Fundamentals of Statistical And Thermal Physics

Fall, 2014

Reference

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Chapter 6

Basic methods and results of statistical mechanics

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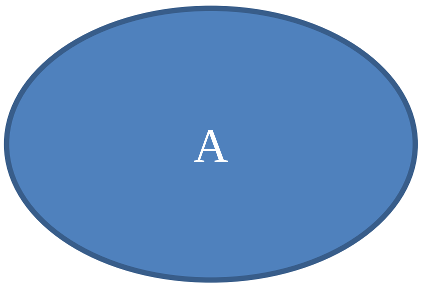
Microcanonical Distrabution

The isolated system A consists of a given number N of particles in a specified Volume V, and the constant energy of the systerm lying in the range between E and $E+\delta E$. The probability P_r of the state r with the energy denoted by E_r is



Isolated system

$$P_r = \begin{cases} C & \text{if} \quad E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

C is a constant and $\sum_r P_r = 1$

For a quantum statistical isolated system,

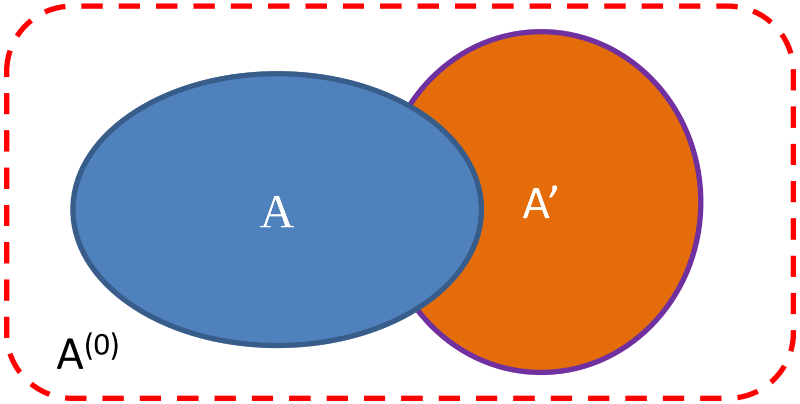
$$P_r = \begin{cases} C & \text{if} \quad E_r = E \\ 0 & \text{if} \quad E_r \neq E \end{cases}$$

So, $\sum_r P_r = C\Omega(E, V, N) = 1$

$$C = \frac{1}{\Omega(E, V, N)}$$

Canonical Distrabution

The isolated system $A^{(0)}$ consists of a small system A and a heat reservoir A' ($A^{(0)} = A + A'$), and the total energy of the systerm lying in the range between $E^{(0)}$ and $E^{(0)} + \delta E$. The conservation of energy can be written as $E_r + E' = E^{(0)}$. Where E' denoted the energy of reservior A'. The probability P_r of A being in the state r with the energy denoted by E_r is



Isolated system

$$P_r = C'\Omega'(E^{(0)} - E_r)$$

C' is a constant of propotionality independent of r and $\sum_r P_r = 1$

$$\because \ E_r \ll E^{(0)}$$

$$\therefore \ \ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 E_r \cdots$$

$$\text{where } \left[\frac{\partial \ln \Omega'}{\partial E'}\right]_0 \equiv \beta$$

$$\therefore \ \ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \beta E_r$$

$$or \ \ \Omega'(E^{(0)} - E_r) = \Omega'(E^{(0)}) \ e^{-\beta E_r}$$

Since $\Omega'(E^{(0)})$ is just a consistant independent of r

$$P_r = C e^{-\beta E_r}$$

$$C^{-1} = \sum_r e^{-\beta E_r} \qquad P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

Canonical Distrabution

The probability P(E) that A has an energy in a small range between E and $E+\delta E$ is then simply obtained by adding the probabilities for all states whose energy lies in this range; i.e.,

$$P(E) = \sum_r P_r = C\,\Omega(E)\,e^{-\beta E}$$

For example, let y be any quantity assuming the value y_r in state r of the system A. The mean value of y is

$$\bar{y} = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}}$$

Example: Paramagnetism

In the ($\pm$) state, the atomic magnetic moment $\mu_H = \pm\mu$, and the corresponding magnatic energy of the atom is $\varepsilon_\pm = \mp \mu H$.

$$P_\pm = C e^{-\beta \varepsilon_\pm} = C e^{\pm \beta \mu H}$$

$$\bar{\mu}_H = \frac{P_+ \mu + P_-(-\mu)}{P_+ + P_-}$$

$$= \mu \frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} - e^{-\beta\mu H}} = \mu \tanh \frac{\mu H}{kT}$$

The "magnetization" or mean magnetic moment per unit volume $\bar{M}_0$ in H is $\bar{M}_0 = N_0 \bar{\mu}_H$

$$\text{if } \frac{\mu H}{kT} \ll 1,\ \bar{\mu}_H = \frac{\mu^2 H}{kT} \qquad \bar{M}_0 = \chi H$$

$$here\ \chi = \frac{N_0 \mu^2}{kT}, \quad \chi \propto T^{-1} \cdots\cdots \text{Curie's law}$$

$$\text{if } \frac{\mu H}{kT} \gg 1,\ \bar{\mu}_H = \mu\ \bar{M}_0 \to N_0 \mu$$

Canonical Distrabution

$$P_r = Ce^{-\beta E_r} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \Rightarrow \overline{E} = \frac{\sum_r e^{-\beta E_r} E_r}{\sum_r e^{-\beta E_r}}$$

$$\sum_r e^{-\beta E_r} E_r = -\sum_r \frac{\partial}{\partial \beta}(e^{-\beta E_r}) = -\frac{\partial}{\partial \beta} Z$$

$$\boxed{\text{here } Z \equiv \sum_r e^{-\beta E_r} \quad \cdots\cdots \quad \text{partition function}}$$

$$\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta};$$

$$\overline{E^2} = -\frac{\partial \overline{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial^2 \beta}$$

$$\Delta_x E_r = \frac{\partial E_r}{\partial x} dx \Rightarrow dW = \frac{\sum_r e^{-\beta E_r}(-\frac{\partial E_r}{\partial x} dx)}{\sum_r e^{-\beta E_r}}$$

$$\sum_r e^{-\beta E_r} \frac{\partial E_r}{\partial x} = -\frac{1}{\beta}\frac{\partial}{\partial x}(\sum_r e^{-\beta E_r}) = -\frac{1}{\beta}\frac{\partial Z}{\partial x}$$

$$\Rightarrow dW = -\frac{1}{\beta Z}\frac{\partial Z}{\partial x} dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x} dx$$

$\because dW = \overline{X} dx$, & the mean generalized force $X = -\overline{\frac{\partial E}{\partial x}}$

$$\therefore \overline{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}$$

if $x = V$,

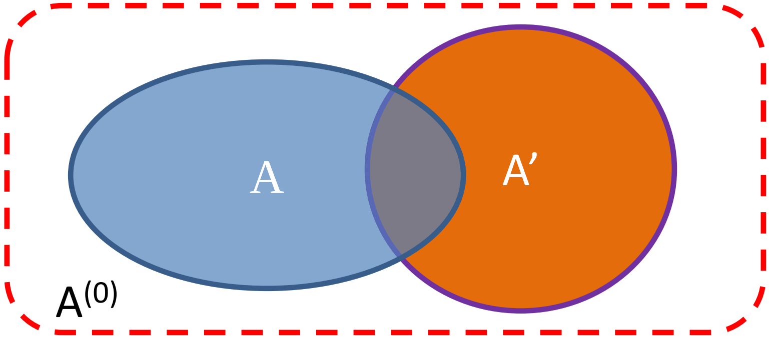
$$dW = \overline{p} dV = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} dV$$

$$\Rightarrow \overline{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

$$\boxed{S \equiv k(\ln Z + \beta \overline{E}) \qquad F \equiv \overline{E} - TS = -kT \ln Z}$$

Grand Canonical Distrabution

The isolated system $A^{(0)}$ consists of a small system A and a heat reservoir A' ($A^{(0)} = A + A'$). Then neither the energy E of A nor the number N of particles in A are fixed, but the total energy $E^{(0)}$ and the total number $N^{(0)}$ of $A^{(0)}$ are fixed. $E + E' = E^{(0)} =$ constant, $N + N' = N^{(0)} =$ constant. where E' and N' denoted the energy and the numberof particles reservior A'.



Isolated system

$$P_r(E_r, N_r) = C'\Omega'(E^{(0)} - E_r, N^{(0)} - N_r)$$

C' is a constant of propotionality independent of r and $\sum_r P_r = 1$

$$\because E_r \ll E^{(0)}, N_r \ll N^{(0)}$$

$$\therefore \ln\Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \ln\Omega'(E^{(0)}, N^{(0)}) - \left[\frac{\partial \ln\Omega'}{\partial E'}\right]_0 E_r - \left[\frac{\partial \ln\Omega'}{\partial N'}\right]_0 N_r \cdots$$

$$\text{where } \left[\frac{\partial \ln\Omega'}{\partial E'}\right]_0 \equiv \beta, \left[\frac{\partial \ln\Omega'}{\partial N'}\right]_0 \equiv \alpha$$

$$\therefore \ln\Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \ln\Omega'(E^{(0)}, N^{(0)}) - \beta E_r - \alpha N_r$$

$$or \quad \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \Omega'(E^{(0)}, N^{(0)}) \; e^{-\beta E_r - \alpha N_r}$$

Since $\Omega'(E^{(0)})$ is just a consistant independent of r

$$P_r = C e^{-\beta E_r - \alpha N_r}$$

$$C^{-1} = \sum_r e^{-\beta E_r - \alpha N_r}, \qquad P_r = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

Grand Canonical Distrabution

$$P_r = C e^{-\beta E_r - \alpha N_r} = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\Rightarrow \bar{E} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} E_r}{\sum_r e^{-\beta E_r - \alpha N_r}}, \bar{N} = \frac{\sum_r e^{-\beta E_r - \alpha N_r} N_r}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\sum_r e^{-\beta E_r - \alpha N_r} E_r = -\sum_r \frac{\partial}{\partial \beta}(e^{-\beta E_r - \alpha N_r}) = -\frac{\partial}{\partial \beta}\Xi$$

$$\sum_r e^{-\beta E_r - \alpha N_r} N_r = -\sum_r \frac{\partial}{\partial \alpha}(e^{-\beta E_r - \alpha N_r}) = -\frac{\partial}{\partial \alpha}\Xi$$

here $\Xi \equiv \sum_r e^{-\beta E_r - \alpha N_r}$ $\cdots\cdots$ grand partition function

also $\Xi \equiv \sum_r e^{-\beta E_r - \alpha N_r} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N - \beta E_s}$

$$\Xi = \sum_{N=0}^{\infty} e^{-\alpha N} \sum_s e^{-\beta E_s} = \sum_{N=0}^{\infty} e^{-\alpha N} Z_N$$

here $Z_N = \sum_s e^{-\beta E_s}$

$$\bar{E} = -\frac{1}{\Xi}\frac{\partial \Xi}{\partial \beta} = -\frac{\partial \ln \Xi}{\partial \beta};$$

$$\bar{N} = -\frac{1}{\Xi}\frac{\partial \Xi}{\partial \alpha} = -\frac{\partial \ln \Xi}{\partial \alpha};$$

$$\overline{E^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln \Xi}{\partial^2 \beta};$$

$$\overline{N^2} = -\frac{\partial \bar{N}}{\partial \alpha} = \frac{\partial^2 \ln \Xi}{\partial^2 \alpha};$$

$$dW = -\frac{1}{\beta Z}\frac{\partial \Xi}{\partial x} dx = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial x} dx = \bar{X} dx$$

$\bar{X} = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial x}$; if $x = V$, $\bar{p} = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial V}$

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

$S \equiv k(\ln \Xi + \beta \bar{E} + \alpha \bar{N})$, & $\alpha = -\frac{\mu}{kT}$

$$F \equiv \bar{E} - TS = -kT \ln \Xi + kT\alpha \frac{\partial \ln \Xi}{\partial \alpha}$$

$$\Psi \equiv F - G = F - \bar{N}\mu = -kT \ln \Xi$$

Summary

- Microcanonical distrabution: $$P_r = \begin{cases} C & \text{if } E < E_r < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$
- Canonical distribution: $$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

  Partition function: $$Z \equiv \sum_r e^{-\beta E_r}$$
- Grand danonical distribution: $$P_r = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

  Grand partition function: $$\Xi \equiv \sum_r e^{-\beta E_r - \alpha N_r} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N - \beta E_s}$$

Thanks for your attention!