative of the grand partition function? Justify your answer (e.g. does not just copy it from your notes)

$$\langle N \rangle = \sum_{s,N} P(s,N)\, N = \sum_{sN} N \frac{e^{-\frac{(\varepsilon-\mu)}{\tau}N}}{\mathcal{Z}}$$

$$= \tau \frac{\partial \log \mathcal{Z}}{\partial \mu}$$

c) (5 points) Deduce from this result that the mean number of particles in state s with energy ε_s per particle (and one spin orientation) is for half-integer spin particles

$$\langle N_s \rangle = \frac{1}{\exp\left(\frac{\varepsilon_s - \mu}{\tau}\right) + 1}$$

In the case above

$$\langle N_s \rangle = \tau \frac{\partial \log}{\partial \mu} \left[1 + e^{-\frac{(\varepsilon_s - \mu)}{\tau}} \right]$$

$$= \frac{e^{-\frac{(\varepsilon_s-\mu)}{\tau}}}{1 + e^{-\frac{(\varepsilon_s-\mu)}{\tau}}} = \frac{1}{e^{\frac{\varepsilon_s-\mu}{\tau}} + 1}$$

d) (5 points) In order to know the total number of particles in the system we have to sum over the density of states

$$\langle N\rangle = \sum_{s,spins} \frac{1}{\exp\left(\frac{\varepsilon_s - \mu}{\tau}\right)+1}$$

We will call g_s is the number of independent spin states (2 for spin 1/2), and perform the appropriate integral over phase space to sum over spatial quantum states. Express <*N*> as a function of g_s, the volume V and an integral over d^3p.

$$\langle N\rangle = \sum_{s,\,spins} \frac{1}{\exp\left(\frac{\varepsilon_s-\mu}{\tau}\right)+1}$$

using the density of spatial states per unit phase space

$$\langle N\rangle = \int \frac{g_s}{\exp\left(\frac{\varepsilon_s-\mu}{\tau}\right)+1} \frac{d^3p\, d^3x}{h^3} = \frac{V g_s}{h^3} \int \frac{d^3p}{\exp\left(\frac{\varepsilon_s(p)-\mu}{\tau}\right)+1}$$

e) (5 points) What is the condition for $\langle N_s\rangle \ll 1$. If this low occupation number is correct for most of the states show that

$$\langle N\rangle = g_s V \exp\left(\frac{\mu}{\tau}\right)\left(\frac{2\pi M\tau}{h^2}\right)^{\frac{3}{2}} = g_s V \exp\left(\frac{\mu}{\tau}\right) n_Q$$

$$\text{or } \mu = \tau \log\left(\frac{n}{g_s n_Q}\right) \text{ where } n = \frac{\langle N\rangle}{V}$$

This is the classical result (the g_s factor comes from the spin degrees of freedom and is also present classically). This rigorous result justifies the Gibbs *ansatz* of dividing by *N!* the naïve partition function for a system of *N* undistinguishable particles.
In this derivation, you may want to use the fact that

$$\int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right)dx = \sqrt{2\pi}\sigma$$

for $\langle N_s\rangle \ll 1$ we need to have $\exp\left(\frac{\varepsilon_s-\mu}{\tau}\right) \gg 1$

$\varepsilon_s - \mu \gg \tau$

We have then

$$\langle N\rangle = g_s V e^{+\frac{\mu}{\tau}} \int e^{-\frac{\varepsilon(p)}{\tau}} \frac{d^3p}{h^3} = g_s V e^{\frac{\mu}{\tau}} \int_{-\infty}^{+\infty} e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2M\tau}} dp_x dp_y dp_z$$

$$= g_s V \frac{(2\pi M\tau)^{3/2}}{h^3} e^{\frac{\mu}{\tau}} = g_s V \left(\frac{2\pi M\tau}{h^2}\right)^{3/2} e^{\frac{\mu}{\tau}}$$

$h^3 = (4\pi^2\hbar^2)^{3/2}$

$$= g_s V \underbrace{\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}}_{n_Q} e^{\frac{\mu}{\tau}}$$

$$\boxed{\Rightarrow \mu = \tau \log\left(\frac{n}{g_s n_Q}\right)}$$