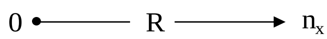
Advanced Thermodynamics (Final Exam.)

M2794.007900-001 **June 18, 2019**

1. If quantum numbers are large and the energy levels are closely located, what will be the density of quantum states, g(ϵ) for the particles moving in <u>one dimensional space</u> whose length is *L*? n indicate quantum numbers. **(10 pt)**

Note: $n^2 = \left(\frac{8mL^2}{h^2}\right)\epsilon \equiv R^2$



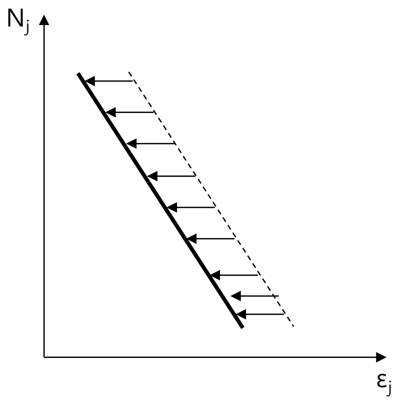
$$g(\epsilon) = n(\epsilon + d\epsilon) - n(\epsilon) \approx \frac{dn(\epsilon)}{d\epsilon} d\epsilon$$

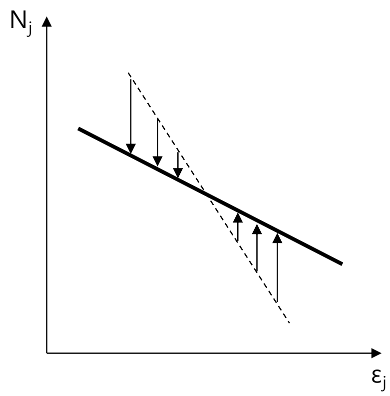
$$n(\epsilon) = \frac{1}{2} \times 2R = \frac{2\sqrt{2}L}{h} m^{1/2} \epsilon^{1/2}$$

$$\therefore g(\epsilon) = \frac{dn(\epsilon)}{d\epsilon} = \sqrt{2}\frac{L}{h} m^{1/2} \epsilon^{-1/2}$$

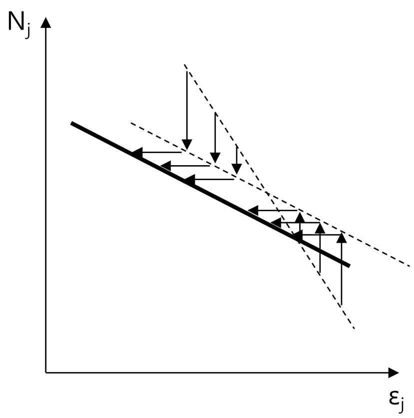
2. There are *N* indistinguishable particles in a piston of volume *V*. When the piston is heated and doing work simultaneously, describe what will be the system's new states in a statistical viewpoint. **(10 pt)**

$dQ = \sum \epsilon_i dN_i$, $dW = \sum N_i d\epsilon_i$





Work done from the systemHeat added to the system



Heat added to the system and simultaneously work done from the system

3. Helium follows Maxwell-Boltzmann statistics. Find out the followings when the gas is confined in a space with volume of V. **(20 pt)**

(1) Partition function (translation)

(2) Internal energy

(3) Entropy

(4) Enthalpy

(5) Chemical potential

(6) Pressure

(7) Heat capacity at constant volume

(1) Partition function

$$Z=\sum g(\epsilon)e^{-\epsilon/kT}=\int_0^\infty g(\epsilon)e^{-\epsilon/kT}d\epsilon=\frac{4\sqrt{2}\pi V}{h^3}\int_0^\infty \epsilon^{1/2}e^{-\epsilon/kT}d\epsilon$$

because $\int_0^\infty \epsilon^{1/2}e^{-\epsilon/kT}d\epsilon=\frac{kT}{2}\sqrt{\pi kT}$

$$\therefore Z=(\frac{2\pi mkT}{h^2})^{3/2}V$$

(2) Internal energy

$$U=NkT^2(\frac{\partial \ln Z}{\partial T})_V$$

because $\ln Z=\frac{3}{2}\ln T+\ln V+\frac{3}{2}ln(\frac{2\pi mk}{h^2})$

$$U=NkT^2\times\frac{3}{2T}=\frac{3}{2}NkT$$

(3) Entropy

$$S=\frac{U}{T}+Nk(\ln Z-\ln N+1)=\frac{3}{2}Nk+Nk+\ln\frac{V(2\pi mkT)^{3/2}}{Nh^3}$$

$$\therefore S=Nk[\frac{5}{2}+\ln\frac{V(2\pi mkT)^{3/2}}{Nh^3}]$$

(4) Enthalpy

$$H=NkT[1+T(\frac{\partial \ln Z}{\partial T})_V]=\frac{5}{2}NkT$$

(5) Chemical potential

$$\mu=-kT(\ln Z-\ln N)=-kT\ln\frac{V(2\pi mkT)^{3/2}}{Nh^3}$$

(6) Pressure

$$P=-\frac{\partial F}{\partial V})_T=\frac{NkT}{V}$$

(7) Heat capacity

$$C_V=\frac{\partial U}{\partial T})_V=\frac{3}{2}Nk$$

4. Diatomic ideal gas is moving in <u>one-dimensional plane</u> which follows Maxwell-Boltzmann distribution. Find out the speed distribution $N(v)dv$, which implies the number of particles whose speed is in the range from v to $v+dv$. The number of particles is *N*, and the length of 1-dimensional plane is *L*. (※ Use the result in problem 1) **(10 pt)**

$$Z=\int_0^\infty g(\epsilon)e^{-\epsilon/kT}d\epsilon=\sqrt{2}\frac{L}{h}m^{1/2}\int_0^\infty \epsilon^{-1/2}e^{-\epsilon/kT}d\epsilon$$

because $\int_0^\infty \epsilon^{-1/2}e^{-\epsilon/kT}d\epsilon=\sqrt{\pi kT}$

$$Z=(\frac{2\pi mkT}{h^2})^{1/2}L$$

$$N(\epsilon)d\epsilon=f(\epsilon)g(\epsilon)d\epsilon$$

$f(\epsilon)=\frac{N}{Z}e^{-\epsilon/kT}$, $Z=(\frac{2\pi mkT}{h^2})^{1/2}L$

from problem #1 $g(\epsilon)=\sqrt{2}\frac{L}{h}m^{1/2}\epsilon^{-1/2}$

$$N(\epsilon)d\epsilon=f(\epsilon)g(\epsilon)d\epsilon=\frac{Ne^{-\epsilon/kT}}{\sqrt{\pi kT}}\epsilon^{-1/2}d\epsilon$$

Converting energy distribution to velocity distribution

$\epsilon=\frac{1}{2}mv^2$, $d\epsilon=mvdv$

$$\epsilon^{-1/2}d\epsilon=\sqrt{2}m^{1/2}dv$$

$$\therefore N(v)dv=N(\frac{2m}{\pi kT})^{1/2}e^{-mv^2/2kT}dv$$

5. One mole of oxygen and two moles of nitrogen are mixed in a constant temperature and pressure condition. If these gases follow Maxwell-Boltzmann distribution, what will be the entropy of mixing? Obtain the entropy of mixing by using a concept of <u>system partition function</u>. **(10 pt)**

$n_{O_2}=1mol$, $n_{N_2}=2mol$

Number of molecules of each species:

$$N_{O_2}=N_A\times n_{O_2}=N$$

$$N_{N_2}=N_A\times n_{N_2}=2N$$

$Z_{sys}=Z_{sys}^{O_2}Z_{sys}^{N_2}$, $Z_{sys}^{O_2}=\frac{Z_{O_2}^{N!}}{N!}$, $Z_{sys}^{N_2}=\frac{Z_{N_2}^{2N!}}{(2N)!}$

$$S_{sys}=\frac{U}{T}+k\ln Z_{sys}$$

$$S_i=\frac{U}{T}+Nk\ln Z_{O_2}+2Nk\ln Z_{N_2}-k\ln (N+2N)!$$

$$S_d=\frac{U}{T}+Nk\ln Z_{O_2}+2Nk\ln Z_{N_2}-k\ln [N!+(2N)!]$$

$$\triangle S=S_i-S_d=k(N+2N)\ln(N+2N)-kN\ln N-2kN\ln 2N$$

$$\triangle S=Nk(3\ln 3N-\ln N-2\ln 2N)$$

$\therefore \triangle S=Nk\ln\frac{27}{4}$ or $\therefore \triangle S=-Nk(\ln\frac{1}{3}+2\ln\frac{2}{3})$

6. For one-dimensional solid as an assembly of 2N distinguishable oscillators, half of them vibrate with a frequency, ν, and the other half with 2ν. Find out the followings. **(20 pt)**

(1) Partition function

(2) Internal energy, U.

(3) Heat capacity at constant volume, C_V.

(4) Helmholtz energy, F.

(5) Entropy, S.

(6) Find out the behavior of S at high temperature.

(1) Partition function

$$\theta_E = \frac{h\upsilon}{kT}$$

$$Z_1 = \frac{e^{-\theta_E/2T}}{1-e^{-\theta_E/T}}, \quad Z_2 = \frac{e^{-\theta_E/T}}{1-e^{-2\theta_E/T}}$$

$$Z = Z_1 Z_2 = \frac{e^{-3\theta_E/2T}}{1-e^{-\theta_E/T}-e^{-2\theta_E/T}+e^{-3\theta_E/T}}$$

(2) Internal energy

$$U = U_1 + U_2$$

$$U_1 = NkT^2\left(\frac{\partial \ln Z_1}{\partial T}\right)_V = Nk\theta_E\left(\frac{1}{2}+\frac{1}{e^{\theta_E/T}-1}\right)$$

$$U_2 = NkT^2\left(\frac{\partial \ln Z_2}{\partial T}\right)_V = Nk\theta_E\left(1+\frac{2}{e^{2\theta_E/T}-1}\right)$$

$$\therefore U = Nk\theta_E\left(\frac{3}{2}+\frac{1}{e^{\theta_E/T}-1}+\frac{2}{e^{2\theta_E/T}-1}\right)$$

(3) Heat capacity

$$C_V = Nk\left(\frac{\theta_E}{T}\right)^2\left[\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}+\frac{4e^{2\theta_E/T}}{(e^{2\theta_E/T}-1)^2}\right]$$

(4) Helmholtz energy

$$F = U - TS = -NkT\ln Z$$

$$\therefore F = NkT\left[\frac{3\theta_E}{2T}+\ln(1-e^{-\theta_E/T})+\ln(1-e^{-2\theta_E/T})\right]$$

(5) Entropy

For distinguishable oscillators

$$w = N!\prod_i \frac{g_i^{N_i}}{N_i!}$$

$$S = k\ln w = k\ln N! + \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$S = \frac{U}{T} + Nk\ln Z$$

$$S = \frac{U}{T} + Nk\left[-\frac{3\theta_E}{2T} - \ln(1-e^{-\theta_E/T}) - \ln(1-e^{-2\theta_E/T})\right]$$

(6) behavior of S at high temperature

$$S=\frac{U}{T}+Nk[-\frac{3\theta_E}{2T}-\ln(1-e^{-\theta_E/T})-\ln(1-e^{-2\theta_E/T})]$$

from (2) $U=Nk\theta_E(\frac{3}{2}+\frac{1}{e^{\theta_E/T}-1}+\frac{2}{e^{2\theta_E/T}-1})$

at high temperature

$\theta_E \ll T$, $e^{\theta_E/T}-1\approx\frac{\theta_E}{T}$

$$U=Nk\theta_E(\frac{3}{2}+\frac{1}{e^{\theta_E/T}-1}+\frac{2}{e^{2\theta_E/T}-1})\approx Nk\theta_E(\frac{3}{2}+\frac{2T}{\theta_E})$$

$$Nk[-\frac{3\theta_E}{2T}-\ln(1-e^{-\theta_E/T})-\ln(1-e^{-2\theta_E/T})]\approx-\frac{3Nk\theta_E}{2T}-Nk\ln 2(\frac{\theta_E}{T})^2$$

$\therefore S\approx 2Nk-Nk\ln 2(\frac{\theta_E}{T})^2$ (high temperature)

7. The total number of photons are not conserved, which means $\Sigma N_i = N$ can not be applied. **(20 pt)**

(1) Find out the number of photons for each quantum state.

(2) Find out the partition function, *Z*.

(3) Calculate the internal energy, *U*.

(4) Calculate the entropy, *S*.

(5) Calculate the Helmholtz energy, *F*.

(6) Calculate the pressure, *P*.

Note: $g(\nu)d\nu=\frac{8\pi V}{c^3}\nu^2 d\nu$, $\int_0^\infty\frac{x^3dx}{e^x-1}=\frac{\pi^4}{15}$

(1) the number of photons for each quantum state

$$f(\nu)=\frac{N(\nu)}{g(\nu)}=\frac{1}{e^{h\nu/kT}-1}$$

$$N(\nu)d\nu=\frac{g(\nu)}{e^{h\nu/kt}-1}d\nu=\frac{8\pi V}{c^3}\times\frac{\nu^2}{e^{h\nu/kT}-1}d\nu$$

(2) Partition function

$$\ln Z=\int_0^\infty -g(\nu)\ln(1-e^{-h\nu/kT})d\nu=-\int_0^\infty\frac{8\pi V}{c^3}\nu^2\ln(1-e^{-h\nu/kT})d\nu$$

$$\int_0^\infty x^2 \ln(1-e^{-x})dx = -\frac{x^3}{3}\ln(1-e^{-x})|_0^\infty + \int_0^\infty \frac{1}{3}\frac{x^3}{e^x-1}dx = \int_0^\infty \frac{1}{3}\frac{x^3}{e^x-1}dx$$

$$\ln Z = \frac{8\pi V}{3}(\frac{kT}{hc})^3 \frac{\pi^4}{15} = \frac{8\pi^5 V}{45}(\frac{kT}{hc})^3$$

$$\therefore Z = \exp[\frac{8\pi^5 V}{45}(\frac{kT}{hc})^3]$$

(3) Internal energy

$$U = \int_0^\infty u(\nu)d\nu$$

$$u(\nu)d\nu = N(\nu)d\nu \times h\nu = \frac{8\pi V h}{c^3} \times \frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$$

when defining $x = \frac{h\nu}{kT} \Rightarrow \nu = (\frac{kT}{h})x,\ d\nu = (\frac{kT}{h})dx$

$$U = \frac{8\pi V}{(ch)^3}(kT)^4 \int_0^\infty \frac{x^3 dx}{e^x-1}$$

$$\therefore U = \frac{8\pi^5 k^4 T^4}{15h^3c^3} V$$

(4) Entropy

$$S = \int_0^T \frac{C_V}{T} dT,\quad C_V = \frac{\partial U}{\partial T})_V$$

When defining $a = \frac{8\pi^5 k^4}{15h^3c^3}$, $U = aT^4 V$

$$C_V = \frac{\partial U}{\partial T})_V = 4aT^3 V$$

$$S = \int_0^T \frac{C_V}{T} dT = 4aV\int_0^T T^2 dT = \frac{4}{3}aT^3 V$$

$$\therefore S = \frac{32\pi^5 k^4}{45h^3c^3} T^3 V$$

(5) Helmholtz energy

$$F = U - TS = -\frac{1}{3}aT^4 V$$

$$\therefore F = -\frac{8\pi^5 k^4}{45h^3c^3} T^4 V$$

(6) Pressure

$$\therefore P = -\frac{\partial F}{\partial V})_T = \frac{1}{3}aT^4 = \frac{8\pi^5 k^4}{45h^3c^3} T^4$$

8. For Bosons, the equilibrium distribution is expressed as $f(\epsilon) = \frac{N(\epsilon)}{g(\epsilon)} = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$. **(10 pt)**

(1) Describe the procedure how to handle Bose-Einstein condensation phenomena.

(2) What will be the variation of the number of particles with temperature in the ground state and the excited state for Boson gases?

(1)

When $T \to 0$, energy state of bosons places in the ground state $\epsilon = 0$ also $N_0 \approx N$

$$N_0 \approx \frac{1}{e^{-\mu/kT}-1}$$

When $T \to \infty$, energy state of bosons are excited

$$N_{ex} = V\frac{2}{\sqrt{\pi}}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\int_0^\infty \frac{x^{1/2}dx}{e^x-1} = 2.612\,V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

Bose temperature is the temperature above which all the bosons should be in excited states.

$$N = 2.612\,V\left(\frac{2\pi mkT_B}{h^2}\right)^{3/2}$$

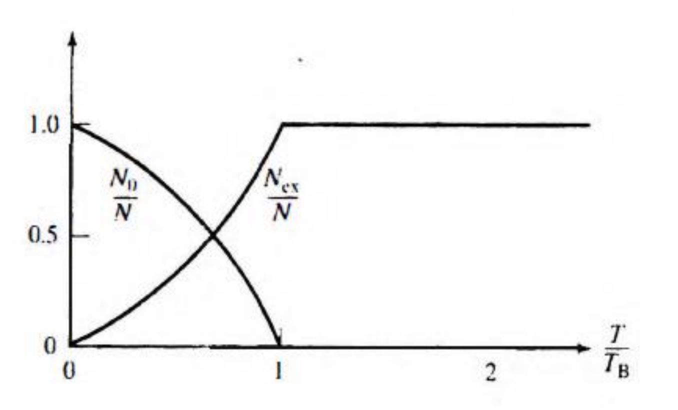
Define that total number of bosons consists of N_0 in the ground state and N_{ex} in the excited state

$$N = N_0 + N_{ex}$$

$$\frac{N_0}{N} = 1 - \frac{N_{ex}}{N} = 1 - \left(\frac{T}{T_B}\right)^{3/2}$$

(2)

In the temperature of the ground state, the number of particles are close to N_0, but above the Bose temperature, the number of particles are the same with N_{ex}



9. A system with two nondegenerate energy levels ε_0 and ε_1 ($\varepsilon_1 > \varepsilon_0 > 0$) is populated by N distinguishable particles at temperature T. **(20 pt)**

(1) Show that the average energy per particle is given by

$$u = \frac{U}{N} = \frac{\epsilon_0 + \epsilon_1 e^{-\beta\triangle\epsilon}}{1 + e^{-\beta\triangle\epsilon}},\ \triangle\epsilon = \epsilon_1 - \epsilon_0,\ \beta = 1/kT$$

(2) Show that when T → 0

$$u \approx \epsilon_0 + \triangle\epsilon\, e^{-\beta\triangle\epsilon}$$

and when T → ∞

$$u \approx \frac{1}{2}(\epsilon_0 + \epsilon_1) - \frac{1}{4}\beta(\triangle\epsilon)^2$$

(3) Show that the specific heat capacity at constant volume, c_v is

$$c_v = k\left(\frac{\triangle\epsilon}{kT}\right)^2 \frac{e^{-\triangle\epsilon/kT}}{(1 + e^{-\triangle\epsilon/kT})^2}$$

(4) Compute c_v in the limits T → 0 and T → ∞ and make a careful sketch of c_v versus $\triangle\varepsilon/kT$

(1)

$$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\epsilon_j/kT} = N\frac{g_j}{Z} e^{-\epsilon_j/kT},\quad \left(Z = \sum_{j=1}^{2} g_j e^{-\epsilon_j/kT}\right)$$

$$N_0 = N\frac{e^{-\epsilon_0/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}},\quad N_1 = N\frac{e^{-\epsilon_1/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}}$$

$$U = \sum N_j\epsilon_j = N\frac{\epsilon_0 e^{-\epsilon_0/kT} + \epsilon_1 e^{-\epsilon_1/kT}}{e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT}} = N\frac{\epsilon_0 + \epsilon_1 e^{-\beta\triangle\epsilon}}{1 + e^{-\beta\triangle\epsilon}}$$

$$u = \frac{U}{N} = \frac{\epsilon_0 + \epsilon_1 e^{-\beta\triangle\epsilon}}{1 + e^{-\beta\triangle\epsilon}},\ \triangle\epsilon = \epsilon_1 - \epsilon_0,\ \beta = 1/kT$$

(2)

when T → 0

$$u = \frac{(\epsilon_0 + \epsilon_0 e^{-\beta\triangle\epsilon}) - \epsilon_0 e^{-\beta\triangle\epsilon} + \epsilon_1 e^{-\beta\triangle\epsilon}}{1 + e^{-\beta\triangle\epsilon}} = \epsilon_0 + \frac{\triangle\epsilon e^{-\beta\triangle\epsilon}}{1 + e^{-\beta\triangle\epsilon}}$$

T → 0, $e^{-\beta\triangle\epsilon} \ll 1$

$$\therefore u \approx \epsilon_0 + \triangle\epsilon e^{-\beta\triangle\epsilon}$$

when T → ∞

$$u = \frac{\frac{1}{2}\epsilon_0 + (\frac{1}{2}\epsilon_0 + \frac{1}{2}\epsilon_0 e^{-\beta\Delta\epsilon}) - \frac{1}{2}\epsilon_0 e^{-\beta\Delta\epsilon} - \frac{1}{2}\epsilon_1 + (\frac{1}{2}\epsilon_1 + \frac{1}{2}\epsilon_1 e^{-\beta\Delta\epsilon}) + \frac{1}{2}\epsilon_1 e^{-\beta\Delta\epsilon}}{1 + e^{-\beta\Delta\epsilon}}$$

$$u = \frac{1}{2}(\epsilon_0 + \epsilon_1) + \frac{\Delta\epsilon}{2} \times \frac{e^{-\beta\Delta\epsilon} - 1}{1 + e^{-\beta\Delta\epsilon}}$$

$T \to \infty$, $e^{-\beta\Delta\epsilon} - 1 \approx -\beta\Delta\epsilon$, $e^{-\beta\Delta\epsilon} \to 1$

$$\therefore u = \frac{1}{2}(\epsilon_0 + \epsilon_1) - \frac{1}{4}\beta(\Delta\epsilon)^2$$

(3)

$$c_V = \frac{\partial u}{\partial T})_V$$

$$\frac{\partial u}{\partial T})_V = \frac{\epsilon_1 (\frac{\Delta\epsilon}{kT^2}) e^{-\Delta\epsilon/kT}}{1 + e^{-\Delta\epsilon/kT}} - (\epsilon_0 + \epsilon_1 e^{-\Delta\epsilon/kT}) \frac{(\frac{\Delta\epsilon}{kT^2}) e^{-\Delta\epsilon/kT}}{(1 + e^{-\Delta\epsilon/kT})^2}$$

$$\frac{\partial u}{\partial T})_V = \frac{\Delta\epsilon (\frac{\Delta\epsilon}{kT^2}) e^{-\Delta\epsilon/kT}}{(1 + e^{-\Delta\epsilon/kT})^2} = k(\frac{\Delta\epsilon}{kT^2})^2 \frac{e^{-\Delta\epsilon/kT}}{(1 + e^{-\Delta\epsilon/kT})^2}$$

(4)

if $x = \frac{\Delta\epsilon}{kT}$

then $c_v = kx^2 \frac{e^{-x}}{(1 + e^{-x})^2}$

$T \to 0 \Rightarrow x \to \infty$, $e^{-x} \to 0$, $c_v \to 0$

$c_v = kx^2 e^{-x}$

$T \to \infty \Rightarrow x \to 0$, $e^{-x} \to 1$, $c_v \to 0$

$$c_v = kx^2 \frac{e^{-x}}{(1 + e^{-x})^2} \approx kx^2 \frac{1 - x}{(2 - x)^2} = \frac{1}{4}kx^2$$