

A partition function describes the statistical properties of a system in thermodynamic equilibrium. It is a function of the thermodynamic state variables, such as the temperature and volume. Most of the thermodynamic variables of the system, such as the total energy, free energy, entropy and pressure can be expressed in terms of the partition function or its derivatives. It is dimensionless, it is a pure number. The Boltzmann factor is used to approximate the fraction of particles in a large system. The Boltzmann factor is

$$Z \equiv \exp(-\beta E_0)$$

where $\beta = 1/T$ where $T = \text{statistical temp}$. Let us consider a system with energy $E(q_1, \dots, q_f, p_1, \dots, p_f)$ which depends on some f generalised coordinates and momenta. If the phase space is subdivided into cells of volume h^f , the partition function Z expressed in terms of equation (1)

This equation is evaluated by summing over the number $(dq_1, \dots, dq_f, dp_1, \dots, dp_f) / h^f$

of cells of phase space which lie in the element of volume (dq_1, \dots, dq_f) at the point (q_1, \dots, q_f) and which have the same energy $E(q_1, \dots, q_f, p_1, \dots, p_f)$.

and then summing or integrating over all such elements of volume. Thereby

$$Z = \iint e^{-\beta E(v_1, \dots, p_f)} (dv_1, \dots, dp_f) \Big|_{H}$$

~~Thermodynamic functions for canonical ensemble~~ →

Properties →

Effect of shifting the zero level of energy on the partition function, mean energy, specific heat and entropy →

Suppose the standard state changes by an amount ϵ_0 , the energy of each state γ becomes $E'_\gamma = E_\gamma + \epsilon_0$

The partition function becomes

$$\begin{aligned} Z' &= \sum_{\gamma} \epsilon e^{-\beta (E_\gamma + \epsilon_0)} \\ &= \sum_{\gamma} \epsilon e^{-\beta E_\gamma} \cdot e^{-\beta \epsilon_0} \\ &= e^{-\beta \epsilon_0} Z \end{aligned}$$

$$\log Z' = \log Z - \beta \epsilon_0$$

which shows that the partition function is changed.

The mean energy.

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Day (054-311)

$$\langle E \rangle = \frac{\sum_{\sigma} e^{-\beta E_{\sigma}} E_{\sigma}}{\sum_{\sigma} e^{-\beta E_{\sigma}}}$$

$$\sum_{\sigma} e^{-\beta E_{\sigma}} \langle E \rangle = \sum_{\sigma} e^{-\beta E_{\sigma}} E_{\sigma}$$

where the sums are over all accessible states σ of the system, irrespective of their energy

$$- \sum_{\sigma} \frac{\partial}{\partial \beta} (e^{-\beta E_{\sigma}}) = \sum_{\sigma} e^{-\beta E_{\sigma}} E_{\sigma}$$

$$- \frac{\partial^2}{\partial \beta^2} = \sum_{\sigma} e^{-\beta E_{\sigma}} E_{\sigma}$$

$$\text{Therefore } \langle E \rangle = - \frac{1}{2} \frac{\partial^2}{\partial \beta^2} = - \frac{\partial}{\partial \beta} (\log Z)$$

on this case when the energy is shifted by E_0 we find that new mean energy is

$$\bar{E}' \text{ or } \langle E' \rangle = - \frac{\partial}{\partial \beta} \log Z'$$

$$= - \frac{\partial}{\partial \beta} (\log Z) + E_0$$

$$= \langle E \rangle + E_0$$

The Mean Energy is shifted by

an amount E_0

March

T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S							
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31

$$C_V = \frac{\partial \bar{E}}{\partial T}$$

$$C'_V = \frac{\partial}{\partial T} (\bar{E} + \epsilon_0) = \frac{\partial \bar{E}}{\partial T}$$

This implies that specific heat at constant volume remains unchanged on shifting the zero level of energy.

Thermodynamic function for canonical Ensemble \rightarrow

Let the probability in canonical ensemble for a system to have energy in the range $E \leq \epsilon \leq E + \delta E$
 $= \omega(E) \delta E$

25 $P(E)$ is the probability density or distribution function or occupancy probability of a unit volume of phase space at energy E

Then probability of a volume $d\tau$ of phase space corresponding to energies between E and $E + dE = P(E) d\tau$

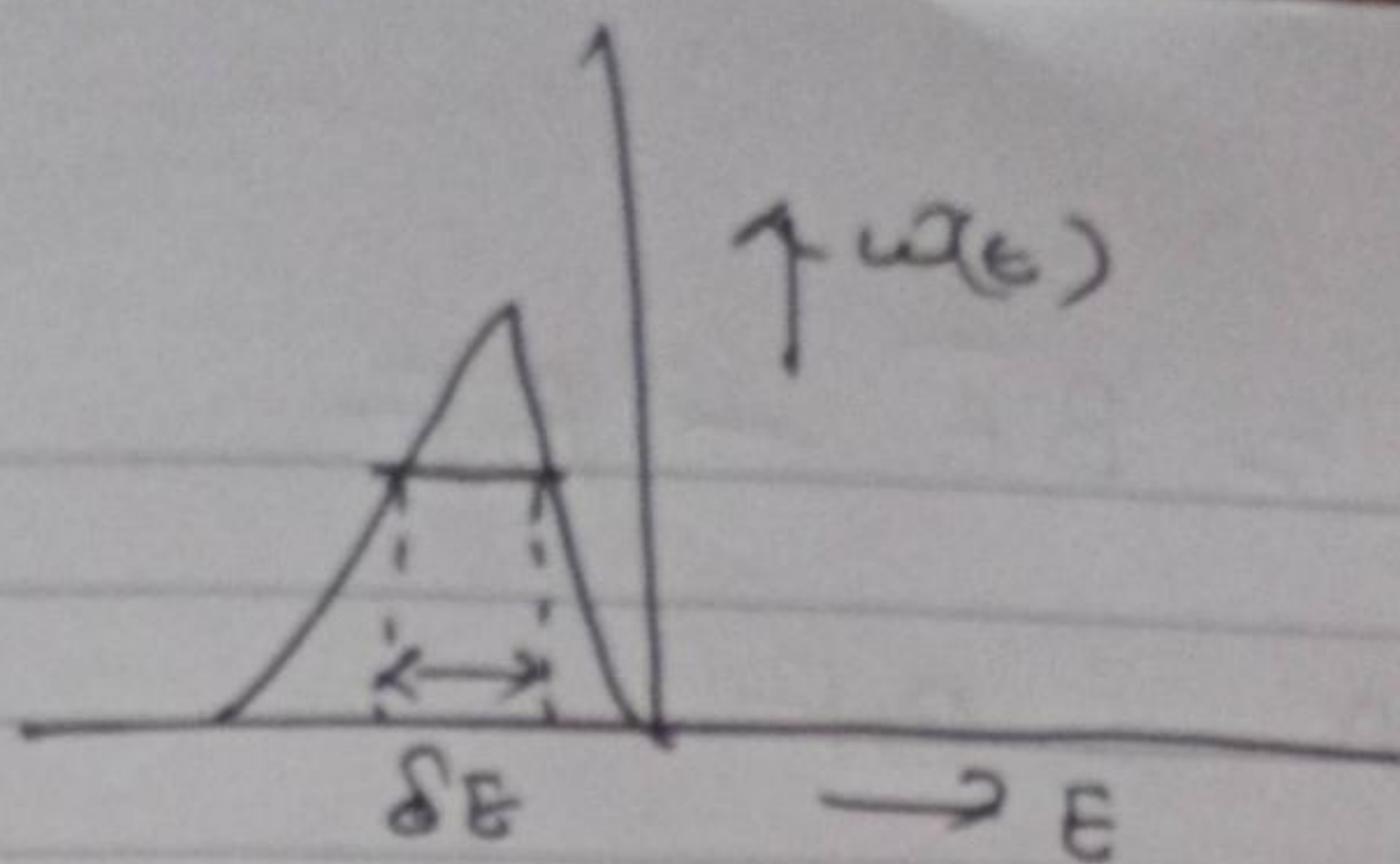
So

$$\omega(E) \delta(E) = P(E) d\tau$$

$\tau(E) =$ The volume of phase space corresponding to the energies less than or equal to E

The phase space volume, contained in the probable energy range δE will be

$$d\tau = \left(\frac{\partial \tau(E)}{\partial E} \right) \delta E$$



$w(E)$ function of E

The normalization condition

$$\int w(E) dE = 1$$

Means geometrically that the area under the curve $w = w(E)$ is equal to unity.

$$w(\bar{E}) d\bar{E} = 1$$

where \bar{E} corresponds to the maximum of the curve

$$P(\bar{E}) \Delta T = 1$$

$$\Delta T = \frac{1}{P(\bar{E})}$$

$$= A^{-1} e^{\bar{E}/T}$$

$$= A^{-1} e^{\beta \bar{E}}$$

$$\beta = 1/T$$

Now the expression for Statistical entropy

$$S = \log \Delta T$$

$$= \log (A^{-1} e^{\beta \bar{E}})$$

Helmholtz free energy

$$F = \bar{E} - T S = \bar{E} - S/\beta$$

$$G = B\bar{E} - BF$$

$$\log A = BF$$

$$A = e^{BF}$$

The canonical distribution function assumes the form

$$P(E) = A e^{-\beta E}$$

$$= e^{BF} e^{-\beta E}$$

$$= e^{\beta(F-E)}$$

which on normalisation becomes

$$\int P(E) d\tau = \int e^{\beta(F-E)} d\tau = 1$$

$$e^{-\beta F} = \int e^{-\beta E} P(E) d\tau$$

The partition function

$$Z = \int e^{-\beta E} P(E) d\tau$$

$$e^{-\beta F} = Z$$

$$F = -\frac{1}{\beta} \log Z$$

$$F = -\gamma \log Z$$

Here Helmholtz free energy

The entropy of a system in a canonical ensemble

$$S = -k \left(\frac{\partial F}{\partial \tau} \right)_V$$

$$= k \frac{\partial}{\partial \tau} (\tau \log 2)$$

$$= k \left[\log 2 + \tau \frac{\partial}{\partial \tau} (\log 2) \right]$$

$$\log 2 = \log \sum_{\epsilon} e^{-\epsilon \tau / \tau}$$

$$\frac{\partial}{\partial \tau} (\log 2) = \frac{1}{\tau^2} \frac{\sum_{\epsilon} \epsilon \cdot e^{-\epsilon \tau / \tau}}{\sum_{\epsilon} e^{-\epsilon \tau / \tau}}$$

$$= \frac{1}{\tau^2} \langle \epsilon \tau \rangle$$

$$S = k \left[\log 2 + \tau \frac{1}{\tau^2} \langle \epsilon \tau \rangle \right]$$

$$= k \left[\log 2 + \beta \langle E \rangle \right]$$

$$\beta = 1/\tau$$