PHYS 3014: Statistical Mechanics

Lecture Notes
Part 7

Canonical Ensemble: Calculation of Partition Function

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Calculation of partition function Z of the system

(a) Two level system

The energy of system be either $-\frac{\Delta}{2}$ or $\frac{\Delta}{2}$

then

$$Z = \sum_r \exp(-\beta E_r)$$

$$= e^{\beta\frac{\Delta}{2}} + e^{-\beta\frac{\Delta}{2}}$$

$$= 2\cosh\left(\frac{\beta\Delta}{2}\right)$$

Internal energy $U = -\frac{\partial}{\partial\beta}\ln Z$

$$= -\frac{\Delta}{2}\tanh\left(\frac{\beta\Delta}{2}\right)$$

heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial\beta}\right)_V \frac{\partial\beta}{\partial T}$

$$= -\left(\frac{\Delta}{2}\right)^2 \operatorname{sech}^2\left(\frac{\beta\Delta}{2}\right)\cdot\left(-\frac{1}{KT^2}\right)$$

$$= K\left(\frac{\beta\Delta}{2}\right)^2 \operatorname{sec}^2\left(\frac{\beta\Delta}{2}\right)$$

Helmholtz free energy

$$F = -KT \ln Z$$
$$= -KT \ln\left\{2\cosh\left(\frac{\beta\Delta}{2}\right)\right\}$$

Entropy

$$S = \frac{U-F}{T}$$
$$= -\frac{\Delta}{2T}\tanh\left(\frac{\beta\Delta}{2}\right) + K\ln\left\{2\cosh\left(\frac{\beta\Delta}{2}\right)\right\}$$

(b) Simple harmonic Oscillator

The energy of the system is $(n+\frac{1}{2})\hbar\omega$ where $n = 0, 1, 2, \ldots$

$$\therefore \quad Z = \sum_r \exp(-\beta E_r) = \sum_{n=0}^{\infty} \exp -\beta(n+\tfrac{1}{2})\hbar\omega$$
$$= e^{-\beta\frac{\hbar\omega}{2}} \cdot \sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega) = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-\exp(-\beta\hbar\omega)}$$
$$= \frac{1}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}$$

internal energy $U = -\dfrac{\partial \ln z}{\partial \beta}$

$$\ln z = -\frac{1}{2}\beta\hbar\omega - \ln\{1 - e^{-\beta\hbar\omega}\}$$

$$\therefore \quad U = \frac{1}{2}\hbar\omega + \frac{e^{-\beta\hbar\omega}\cdot\hbar\omega}{1 - e^{-\beta\hbar\omega}}$$

$$= \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$

specific heat $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

$$= \hbar\omega \frac{(-1)\,\hbar\omega}{[e^{\beta\hbar\omega} - 1]^2} e^{\beta\hbar\omega}\left(-\frac{1}{kT^2}\right)$$

$$= k\,(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}$$

At high temperature $\beta\hbar\omega << 1$

$$\therefore \quad e^{\beta\hbar\omega} \simeq 1 + \beta\hbar\omega$$

$\therefore \quad C_v = K \frac{(\beta\hbar\omega)^2 \cdot [1+\beta\hbar\omega]}{(\beta\hbar\omega)^2}$

$= K$

and $\quad U \simeq \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\beta\hbar\omega} = KT\left[1 + \frac{\hbar\omega}{2KT}\right]$

$\simeq KT$

Helmholtz function

$F = -KT \ln Z$

$= -KT\left[-\frac{1}{2}\beta\hbar\omega - \ln\{1 - e^{-\beta\hbar\omega}\}\right]$

$= \frac{1}{2}\hbar\omega + KT\ln\{1 - e^{-\beta\hbar\omega}\}$

Entropy $\quad S = \frac{U-F}{T} = K\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln\{1 - e^{-\beta\hbar\omega}\}\right]$

At absolute zero, $U \rightarrow \frac{\hbar\omega}{2}$, $C_v \rightarrow 0$ and $S \rightarrow 0$

(c) N - level System

Let the energy levels of the system be $0, \hbar\omega, 2\hbar\omega, \ldots (N-1)\hbar\omega$. Then partition function of the system is

$$Z = \sum_r \exp(-\beta E_r)$$

$$= \sum_{r=0}^{N-1} \exp(-\beta r\hbar\omega)$$

$$= \frac{1 - e^{-N\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

(d) Rotational Energy levels

The energies of rotational energy levels of a molecule with moment of inertia I is

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$ where $J = 0, 1, 2, \ldots$ are angular momentum quantum no.

Energy level E_J has degeneracy $2J+1$.

its partition function is

$$Z = \sum_{J=0}^{\infty} (2J+1) \exp\left(-\beta E_J\right)$$

$$= \sum_{J=0}^{\infty} (2J+1) \exp\left\{-\beta \hbar^2 J(J+1)/2I\right\}$$

(e) System consists of three independent particles. Each particle has two states of energy 0 and ϵ

Total max. energy that could be possible $= 3\epsilon$
Min energy that could be possible $= 0$

Configuration Level	Total Energy of system	No. of particles in 0 energy state	No. of particles in ϵ energy state	Degeneracy
1	0	3	0	1
2	ϵ	2	1	3
3	2ϵ	1	2	3
4	3ϵ	0	3	1

partition function of system

$$Z = \sum_r g_r \exp(-\beta E_r)$$

$$= 1 \times \exp(-\beta \cdot 0) + 3 \times \exp(-\beta \cdot \epsilon)$$
$$+ 3 \times \exp(-\beta \cdot 2\epsilon) + 1 \times \exp(-\beta \cdot 3\epsilon)$$

$$= 1 + 3e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

$$= (1 + e^{-\beta\epsilon})^3$$

The partition function for one particle system

$$Z_1 = 1 + e^{-\beta\epsilon}$$

∴ partition function of complete system consisting of three distinguishable particles

$$Z_3 = (1 + e^{-\beta\epsilon})^3 = (Z_1)^3$$

Similarity for two distinguishable particles

$$Z_2 = (1 + e^{-\beta\epsilon})^2 = (Z_1)^2$$

probability that the system is in state of energy E_r

$$P_r = \frac{g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)}$$

(f) A single particle system with three energy levels of energies 0, ϵ and 2ϵ. The degeneracies are 1, 3, 1 for energy levels 0, ϵ and 2ϵ respectively.

partition function of the system

$$Z_1 = \sum_r g_r \exp(-\beta E_r)$$

$$= 1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}$$

Mean energy of single particle $\langle E_r \rangle = \dfrac{\sum_r E_r g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)}$

$$\bar{E} = \frac{0 + 3\epsilon e^{-\beta\epsilon} + 2\epsilon e^{-2\beta\epsilon}}{1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}}$$

Partition function for a gas molecule (monoatomic)
(Single particle partition function)

Consider a gas molecule is confined in a space of volume V and in equilibrium at temperature T.

The hamiltonian of the molecule is

$$H(q,p) = \sum_{i=1}^{3} \frac{p_i^2}{2m}$$

It is also the energy of the molecule.

The single particle partition function is

$$Z(T,V,1) = Z_1 = \frac{1}{h^3} \int d^3q \, d^3p \, \exp\{-\beta H(q,p)\}$$

$$= \frac{V}{h^3} \iiint \exp\left\{-\frac{1}{2mKT}(p_x^2 + p_y^2 + p_z^2)\right\} dp_x dp_y dp_z$$

$$= \frac{V}{h^3} (2\pi mKT)^{3/2}$$

$$\therefore \quad Z_1 = Z(T,V,1) = \frac{V}{\lambda^3} \quad \text{where } \lambda = \frac{h}{\sqrt{2\pi m k T}}$$

is the thermal de-Broglie wavelength of the molecule. The quantity $\sqrt{2\pi m k T}$ has the character of an average thermal momentum of a molecule.

System of N non-interacting particles

Consider a system of N non-interacting particles which are confined in a space of volume V and are in equilibrium at temperature T. The hamiltonian of the system is sum of N one particle hamiltonians.

$$H(q_1 \cdots q_{3N}, p_1 \cdots p_{3N}) = \sum_{i=1}^{N} h(q_i, p_i)$$

$$\therefore \quad H(q,p) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad \text{for N particles.}$$

Particles of the system are distinguishable.

$\therefore$ partition function of the system

$$Z_N = Z(T,V,N) = \frac{1}{h^{3N}} \int \cdots \int e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} d^{3N}p \, d^{3N}q$$

$$= \frac{V^N}{h^{3N}} \int \cdots \int e^{-\beta\left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots + \frac{p_{3N}^2}{2m}\right)} \cdot dp_1 dp_2 \cdots dp_{3N}$$

$$= \frac{V^N}{h^{3N}} \left(\sqrt{2\pi m KT}\right)^{3N}$$

$$= \left[\frac{V}{h^3}(2\pi m KT)^{3/2}\right]^N$$

$$= \left[Z(T,V,1)\right]^N = Z_1^N$$

If the particles of the system are indistinguishable, then partition function of the system is

$$Z_N = Z(T,V,N) = \frac{1}{\underline{|N}} \left[Z(T,V,1)\right]^N$$

$$= \frac{1}{\underline{|N}} \left(\frac{V}{\lambda^3}\right)^N = \frac{1}{\underline{|N}} \left[\frac{V}{h^3}(2\pi m KT)^{3/2}\right]^N$$

Now, $$Z(T,V,N) = \frac{1}{\lfloor N} \left[\frac{V}{h^3}(2\pi mKT)^{3/2}\right]^N$$

$$\ln Z(T,V,N) = N \ln\left[\frac{V}{h^3}(2\pi mKT)^{3/2}\right] - \ln \lfloor N$$

$$= N \ln\left[\frac{V}{h^3}(2\pi mKT)^{3/2}\right] - N\ln N + N$$

$$= N\left[\ln\left[\frac{V}{Nh^3}(2\pi mKT)^{3/2}\right] + 1\right]$$

$\therefore$ Helmholtz free energy

$$F(T,V,N) = -KT \ln\{Z(T,V,N)\}$$

$$= NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right\} - 1\right]$$

Internal energy $$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}NKT$$

Specific heat $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}NK$$

pressure $\quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NKT}{V}$

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = \frac{U-F}{T}$$

$$= NK\left[\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right]\right]$$

chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = KT\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right\}$$

Gibbs function

$$G = H - TS$$

$$= U + PV - TS$$

$$= F + PV$$

$$= NKT\left[\ln\left\{\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right\}\right]$$

References:

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Thank You

For any questions/doubts/suggestions and submission of assignments

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