Intermediate Exam T5 Thermodynamics and Statistical Physics 2018-2019

Friday December 21, 2018
9:00-11:00

Read these instructions carefully before making the exam!

- **Write your name and student number on *every* sheet.**
- ***Make sure to write readable for other people than yourself. Points will NOT be given for answers in illegible writing.***
- ***Language*; your answers have to be in English.**
- **Use a *separate* sheet for each problem.**
- **Use of a (graphing) calculator is allowed.**
- **This exam consists of 3 problems.**
- **The weight of the problems is Problem 1 (P1=30 pts); Problem 2 (P2=30 pts); Problem 3 (P3=30 pts). Weights of the various subproblems are indicated at the beginning of each problem.**
- **The grade of the exam is calculated as (P1+P2+P3 +10)/10.**
- **For all problems you have to write down your arguments and the intermediate steps in your calculation, *else the answer will be considered as incomplete and points will be deducted.***

PROBLEM 1 Name S-number	

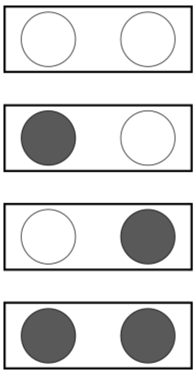
PROBLEM 2 Name S-number	

PROBLEM 3 Name S-number	

PROBLEM 1

Score: a+b+c+d+e+f=5+5+5+5+5+5=30

A system with two distinguishable absorption sites is in equilibrium with a large heat reservoir with temperature T and a particle reservoir with chemical potential μ. If 0, 1, or 2 particles are absorbed to the system, the energy of the system is 0, -ε and -2ε, respectively (see figure).



$E = 0$

$E = -\varepsilon$

$E = -\varepsilon$

$E = -2\varepsilon$

a) Show that the grand partition function $\mathcal{z}$ for this system is given by,

$$\mathcal{z} = (1 + x)^2 \text{ with } x = e^{\beta(\mu+\varepsilon)}$$

b) Give expressions for the probabilities $P(0)$; $P(-\varepsilon)$ and $P(-2\varepsilon)$ that the system has an energy of 0, $-\varepsilon$ and -2ε, respectively. Express your answers in terms of x.

c) In case $\mu + \epsilon > 0$, calculate the probabilities from b) in the limits $T \to 0$ and $T \to \infty$.

d) Calculate the mean number $\langle N \rangle$ of particles absorbed to the system. Express your answer in terms of x.

Suppose we add particles of a second type to the particle reservoir. The chemical potential of this type of particles is also μ. However, this second particle type binds twice as strong (thus with binding energy -2ε) to the absorption sites of the system as the original (first) particle type.

e) Give an expression of the grand partition function $\mathcal{z}$ for this new situation. Express your answer in terms of x and $y = e^{\beta(\mu+2\varepsilon)}$.

f) Calculate the ratio R of the probability that both adsorption sites are occupied by a particle of the first type and the probability that both sites are occupied by a particle of the second type. Explain what happens with this ratio in case $T \to 0$.

$$R = \frac{P_{\text{first}}(2 \text{ sites occupied})}{P_{\text{second}}(2 \text{ sites occupied})}$$

PROBLEM 2

Score: a+b+c+d+e =7+7+7+3+6=30

A gas of photons is confined to a cavity with volume V. The cavity is kept at a constant temperature T.

HINT 1: The density of states for a *spinless* particle confined to an enclosure with volume V is (expressed as a function of the particle's momentum p):

$$g(p)dp = \frac{V}{h^3} 4\pi p^2 dp$$

HINT 2: The mean number of photons in a state with energy $\varepsilon = \hbar\omega$ is equal to: $\frac{1}{e^{\beta\varepsilon}-1}$

a) Show that density of states of a photon in the cavity can be written as,

$$g(\omega)d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3}$$

b) Show that the mean number of photons in the cavity is given by,

$$N = b\ \frac{Vk^3T^3}{\pi^2\hbar^3c^3}$$

where $b = 2.404$ is a dimensionless constant.

c) Show that the total energy density $u = \frac{U}{V}$ (J m^{-3}) in the cavity is related to the temperature T by,

$$u = aT^4 \text{ with } a = \frac{\pi^2 k^4}{15\hbar^3 c^3}$$

d) Use the first law of thermodynamics and the definition of Helmholtz free energy to derive the expression: $dF = -SdT - PdV$.

The Helmholtz free energy F of the photon gas is $F = -\frac{1}{3}aVT^4$, with a the constant defined in c)

e) Calculate the entropy S directly from the Helmholtz free energy and show that for the photon gas:

$$U = F + TS$$

PROBLEM 3

Score: a+b+c+d+e =3+7+7+6+7=30

Consider an ultrarelativistic atom with mass M confined to (one dimensional) movement along the x-axis between $x = 0$ and $x = L$. The atom is in equilibrium with a heat bath at temperature T.

a) Show that for an ultrarelativistic atom the energy E and momentum p are related by $E = pc$ with c, the velocity of light.

b) Show that for this atom the number of states in which the atom has a momentum with a magnitude between p between p and $p + dp$ is given by:

$$g(p)dp = \frac{2L}{h}dp$$

c) Show that the single atom partition function is given by,

$$Z_1 = \frac{L}{\pi}\left(\frac{kT}{\hbar c}\right)$$

d) Suppose we have a classical ideal gas in 1 dimension of N of these ultrarelativistic atoms. Calculate the internal energy U of this 1-dimensional gas.

e) Derive the equation of state of this 1-dimensional gas. (Use the expression of the Helmholtz free energy and the first law of thermodynamics in one dimension ($dU = TdS - pdL$). With p the 1D pressure (tension) of the gas.

Solutions

PROBLEM 1

a)

$$\mathcal{Z} = \sum_{N=0}^{\infty}\sum_{r} e^{\beta(\mu N - E_r(N))} = e^{\beta(\mu\times 0-0)} + e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 2+2\varepsilon)}$$

$$= 1 + 2e^{\beta(\mu+\varepsilon)} + e^{2\beta(\mu+\varepsilon)} = 1 + 2x + x^2 = (1+x)^2$$

b)

$$P(0) = \frac{e^{\beta(\mu\times 0-0)}}{\mathcal{Z}} = \frac{1}{\mathcal{Z}} = \frac{1}{(1+x)^2}$$

$$P(-\varepsilon) = \frac{e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 1+\varepsilon)}}{\mathcal{Z}} = \frac{2x}{(1+x)^2}$$

$$P(-2\varepsilon) = \frac{e^{\beta(\mu\times 2+2\varepsilon)}}{\mathcal{Z}} = \frac{x^2}{(1+x)^2}$$

c)

In the limit $T \to 0$ we have $x = e^{\beta(\mu+\varepsilon)} \to \infty;$ because $\mu + \varepsilon > 0$.

Thus,

$$P(0) = \frac{1}{(1+x)^2} \to 0$$

$$P(-\varepsilon) = \frac{2x}{(1+x)^2} = \frac{2x}{1+2x+x^2} = \frac{2}{\frac{1}{x}+2+x} \to 0$$

$$P(-2\varepsilon) = \frac{x^2}{(1+x)^2} = \frac{x^2}{1+2x+x^2} = \frac{1}{\frac{1}{x^2}+\frac{2}{x}+1} \to 1$$

At low temperature both adsorption sites are occupied (situation with the lowest energy).

In the limit $T \to \infty$ we have $x = e^{\beta(\mu+\varepsilon)} \to 1$.

Thus,

$$P(0) = \frac{1}{(1+x)^2} \to \frac{1}{4}$$

$$P(-\varepsilon) = \frac{2x}{(1+x)^2} \to \frac{2}{4}$$

$$P(-2\varepsilon) = \frac{x^2}{(1+x)^2} \to \frac{1}{4}$$

At high energies all the four situations as pictured in the figure are equally probable.

d)

There are two ways to do this,

Using either $\langle N \rangle = \sum_{all\ states} P_i\, N_i$ or $\langle N \rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta$

In the first approach we use the probabilities for 0, 1 or 2 particle absorbed:

$$P(N=0) = \frac{1}{(1+x)^2}$$

$$P(N=1) = \frac{2x}{(1+x)^2}$$

$$P(N=2) = \frac{x^2}{(1+x)^2}$$

$$\langle N \rangle = P(N=0) \times 0 + P(N=1) \times 1 + P(N=2) \times 2 = \frac{2x}{(1+x)^2} + \frac{2x^2}{(1+x)^2} \Rightarrow$$

$$\langle N \rangle = \frac{2x(1+x)}{(1+x)^2} = \frac{2x}{1+x}$$

Using the other expression gives,

$$\langle N \rangle = \frac{1}{\beta}\left(\frac{\partial \ln z}{\partial \mu}\right)_\beta = \frac{1}{\beta}\left(\frac{\partial \ln[(1+x)^2)]}{\partial \mu}\right)_\beta = \frac{1}{\beta}\frac{2}{1+x}\left(\frac{\partial x}{\partial \mu}\right)_\beta = \frac{1}{\beta}\frac{2}{1+x}\left(\frac{\partial e^{\beta(\mu+\varepsilon)}}{\partial \mu}\right)_\beta$$
$$= \frac{1}{\beta}\frac{2}{1+x}\beta e^{\beta(\mu+\varepsilon)} = \frac{2x}{1+x}$$

e)

The grand partition function in this situation becomes:

$$\mathcal{Z} = \sum_{N=0}^{\infty}\sum_{r} e^{\beta(\mu N - E_r(N))} = e^{\beta(\mu\times 0-0)} + e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 2+2\varepsilon)}$$
$$+ e^{\beta(\mu\times 1+2\varepsilon)} + e^{\beta(\mu\times 1+2\varepsilon)} + e^{\beta(\mu\times 2+4\varepsilon)} + e^{\beta(\mu\times 2+3\varepsilon)} + e^{\beta(\mu\times 2+3\varepsilon)}$$
$$= 1 + 2e^{\beta(\mu+\varepsilon)} + e^{2\beta(\mu+\varepsilon)} + 2e^{\beta(\mu+2\varepsilon)} + e^{2\beta(\mu+2\varepsilon)} + 2e^{\beta(2\mu+3\varepsilon)}$$
$$= 1 + 2x + x^2 + 2y + y^2 + 2xy = (1 + x + y)^2$$

f)
We have

$$P_{\text{first}}(2 \text{ sites occupied}) = \frac{e^{2\beta(\mu+\varepsilon)}}{\mathcal{Z}}$$

And

$$P_{\text{second}}(2 \text{ sites occupied}) = \frac{e^{2\beta(\mu+2\varepsilon)}}{\mathcal{Z}}$$

$$R = \frac{e^{2\beta(\mu+\varepsilon)}}{e^{2\beta(\mu+2\varepsilon)}} = e^{-2\beta\varepsilon}$$

In case $T \to 0$ then $\beta \to \infty$ and thus $R \to 0$; all sites are occupied by the stronger binding particle.

PROBLEM 2

a)
For photons the momentum p is related to energy $\varepsilon = \hbar\omega = pc$. Using this in HINT 1 in combination with the fact that the photon has two polarization states (extra factor of two in the density of states) leads to,

$$g(\omega)d\omega = 2\frac{V}{h^3}4\pi\left(\frac{\hbar\omega}{c}\right)^2 d\left(\frac{\hbar\omega}{c}\right) = \frac{V}{\pi^2\hbar^3}\left(\frac{\hbar}{c}\right)^3\omega^2 d\omega = \frac{V\omega^2 d\omega}{\pi^2 c^3}$$

b)
Using the density of states in a) and the mean number of photons in each state $n(\omega)$ (from HINT 2) we find,

$$N = \int_0^\infty n(\omega)g(\omega)d\omega = \int_0^\infty \frac{1}{e^{\beta\hbar\omega}-1}\frac{V\omega^2 d\omega}{\pi^2 c^3}$$

With the substitution $x = \beta\hbar\omega$ this leads to,

$$N = \frac{V}{\pi^2 c^3}\frac{1}{(\beta\hbar)^3}\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2.404\frac{Vk^3T^3}{\pi^2\hbar^3 c^3}$$

with the value of the integral from the table of integrals.

c)
The total energy U in the cavity is,

$$U = \int_0^\infty \hbar\omega\, n(\omega)g(\omega)d\omega = \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\frac{V\omega^2 d\omega}{\pi^2 c^3}$$

Again using the substitution $x = \beta\hbar\omega$ this leads to,

$$U = \frac{\hbar V}{\pi^2 c^3}\frac{1}{(\beta\hbar)^3}\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{Vk^4T^4}{\pi^2\hbar^2 c^3}\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{Vk^4T^4}{\pi^2\hbar^2 c^3}\times\frac{\pi^2}{15} = \frac{V\pi^2 k^4}{15\hbar^3 c^3}T^4 \Rightarrow$$

$$u = \frac{U}{V} = \frac{\pi^2 k^4}{15\hbar^3 c^3}T^4 = aT^4$$

The value of the integral was taken from the table of integrals.

d)

From $F = U - TS$ we have

$$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$$

e)

From d) and the given expression for F we find,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial\left(-\frac{1}{3}aVT^4\right)}{\partial T}\right)_V = \frac{4}{3}aVT^3$$

And,

$$F = -\frac{1}{3}aVT^4 = aVT^4 - T\frac{4}{3}aVT^3 = U - TS$$

Check.

PROBLEM 3

a)

For an ultrarelativistic atom the rest mass energy is much smaller than the energy term related to the momentum of the particle thus,

$$E^2 = p^2c^2 + m^2c^4 \approx (pc)^2 \Rightarrow E = pc$$

b)

From the solution of the 1D-wave equation: $\varphi = A \sin k_x x$ and taking this function to vanish at $x = 0$ and at $x = L$ results in,

$k_x = \frac{n_x \pi}{L}$ with n_x a non-zero positive integers.

The total number of states $\Phi(k)$ with $|\vec{k}| < k$ is then given by the length k (only positive integers) divided by the unit distance between two states in k-space.

$$\Phi(k) = \frac{k}{\left(\frac{\pi}{L}\right)} = \frac{L}{\pi}k$$

The number of states between $k + dk$ and k is:

$$g(k)dk = \Phi(k + dk) - \Phi(k) = \frac{\partial \Phi}{\partial k}dk = \frac{L}{\pi}dk$$

Converting to momentum $p = \hbar k = \frac{h}{2\pi}k$ we find,

$$g(p)dp = \frac{2L}{h}dp$$

c)

Single atom partition function:

$$Z_1 = \int_0^\infty g(p)e^{-\beta pc}dp = \int_0^\infty \frac{2L}{h}e^{-\beta pc}\,dp = \frac{2L}{h}\int_0^\infty e^{-\beta pc}\,dp = \left(\frac{2L}{h}\right)\left(\frac{1}{\beta c}\right)\int_0^\infty e^{-z}\,dz$$
$$= \left(\frac{2L}{h}\right)\left(\frac{1}{\beta c}\right)(-e^{-z})|_0^\infty = \left(\frac{2L}{h}\right)\left(\frac{1}{\beta c}\right) = \left(\frac{L}{\pi}\right)\left(\frac{kT}{\hbar c}\right)$$

d)

The partition function of the classical ideal gas of N atoms is:

$$Z_N = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left(\left(\frac{L}{\pi}\right)\left(\frac{kT}{\hbar c}\right)\right)^N = \frac{1}{N!}\left(\frac{L}{\beta\pi\hbar c}\right)^N$$

The internal energy of the gas is:

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[N \ln\left(\frac{L}{\beta\pi\hbar c}\right) - \ln(N!)\right] = N\frac{\partial}{\partial \beta}[\ln(\beta)] = \frac{N}{\beta} = NkT$$

e)
From $F = U - TS \Rightarrow dF = dU - TdS - SdT$ and the first law for the 1-dimensional gas $dU = TdS - pdL$) we find:

$$dF = -SdT - pdL$$

And thus,

$$p = -\left(\frac{\partial F}{\partial L}\right)_T$$

Using,

$$F = -\frac{\ln Z}{\beta}$$

We find:

$$p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial L} = \frac{1}{\beta}\frac{\partial}{\partial L}\left(N \ln\left(\frac{L}{\beta\pi\hbar c}\right) - \ln(N!)\right) = \frac{N}{\beta L} = \frac{NkT}{L}$$