Intermediate Exam T5 Thermodynamics and Statistical Physics 2019-2020

Friday December 19, 2019
19:00-21:00

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	

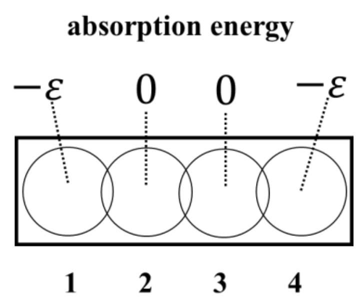
PROBLEM 2 Name S-number	

PROBLEM 3 Name S-number	

PROBLEM 1

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

A system with four distinguishable absorption sites (site 1, 2, 3, and 4) is in equilibrium with a large heat reservoir with temperature T and a particle reservoir with chemical potential μ. The energies for absorption of a particle to site 1, 2, 3 and 4 are $-\varepsilon$, 0, 0, and $-\varepsilon$, respectively, with $\varepsilon > 0$. The surface area of the absorption sites is such that absorption of two particles directly next to each other does not occur (see figure).



a) Show that the grand partition function z for this system is given by,

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

b) Give an expression for the probability $P(N = 1)$ that one particle is absorbed to the system and give an expression for the probability $P(E = 0)$ that the system has zero energy. Express your answers in terms of x and y.

c) Calculate the mean number of particles $\langle N \rangle$ of the system. Express your answer in terms of x and y.

d) In case $\mu < 0$ and $\mu + \epsilon > 0$, calculate the mean number of particles $\langle N \rangle$ of the system in the limits $T \to 0$ and $T \to \infty$.

PROBLEM 2

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

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

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

Consider a 2-dimensional square crystal that consist of N atoms. Both sides of the crystal have length L. Assume that the crystal can be described as a system of $2N$ *independent* oscillators all with the same frequency ω.

b) Derive the following expression for the *molar* heat capacity of the 2D square crystal,

$$C_V = 2R\frac{x^2e^x}{(e^x-1)^2} \text{ with } x = \frac{\hbar\omega}{kT} \text{ and } R \text{ the gas constant.}$$

Now consider the same 2D square crystal that consist of N atoms but in this case, we assume that the crystal can be described as a system of $2N$ *coupled* oscillators.

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

$$g(\omega)d\omega = \frac{L^2\omega}{\pi v_0^2}d\omega$$

In this expression v_0 is the velocity of the transverse and longitudinal waves which are assumed to be equal. Assume that the waves have one transversal and one longitudinal mode.

d) Prove that the Debye frequency ω_D for this 2D crystal is: $\omega_D = \sqrt{4\pi N}\frac{v_0}{L}$

e) Show that the internal energy U *per mole* of the 2D crystal can be written as,

$$U = \frac{2}{3}R\,\Theta_D + 4R\Theta_D\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\left(\frac{x^2}{e^x-1}\right)dx \text{ with } \Theta_D = \frac{\hbar\omega_D}{k}$$

and show that in case $T \to 0$ than $C_V \approx \text{const} \times \left(\frac{T}{\Theta_D}\right)^2$. Calculate the constant.

PROBLEM 3

Score: a+b+c =10+10+10=30

A gas of photons is confined to a 2-dimensional cavity with surface area A. The cavity is kept at a constant temperature T.

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

$$g(p)dp = \frac{2\pi A}{h^2} p dp$$

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) Assume that in 2 dimensions the photons still have two polarization directions. Show that the density of states of a photon in the cavity can be written as,

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

b) Show that the internal energy U of the photon gas in the cavity is given by,

$$U = aAT^3$$

and derive an expression for a in terms of fundamental constants.

c) Show that the internal energy U is related to the mean number of photons N by,

$$U = bNkT$$

with b a dimensional constant. Calculate the value of b.

Solutions

PROBLEM 1

a)

$$z = \sum_{N=0}^{\infty} \sum_{r} e^{\beta\left(\mu N - E_r(N)\right)} = e^{\beta(\mu\times 0-0)} + e^{\beta(\mu\times 1+0)} + e^{\beta(\mu\times 1+0)} + e^{\beta(\mu\times 1+\varepsilon)}$$

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

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

$$= 1 + 2x(1 + y + xy) + x^2y^2$$

b)

There are four situations in which one particle is absorbed:

$$P(N=1) = \frac{e^{\beta(\mu\times 1-0)} + e^{\beta(\mu\times 1-0)} + e^{\beta(\mu\times 1+\varepsilon)} + e^{\beta(\mu\times 1+\varepsilon)}}{z}$$

$$= \frac{2x(1+y)}{1 + 2x(1 + y + xy) + x^2y^2}$$

There are three situations with zero energy:

$$P(E=0) = \frac{e^{\beta(\mu\times 0-0)} + e^{\beta(\mu\times 1-0)} + e^{\beta(\mu\times 1-0)}}{z} = \frac{1+2x}{1 + 2x(1 + y + xy) + x^2y^2}$$

c)

There are two ways to do this,

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

In the first approach we use the probabilities for number of particles 0, 1 or 2:

$$P(N=0) = \frac{1}{z}$$

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

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

$$\begin{aligned}\langle N\rangle &= P(N=0)\times 0 + P(N=1)\times 1 + P(N=2)\times 2\\ &= \frac{2x(1+y)}{z}\times 1 + \frac{x^2(2y+y^2)}{z}\times 2\\ &= \left(\frac{2x(1+y)+2x^2(2y+y^2)}{z}\right) = \left(\frac{2x(1+y+2xy+xy^2)}{z}\right)\\ &= \left(\frac{2x(1+y+2xy+xy^2)}{1+2x(1+y+xy)+x^2y^2}\right)\end{aligned}$$

With the other expression,

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

Using the other expression gives, with $\left(\frac{\partial x}{\partial \mu}\right)_\beta = \beta x$; $\left(\frac{\partial y}{\partial \mu}\right)_\beta = 0$

$$\begin{aligned}\langle N\rangle &= \frac{1}{\beta}\left(\frac{\partial \ln z}{\partial \mu}\right)_\beta = \frac{1}{\beta}\frac{1}{z}\left(\frac{\partial z}{\partial \mu}\right)_\beta = \frac{1}{\beta}\frac{1}{z}\left(\frac{\partial(1+2x(1+y+xy)+x^2y^2))}{\partial \mu}\right)_\beta\\ &= \frac{1}{\beta}\frac{1}{z}(2\beta x + 2\beta xy + 4\beta x^2 y + 2\beta x^2y^2)\\ &= \frac{1}{z}(2x+2xy+4x^2y+2x^2y^2) = \left(\frac{2x(1+y+2xy+xy^2)}{1+2x(1+y+xy)+x^2y^2}\right)\end{aligned}$$

d)

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

Thus,

$$\begin{aligned}\langle N\rangle &= \left(\frac{2x(1+y+2xy+xy^2)}{1+2x(1+y+xy)+x^2y^2}\right)\\ &= \left(\frac{2\left(\frac{1}{xy^2}+\frac{1}{xy}+\frac{2}{y}+1\right)}{\frac{1}{x^2y^2}+2\left(\frac{1}{xy^2}+\frac{1}{xy}+\frac{1}{y}\right)+1}\right) \xrightarrow[T\to 0]{} \left(\frac{2(0+0+0+1)}{0+2(0+0+0)+1}\right) = 2\end{aligned}$$

The system goes to the lowest energy configuration with a particle at location 1 and a particle at position 4.

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

Thus,

$$\langle N \rangle = \left(\frac{2x(1 + y + 2xy + xy^2)}{1 + 2x(1 + y + xy) + x^2y^2}\right) \xrightarrow[T\to\infty]{} \left(\frac{2(1 + 1 + 2 + 1)}{1 + 2(1 + 1 + 1) + 1}\right) = \left(\frac{10}{8}\right)$$

The high energy limit all 8 configurations are equally probable thus the mena number of particles is:

$$\frac{0 + 1 + 1 + 1 + 1 + 2 + 2 + 2}{8} = \frac{10}{8}$$

PROBLEM 2

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 $x = \beta\hbar\omega$.

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

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)

The total internal energy is of the $2N$ oscillators is $U = 2N\langle\varepsilon\rangle = 2N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)$ and the heat capacity becomes,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 2N\frac{\partial}{\partial T}\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) = 2N\frac{\partial}{\partial\beta}\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)\left(\frac{\partial\beta}{\partial T}\right)$$

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

$$C_V = 2Nk\frac{x^2 e^x}{(e^x - 1)^2} \quad \text{with } x = \frac{\hbar\omega}{kT} = \beta\hbar\omega$$

And for one mole,

$$C_V = 2R\frac{x^2 e^x}{(e^x - 1)^2}$$

c)

In Debye's theory the lattice vibrations are approximated by waves. In the case we have a 2D geometry thus we consider the 2D wave equation. From the solution of the 2D-wave equation: $\varphi = A \sin k_x x \sin k_y y$ and taking this function to vanish at $x = y = 0$ and at $x = y = L$ results in,

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

The total number of states with $|\vec{k}| < k$ is then given by, (the area of a quarter circle e.g. only positive integers, with radius k divided by the area of the unit surface e.g. the surface of one state, in k-space).

$$\Phi(k) = \frac{\frac{1}{4}\pi k^2}{\left(\frac{\pi}{L}\right)^2} = \frac{1}{4}\frac{L^2 k^2}{\pi}$$

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

$$g(k)dk = \Phi(k + dk) - \Phi(k) = \frac{\partial \Phi}{\partial k} dk = \frac{1}{2}\frac{L^2 k}{\pi} dk$$

From the wave equation we also have $\omega = k v_0$, substituting this in the equation above leads to,

$$g(\omega)d\omega = \frac{1}{2}\frac{L^2 \omega}{\pi v_0^2} d\omega$$

There are two independent wave modes for this 2-dimensional crystal (given in the exercise) namely, longitudinal and transversal (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), as we may assume that the wave velocities for these two modes are equal we find.

$$g(\omega)d\omega = \frac{L^2 \omega}{\pi v_0^2} d\omega$$

The clever student may also realise that hint 1 in problem 3 can be used. Namely, use $p = \hbar k$ and $A = L^2$ and directly find,

$$g(k)dk = \frac{1}{2}\frac{L^2 k}{\pi} dk$$

etc.

d)

The total number of frequencies has a limit of $2N$. This is forced in the theory by introducing the Debye frequency,

$$\int_0^{\omega_D} g(\omega)d\omega = 2N = \int_0^{\omega_D} \frac{L^2\omega}{\pi v_0^2} d\omega = \frac{1}{2}\frac{L^2\omega_D^2}{\pi v_0^2}$$

It follows that:

$$\omega_D = \sqrt{4\pi N}\frac{v_0}{L}$$

e)

Using the Debye frequency, we can rewrite the density of states as,

$$g(\omega)d\omega = \frac{L^2\omega}{\pi v_0^2} d\omega = 4N\frac{\omega d\omega}{\omega_D^2}$$

We derive an expression for the internal energy of the *2D*-crystal from,

$$U = \int_0^{\omega_D} g(\omega)\langle\varepsilon\rangle d\omega = \int_0^{\omega_D} 4N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)\frac{\omega d\omega}{\omega_D^2}$$

$$= \frac{4N}{\omega_D^2}\int_0^{\omega_D}\left(\frac{1}{2}\hbar\omega^2 + \frac{\hbar\omega^2}{e^{\beta\hbar\omega}-1}\right)d\omega = \frac{2}{3}N\hbar\omega_D + \frac{4N}{\omega_D^2}\int_0^{\omega_D}\left(\frac{\hbar\omega^2}{e^{\beta\hbar\omega}-1}\right)d\omega$$

Now define $x = \beta\hbar\omega$ and $\Theta_D = \frac{\hbar\omega_D}{k}$ and find,

$$U = \frac{2}{3}Nk\,\Theta_D + \frac{4N}{\omega_D^2}\left(\frac{kT}{\hbar}\right)^3\int_0^{\beta\hbar\omega_D}\left(\frac{\hbar x^2}{e^x-1}\right)dx \Rightarrow$$

$$U = \frac{2}{3}Nk\,\Theta_D + 4Nk\Theta_D\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\left(\frac{x^2}{e^x-1}\right)dx$$

And for 1 mole $Nk = R$ we have

$$U = \frac{2}{3}R\,\Theta_D + 4R\Theta_D\left(\frac{T}{\Theta_D}\right)^3\int_0^{\frac{\Theta_D}{T}}\left(\frac{x^2}{e^x-1}\right)dx$$

When $T \to 0$ then $\frac{\theta_D}{T} \to \infty$ and,

$$U = \frac{2}{3} R\ \Theta_D + 4R\Theta_D \left(\frac{T}{\Theta_D}\right)^3 \int_0^\infty \left(\frac{x^2}{e^x - 1}\right) dx$$

The definite integral is 2.404 and thus,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 12 \times 2.404 \times R \times \left(\frac{T}{\Theta_D}\right)^2 = 28.848R \times \left(\frac{T}{\Theta_D}\right)^2$$

PROBLEM 3

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 leads to,

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

b)

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

The total mean energy U in the cavity is,

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

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

$$U = \frac{A\hbar}{\pi c^2}\frac{1}{(\beta\hbar)^3}\int_0^\infty \frac{x^2dx}{e^x-1} = \frac{Ak^3T^3}{\pi\hbar^2c^2}\int_0^\infty \frac{x^2dx}{e^x-1}$$

The integral is equal to 2.404, this follows from the table with the integrals and constants, thus,

$$U = 2.404\frac{Ak^3T^3}{\pi\hbar^2c^2} = aAT^3$$

Consequently,

$$a = \frac{2.404 \times k^3}{\pi\hbar^2c^2}$$

c)

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

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

$$N = \frac{A}{\pi c^2}\frac{1}{(\beta\hbar)^2}\int_0^\infty \frac{x}{e^x-1}dx$$

The integral is equal to $\frac{\pi^2}{6}$, this follows from the table with the integrals and constants, thus,

$$N = \frac{A}{\pi c^2}\frac{1}{(\beta\hbar)^2}\frac{\pi^2}{6} = \frac{\pi A}{6c^2}\frac{k^2T^2}{\hbar^2}$$

$$U = \frac{6\times 2.404}{\pi^2}kT\frac{\pi A k^2 T^2}{6\hbar^2 c^2} = \frac{6\times 2.404}{\pi^2}NkT$$

Consequently,

$$b = \frac{6\times 2.404}{\pi^2} = 1.46$$