Test Exam for T5

Thermodynamics and Statistical Physics 2018-2019

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

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

The grand partition function for a system in equilibrium with a large reservoir with temperature T and chemical potential μ is given by,

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

with N the number of particles of the system and $E_r(N)$ the energy if the system is in state r and it has N particles.

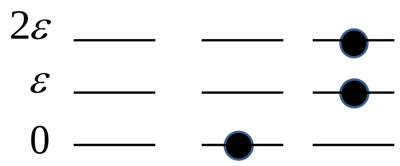
a) Show that the mean number of particles is given by,

$$\langle N \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)_{\beta}$$

b) Show that the mean energy is given by,

$$\langle E \rangle = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{\mu} + \mu \langle N \rangle$$

Suppose that the system can be occupied by particles that can be in three energy states with energies 0, ε and 2ε respectively. The three possible ways the system can be occupied are given in the figure below. Thus, either the system has no particles or it has one particle in the low energy state or it has two particles that are in the two high energy states.



c) Show that the grand partition function of this system is given by,

$$\mathcal{Z} = 1 + x + x^2 e^{-3\beta\varepsilon}$$

with $x = e^{\beta\mu}$

d) What is the probability that this system is in the state with the highest energy? Express your answer in terms of x, β and ε.
e) Calculate the mean particle number $\langle N \rangle$ for this system. Express your answer in terms of x, β and ε.

PROBLEM 2

Score: a+b+c+d =8+7+8+7=30

A gas of photons is confined to a cavity with volume V. The cavity is kept at a temperature T and the gas and the cavity are in thermal equilibrium. The single particle (photon) energy levels are $\varepsilon_i,\ i = 1,2,\cdots$ and the occupation numbers of these energy levels are $n_i,\ i = 1,2,\cdots$. The partition function Z_{ph} for this gas can be expressed as:

$$Z_{ph} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}$$

a) Show that the mean number of photons $\langle n_i \rangle$ in the state with energy ε_i can be found from this partition function by,

$$\langle n_i \rangle = -\frac{1}{\beta}\left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i}\right)_T$$

with $\beta = \frac{1}{kT}$

b) Show that the mean number of photons in the state with energy ε_i is:

$$\langle n_i \rangle = \frac{1}{e^{\beta\varepsilon_i} - 1}$$

c) Derive Plancks's radiation law which gives the distribution of the energy density $u(\omega, T)$ as a function of the photon frequency ω for radiation in thermal equilibrium (e.g. photons in our cavity),

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

HINT: 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):

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

d) Give an equation for the value of the frequency ($\omega = \omega_{max}$) for which the energy density distribution obtains its maximum. You do not have to solve this equation.

PROBLEM 3 *Score: a+b+c+d =9+9+6+6=30*

A harmonic oscillator with energy levels given by $\varepsilon_j = \hbar\omega(j + \frac{1}{2})$ is in equilibrium with a heat bath at temperature T. The angular frequency of the harmonic oscillator is ω.

a) Show that the mean energy $\langle\varepsilon\rangle$ of this oscillator is given by: $\langle\varepsilon\rangle = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$

Now consider a 1-dimensional linear crystal that consists of N atoms. The crystal has length L. Assume that the crystal can be described as a system of N coupled oscillators and that this system can only vibrate in the longitudinal direction.

b) Use Debye's theory to show that the number of angular frequencies between ω and $\omega + d\omega$ is given by:

$$g(\omega)d\omega = \frac{L}{\pi v_0} d\omega$$

In this expression v_0 is the velocity of the longitudinal waves.

c) Explain the meaning of the Debye frequency ω_D and show that for this 1-dimensional crystal,

$$\omega_D = N \frac{\pi v_0}{L}$$

d) Give an expression for the heat capacity C_V of this 1-dimensional crystal and calculate the heat capacity for high temperatures (limit $T \to \infty$).

Solutions

PROBLEM 1

a)

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta = \frac{\sum_{N=0}^{\infty}\sum_r \beta N e^{\beta(\mu N - E_r(N))}}{\mathcal{Z}} = \beta \sum_{N=0}^{\infty}\sum_r N \frac{e^{\beta(\mu N - E_r(N))}}{\mathcal{Z}}$$
$$= \beta \sum_{N=0}^{\infty}\sum_r N P(N,r) = \beta\langle N\rangle \Rightarrow$$

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta$$

b)

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu = \frac{\sum_{N=0}^{\infty}\sum_r \big(\mu N - E_r(N)\big) e^{\beta(\mu N - E_r(N))}}{\mathcal{Z}}$$
$$= -\sum_{N=0}^{\infty}\sum_r E_r(N)\frac{e^{\beta(\mu N - E_r(N))}}{\mathcal{Z}} + \mu \sum_{N=0}^{\infty}\sum_r N \frac{e^{\beta(\mu N - E_r(N))}}{\mathcal{Z}}$$
$$= -\sum_{N=0}^{\infty}\sum_r E_r(N) P(N,r) + \mu \sum_{N=0}^{\infty}\sum_r N P(N,r) = -\langle E\rangle + \mu\langle N\rangle \Rightarrow$$

$$\langle E\rangle = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu\langle N\rangle$$

c)

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

d)

The probability that the system is in a state with N particles and has energy $E(N)$is:

$$P(N, E(N)) = \frac{e^{\beta(\mu N - E(N))}}{\mathcal{Z}}$$

In this case $N = 2$ and $E(N) = 3\varepsilon$, thus,

$$P(2, 3\varepsilon) = \frac{e^{\beta(2\mu - 3\varepsilon)}}{\mathcal{Z}} = \frac{x^2 e^{-3\beta\varepsilon}}{1 + x + x^2 e^{-3\beta\varepsilon}}$$

e)

$$\langle N \rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial x}\right)_\beta \left(\frac{\partial x}{\partial \mu}\right)_\beta = \frac{1}{\beta}\left(\frac{\partial \ln\left(1 + x + x^2 e^{-3\beta\varepsilon}\right)}{\partial x}\right)_\beta \left(\frac{\partial e^{\beta\mu}}{\partial \mu}\right)_\beta$$

$$= \frac{1}{\beta}\left(\frac{1 + 2xe^{-3\beta\varepsilon}}{1 + x + x^2 e^{-3\beta\varepsilon}}\right)\left(\beta e^{\beta\mu}\right) = \frac{x + 2x^2 e^{-3\beta\varepsilon}}{1 + x + x^2 e^{-3\beta\varepsilon}}$$

PROBLEM 2

a)
The partition function is (with $\beta = \frac{1}{kT}$):

$$Z_{ph} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}$$

Differentiating $\ln Z_{ph}$ with respect to ε_i gives:

$$\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} = \frac{-\beta}{Z_{ph}}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)} \Rightarrow$$

$$\begin{aligned}\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} &= -\beta\frac{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}\\ &= -\beta\frac{\sum_{n_i=0}^{\infty} n_i e^{-\beta n_i\varepsilon_i}\sum_{n_1,n_2,\cdots n_{i-1},n_{i+1},\cdots=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}{\sum_{n_i=0}^{\infty} e^{-\beta n_i\varepsilon_i}\sum_{n_1,n_2,\cdots n_{i-1},n_{i+1},\cdots=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}\\ &= -\beta\frac{\sum_{n_i=0}^{\infty} n_i e^{-\beta n_i\varepsilon_i}}{\sum_{n_i=0}^{\infty} e^{-\beta n_i\varepsilon_i}} = -\beta\langle n_i\rangle \Rightarrow\end{aligned}$$

$$\langle n_i\rangle = -\frac{1}{\beta}\left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i}\right)_T$$

b)
The partition function can be further evaluated as

$$Z_{ph} = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)} = \prod_{i=1}^{\infty}\sum_{n_i=0}^{\infty} e^{-\beta(n_i\varepsilon_i)} = \prod_{i=1}^{\infty}\frac{1}{1-e^{-\beta\varepsilon_i}}$$

Taking the logarithm :

$$\ln Z_{ph} = -\sum_{i=1}^{\infty}\ln\left(1-e^{-\beta\varepsilon_i}\right)$$

The mean number of photons then follows from:

$$\langle n_i \rangle = -\frac{1}{\beta}\left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i}\right)_T = \frac{1}{\beta}\left(\frac{-e^{-\beta\varepsilon_i}}{1-e^{-\beta\varepsilon_i}}\right)(-\beta) = \frac{1}{e^{\beta\varepsilon_i}-1}$$

c)
For photons $\varepsilon = \hbar\omega$ and $p = \frac{\varepsilon}{c}$. Using this equation together with the hint we find for the density of states for the photons in terms of frequency ω (remember to multiply with a factor 2 for the two possible polarization states of the photon):

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

The number of photons dN and the energy dE in the range ω to $\omega + d\omega$ are given by,

$$dN = \frac{V}{\pi^2 c^3}\omega^2\frac{1}{e^{\beta\hbar\omega}-1}d\omega$$

And

$$dE = \hbar\omega dN = \frac{V}{\pi^2 c^3}\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

And for the energy density we find,

$$u(\omega, T)d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

d)
The maximum occurs when,

$$\frac{\partial u(\omega,T)}{\partial\omega} = 0 \Rightarrow \frac{3\omega^2}{e^{\beta\hbar\omega}-1} - \frac{\beta\hbar\omega^3 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = 0 \Rightarrow 3\omega^2\left(e^{\beta\hbar\omega}-1\right) - \beta\hbar\omega^3 e^{\beta\hbar\omega} = 0 \Rightarrow$$

$$(3-\beta\hbar\omega)e^{\beta\hbar\omega} = 3$$

This leads to $\omega_{max} = \frac{akT}{\hbar}$, in which a is a constant ($a \approx 2.8$). This means the maximum shifts to higher frequencies if the temperature increases.

PROBLEM 3

a)
The partition function for the oscillator is given by:

$$\mathcal{Z} = \sum_{j=1}^{\infty} e^{-\beta\varepsilon_j} = \sum_{j=1}^{\infty} e^{-\beta\hbar\omega(j+\frac{1}{2})} = e^{-\frac{x}{2}}\sum_{j=1}^{\infty} e^{-jx} = \frac{e^{-\frac{x}{2}}}{1-e^{-x}}$$

With $x = \beta\hbar\omega$.

$$\langle\varepsilon\rangle = -\frac{\partial \ln \mathcal{Z}}{\partial\beta} = -\frac{\partial \ln \mathcal{Z}}{\partial x}\frac{\partial x}{\partial\beta} = -\hbar\omega\frac{\partial}{\partial x}\left(-\frac{x}{2} - \ln(1-e^{-x})\right) = \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-x}}{1-e^{-x}}$$

And putting back $x = \beta\hbar\omega$ we find:

$$\langle\varepsilon\rangle = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

b)
Use the Debye approach and consider elastic waves through the crystal. From the solution of the 1D-wave equation: $\varphi = A\sin q_x x$ and taking this function to vanish at $x = 0$ and at $x = L$ results in,

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

The total number of states with $|\vec{q}| < q$ is then given by the length of the line representing positive integers (thus length q) divided by the unit length of one state, in q-space.

$$\Phi(q) = \frac{q}{\frac{\pi}{L}} = \frac{qL}{\pi}$$

The number of states between $q + dq$ and q is:

$$g(q)dq = \Phi(q+dq) - \Phi(q) = \frac{\partial\Phi}{\partial q}dq = \frac{L}{\pi}dq$$

From the wave equation we also have $\omega = qv_0$, substituting this in the equation above leads to,

$$g(\omega)d\omega = \frac{L}{\pi v_0}d\omega$$

There is only independent wave mode for this 1-dimensional crystal (given in the exercise) namely, longitudinal (in a 3-dimensional crystal there are generally 3 modes, because then transversal waves can exist in both directions perpendicular to the direction of wave propagation, this would give a factor 3 in the equation above).

c)

The total number of frequencies (modes) should be N as there are N atoms. This is forced in the theory by introducing the Debye frequency which is the maximum frequency that cuts off higher modes,

$$\int_0^{\omega_D} g(\omega)d\omega = N = \int_0^{\omega_D} \frac{L}{\pi v_0} d\omega = \frac{L\omega}{\pi v_0}$$

It follows that:

$$\omega_D = N\frac{\pi v_0}{L}$$

Using the Debye frequency we can rewrite,

$$g(\omega)d\omega = \frac{L}{\pi v_0} d\omega = \frac{N d\omega}{\omega_D}$$

d)

First we derive an expression for the energy of the crystal,

$$U = \int_0^{\omega_D} g(\omega)\langle\varepsilon(\omega)\rangle d\omega = \int_0^{\omega_D} \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)\frac{N d\omega}{\omega_D}$$

$$= \frac{N}{\omega_D}\int_0^{\omega_D} \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) d\omega = \frac{1}{2}N\hbar\omega_D + \frac{N}{\omega_D}\int_0^{\omega_D} \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) d\omega$$

The heat capacity follows from,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial T}\right)_V = -\frac{1}{kT^2}\left(\frac{\partial U}{\partial \beta}\right)_V$$

$$= -\frac{1}{kT^2}\frac{\partial}{\partial \beta}\left(\frac{1}{2}N\hbar\omega_D + \frac{N}{\omega_D}\int_0^{\omega_D}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)d\omega\right) =$$

$$= -\frac{1}{kT^2}\frac{N}{\omega_D}\left(\int_0^{\omega_D}\frac{\partial}{\partial \beta}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)d\omega\right)$$

$$= -\frac{1}{kT^2}\frac{N}{\omega_D}\left(\int_0^{\omega_D}\frac{\hbar^2\omega^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}d\omega\right)$$

$$= \frac{\hbar^2}{k^2T^2}\left(\frac{kT}{\hbar}\right)^3\frac{Nk}{x_D}\left(\frac{\hbar}{kT}\right)\left(\int_0^{x_D}\frac{x^2e^x}{(e^x-1)^2}dx\right) = \frac{Nk}{x_D}\left(\int_0^{x_D}\frac{x^2e^x}{(e^x-1)^2}dx\right)$$

With

$$x_D = \frac{\hbar\omega}{kT} = \frac{\theta_D}{T}$$

When $T \to \infty$ then $x_D = \frac{\theta_D}{T} \to 0$ and we can approximate the integrand with,

$$\frac{x^2e^x}{(e^x-1)^2} = \frac{x^2(1+x+..)}{(1+x+\cdots-1)^2} = 1$$

And thus

$$C_V = \frac{Nk}{x_D}\left(\int_0^{x_D}\frac{x^2e^x}{(e^x-1)^2}dx\right) = \frac{Nk}{x_D}\left(\int_0^{x_D}dx\right) = Nk$$