Heat Reservoirs

$\circledast$ $$\beta \stackrel{\Delta}{=} \frac{\partial \ln \Omega(E)}{\partial E}$$

$\tau \stackrel{\Delta}{=} 1/\beta$ is the fundamental temperature.

→ If two systems A and A' are in a pure thermal contact with $A^{(0)} = A \cup A'$ being the isolated system

Large heat bath

then the most probable energy of A after equilb^m is reached is determined by

+ $\tau(E) = \tau'(E')$; $E' = E^{(0)} - E$

* Suppose system of interest A is in thermal equilibrium with a reservoir A'.

→ A' is such that due to any possible exchange of energy with A its temperature is not effected much.

$$\Rightarrow \quad |\Delta \tau'| \ll \tau'$$

Large heat bath

$$\rightarrow \left| \frac{\partial \beta'}{\partial E'} Q' \right| \ll \beta' \quad \text{- - - } \circledast$$

$\frac{\partial \beta'}{\partial E'} Q'$ is the rate of change of β' with energy times the energy Q' absorbed by A'. There this is equal to $\Delta \beta'$; the change in β' due to energy (heat) exchange with A

$$\rightarrow \frac{\partial \beta'}{\partial E'} \approx O\left(\frac{\beta'}{\bar{E}'}\right).$$

$$Q' \approx \bar{E}$$

$\circledast$ is satisfied if $\frac{E}{\bar{E}} \gg 1$.

$\circledast$ A' is a reservoir for A if mean energy of A' is much larger than the energy of A.

Large heat bath

(+) $\ln \Omega'(E' + Q') - \ln \Omega'(E')$

$$= \frac{\partial \ln \Omega'(E')}{\partial E'} \Big| Q' + \frac{1}{2} \frac{\partial^2 \ln \Omega'(E')}{\partial E'^2} \Big| Q'^2$$

$$+ \text{h.o.t.}$$

$$= \beta' Q' + \frac{1}{2} \frac{\partial \beta'}{\partial E'} Q'^2 + \text{h.o.t}$$

$$= Q' \left[\beta' + \frac{1}{2} \frac{\partial \beta'}{\partial E'} Q' \right] + \text{h.o.t}$$

$$\approx Q' \beta'.$$

$$\Rightarrow \quad \Delta \sigma' \approx Q' \beta'$$

Large heat bath

$$\Rightarrow \quad \Delta\sigma' \approx \frac{Q'}{\tau}$$

⊗ Suppose A is the system of interest with energy $E \gg dQ$ that is absorbed by A

$$\Delta\sigma = \ln \Omega(E+dQ) - \ln \Omega(E) \approx \frac{dQ}{\tau}.$$

$$\boxed{\Delta\sigma = \frac{dQ}{\tau}}$$

The Canonical Distribution

* We will now determine the probability of a system A being in a quantum state r that is in a thermal bath A'

* Suppose $A^{(0)} = A \cup A'$ is a closed system and A and A' are in thermal equilibrium.
* Suppose the state r has energy E_r
* $A^{(0)}$ has energy between $E^{(0)}$ and $E^{(0)} + \delta E$

The Canonical distribution

* When A is a particular state r with energy E_r then A' can have energy E' between

$$E^{(0)} - E_r \leq E' \leq E^{(0)} - E_r + \delta_r$$

which is given by $\Omega'(E^{(0)} - E_r)$

* The number of ways in which $A^{(0)}$ can be such that A is in a specific state r is $1 \times \Omega'(E^{(0)} - E_r)$

The canonical distribution

→ Thus probability of A being in a particular state r is

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

with $$\sum_r P_r = 1 \Rightarrow C^{-1} = \sum_r \Omega'(E^{(0)} - E_r)$$

The canonical distribution

→ Suppose the thermal bath (thermal reservoir) A' is so large that any energy level E_r of A is very small compared to the energy E' of the thermal reservoir (satisfied if the energy $\frac{E_r}{E'} \ll 1$).

→ Expanding $\ln P_r$ we have

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

The canonical distribution

$$\textcircled{2}\quad \ln(P_r) = \ln C + \ln \Omega'(E^{(0)} - E_r)$$

$$= \ln C + \ln \Omega'(E^{(0)}) + \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E' = E^{(0)}} (-E_r)$$

$$+ h.o.t$$

$$\Rightarrow \quad \ln(P_r) = \ln C + \ln \Omega'(E^{(0)}) - \beta'(E^{(0)}) E_r + h.o.t$$

$$\Rightarrow \quad \ln P_r = \ln \left[C\, \Omega'(E^{(0)})\, e^{-\beta E_r} \right] + h.o.t.$$

$$\Rightarrow \quad P_r \approx C\, \Omega'(E^{(0)})\, e^{-\beta E_r} \quad [\text{ignoring } h.o.t].$$

The canonical distribution

* Letting $\Lambda := C\,\Omega'(E^{(0)})$ we have

$$P_r = \Lambda\, e^{-\beta E_r}$$

where $\beta = \frac{1}{\tau}$ with τ the temperature of thermal Equilibrium.

* Thus letting $Z := \sum_r e^{-\beta E_r}$

we have

The canonical distribution

①

$$P_r = \frac{e^{-\beta E_r}}{Z} \quad - - - - (*)$$

where $Z = \sum_r e^{-\beta E_r}$

is the partition function.

② $e^{-\beta E_r}$ is the Boltzmann factor; $(*)$ is the canonical distribution and an ensemble of systems that are in thermal equilibrium with a reservoir at temperature T and distributed according to $(*)$ is said to be canonically distributed.

The canonical distribution.

① What is the probability of finding A between E and $E+\delta E$?

$$P(E) = \sum_{\{r : E < E_r \leq E+\delta E\}} P_r$$

However, as δE is small $P_r = \frac{e^{-\beta E_r}}{Z} \simeq \frac{e^{-\beta E}}{Z}$

$$\therefore P(E) = \frac{1}{Z} \sum_{\{r : E \leq E_r \leq E+\delta E\}} e^{-\beta E} = \frac{1}{Z} e^{-\beta E} \sum_{\{r : E \leq E_r \leq E+\delta E\}} 1$$

$$= \frac{1}{Z} e^{-\beta E} \Omega(E)$$

The canonical distribution

$$\Rightarrow \quad P(E) = \frac{\Omega(E)}{Z} e^{-\beta E}$$

The above is the probability of the system A having energy between

E and $E + \delta E$

The Canonical distribution

(*) If a system has states distributed canonically then the expected value of any quantity y that has value y_r in state r is

$$\bar{y} = \sum_r P_r y_r = \frac{1}{Z} \sum_r e^{-\beta E_r} y_r$$

A System with Specified mean Energy

* Consider the situation where the system of interest A is not necessarily in thermal contact with a reservoir but the mean energy of the system A is given as $\bar{E}$

* We will now evaluate the probability of the system A to be in a state r

A System with Specified mean Energy

→ Consider a representative ensemble of 'a' systems that satisfy all the specifications imposed on A and suppose A admits n states.

→ Suppose 'a_r' of 'a' systems in the ensemble are in state r. Then P_r the probability of system A to be in state r is

$$P_r = \frac{a_r}{a}.$$

A system with specified mean energy

→ $P_r = \frac{a_r}{a}$; clearly $\sum_r P_r = 1$. - - - (1)

→ Also, the mean energy is specified and therefore

$$\sum_r P_r E_r = \bar{E}$$

$$\Rightarrow \quad \sum_r \frac{a_r}{a} E_r = \bar{E}$$

$$\Rightarrow \quad \sum_r a_r E_r = a\bar{E} \quad \text{- - - (2)}$$

A System with mean energy specified.

(r) Thus

$$\sum_r a_r E_r = a\bar{E} \quad \text{--} \text{--} (2)$$

$$\sum_r a_r = a \quad \text{--} \text{--} (1)$$

Thus, the n-tuplet $(a_1, a_2, \ldots, a_n)$ have to satisfy (1) and (2).

A System with mean Energy Specified.

→ The possible number of ways of choosing a_1 systems in state 1, a_2 systems in state 2 and so on can be found in the following manner

→ a_1 systems can be chosen from a elements in $\quad {}^{a}C_{a_1} = \dfrac{a!}{a_1!\,(a-a_1)!}$ ways

of the $(a-a_1)$ systems left a_2 systems can be chosen in $\quad {}^{a-a_1}C_{a_2} = \dfrac{(a-a_1)!}{(a-a_1-a_2)!\,a_2!}$

A System with mean energy specified.

Thus, the number of ways of choosing

$(a_1, a_2, \ldots, a_n)$ is

$$\Gamma(a_1, a_2 \ldots a_n) = {}^{a}C_{a_1} \; {}^{a-a_1}C_{a_2} \; {}^{a-a_1-a_2}C_{a_3} \cdots {}^{a-\sum_{j=1}^{n-1} a_j}C_{a_n}$$

$$= \left(\frac{a!}{(a-a_1)!\, a_1!} \right) \frac{(a-a_1)!}{(a-a_1-a_2)!\, a_2!} \cdots \frac{\left(a - \sum_{j=1}^{n-1} a_j\right)!}{0!\, a_n!}$$

$$= \frac{a!}{a_1!\, a_2! \cdots a_n!}$$

A System with mean energy Specified.

→ The most probable distribution is the choice of $a_1, a_2, \ldots, a_n$ that has the maximum number of system $\Gamma(a_1 \ldots a_n)$

→ Thus, the problem becomes

$$\max_{(a_1, a_2, \ldots a_n)} \Gamma(a_1 \ldots a_n)$$

$$\sum_{r=1}^{n} a_r = a$$

$$\sum_{r} a_r E_r = a\bar{E}$$

A System with mean energy specified

$\rightarrow \quad \Gamma(a_1, \ldots a_n) = \dfrac{a!}{a_1!\, a_2! \ldots a_n!}$

assuming a, a_r are large and Stirlings applies

$$\Rightarrow \quad \ln \Gamma(a_1, \ldots a_n) = \ln a! - \ln a_1! - \ln a_2! \ldots - \ln a_n!$$

$$\simeq a \ln a - a - a_1 \ln a_1 + a_1 - \ldots - a_n \ln a_n + a_n$$

$$\approx a \ln a - \sum_r a_r \ln a_r$$

$$= + a \ln a - a \sum_r \frac{a_r}{a} \left[\ln \frac{a_r}{a} + \ln a \right]$$

$$= a \ln a - a \sum_r P_r \ln P_r - a \ln a$$

$$= - a \sum_r P_r \ln P_r$$

A System with mean energy Specified

→ Thus,

$$\ln \Gamma(a_1, \dots a_n) \simeq -a \sum_r P_r \ln P_r$$

Thus, the optimization problem is

$$\max \; -\sum_r P_r \ln P_r$$

$$P_r \geq 0$$

$$\sum_r P_r = 1$$

$$\sum P_r E_r = \bar{E}$$

System with mean Specified Energy

→ Using Lagrange multiplier the solution is obtained by

$$\frac{d}{d_r}\Big[-\sum_r P_r \ln P_r + \lambda\big[\sum_r P_r E_r - E\big]$$
$$+ \alpha\big[\sum_r P_r - 1\big]\Big] = 0$$

$$\Rightarrow \frac{d}{d_r}\left(-P_r \ln P_r + \lambda P_r E_r + \alpha P_r\right) = 0$$

$$\Rightarrow -\frac{P_r}{P_r} + \ln P_r + \lambda E_r + \alpha = 0$$

$$\Rightarrow \ln P_r = -\lambda E_r - \alpha + 1$$

$$\Rightarrow P_r = \left(e^{+1-\alpha}\right) e^{-\lambda E_r}$$

A system with mean specified energy

$\Rightarrow \quad p_r = C\, e^{-\lambda E_r} \quad ; r = 1 \ldots n$

Also as

$$\sum p_r = 1$$

we have

$$C = Z^{-1} = \frac{1}{\sum_r e^{-\lambda E_r}}$$

Also

$$\sum p_r E_r = \bar{E}$$

$$\Rightarrow \quad \sum_r C\, e^{-\lambda E_r} E_r = \bar{E}$$

A System with mean Specified Energy

$$\Rightarrow \quad \sum_r C e^{-\lambda E_r} E_r = \bar{E}$$

$$\Rightarrow \quad \sum_r e^{-\lambda E_r} E_r = Z \bar{E}$$

where $Z = \sum_r e^{-\lambda E_r}$

A System with mean Specified Energy

(*) Thus, the probability P_r that the system is in a state r is given by

$$P_r = \frac{e^{-\lambda E_r}}{Z} \; ; \; Z = \sum_r e^{-\lambda E_r}$$

where λ is determined by the equation

$$\sum e^{-\lambda E_r} E_r = Z \bar{E}$$

which is again a canonical distribution

Canonical distribution in the classical approximation

→ Suppose the energy of the system depends classically on generalized momenta p_i and generalized coordinates q_i with energy $E(q_1, q_2, \ldots q_f, p_1, p_2, \ldots p_f)$ in the elemental volume $dq_1\, dq_2 \ldots dq_f\, dp_1 \ldots dp_f$ at $(q_1, q_2, \ldots q_f, p_1, p_2 \ldots p_f)$. Then the canonical partition function is

$$Z = \int \cdot \int \cdots \int e^{-\beta E(q_1, \ldots p_f)}\, dq_1 \ldots dp_f$$

The Equipartition theorem.

→ Suppose the energy E at $(q_1 \ldots q_f, p_1 \ldots p_f)$ in the volume $dq_1 \ldots dp_f$ is such that

$$E[q_1, \ldots q_f, p_1, \ldots p_f] = \varepsilon_i(p_i) + E'[q_1, \ldots q_f, p_1, \ldots p_f]$$

Then if the system is in thermal Eqlb^{m} then

$$\langle \varepsilon_i \rangle = \frac{\int \varepsilon_i(p_i)\, e^{-\beta E(q_1 \ldots p_f)}\, dq_1 \ldots dp_f}{\int e^{-\beta E(q_1 \ldots p_f)}\, dq_1 \ldots dp_f}$$

Equipartition theorem

$$\langle \varepsilon_i \rangle = \frac{\int \varepsilon_i(p_i)\, e^{-\beta[\varepsilon_i(p_i)+E']} dq_1 \cdots dp_f}{\int e^{-\beta[\varepsilon_i(p_i)+E']} dq_1 \cdots dp_f}$$

$$= \frac{\left(\int_{p_i} \varepsilon_i(p_i)\, e^{-\beta \varepsilon_i(p_i)} dp_i\right) \int e^{-\beta E'} dq_1 \cdots dq_f\, dp_1 \cdots dp_{i-1}\, dp_{i+1} \cdots dp_f}{\int_{p_i} \varepsilon_i(p_i) e^{-\beta \varepsilon_i(p_i)} dp_i \int e^{-\beta E'} dq_1 \cdots dq_f\, dp_1 \cdots dp_{i-1}\, dp_{i+1} \cdots dp_f}$$

Equipartition theorem

$$\langle E_i \rangle = \frac{\int \varepsilon_i(p_i)\, e^{-\beta \varepsilon_i(p_i)}\, dp_i}{\int e^{-\beta \varepsilon_i(p_i)}\, dp_i}$$

$$= \frac{\frac{\partial}{\partial \beta}\left(\int e^{-\beta \varepsilon_i(p_i)}\, dp_i \right)}{\int e^{-\beta \varepsilon_i(p_i)}\, dp_i}$$

Equipartition theorem

$$\circledast \quad \langle \varepsilon_i \rangle = \frac{-\frac{\partial}{\partial \beta} \int e^{-\beta \varepsilon_i(p_i)} dp_i}{\int e^{-\beta \varepsilon_i(p_i)} dp_i}$$

$$= -\frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta \varepsilon_i(p_i)} dp_i \right]$$

Equipartition theorem

⊛ Suppose

$$\varepsilon_i(p_i) = b p_i^2$$

Then

$$\int_{-\infty}^{\infty} e^{-\beta \varepsilon_i} dp_i$$

$$= \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i$$

Let $\beta b p_i^2 = x^2$

$x = \sqrt{\beta b}\; p_i$

$$= \sqrt{\beta b} \int_{-\infty}^{\infty} e^{-x^2} dx$$

$$\therefore \quad \ln\left(\int_{-\infty}^{\infty} e^{-\beta \varepsilon_i} dp_i\right) = \ln\sqrt{\beta b} + \ln \int_{-\infty}^{\infty} e^{-x^2} dx$$

$$= \ln\sqrt{\beta} + \ln\sqrt{b} + \ln \int_{-\infty}^{\infty} e^{-x^2} dx$$

Equipartition theorem

$$\Rightarrow \langle \varepsilon_i \rangle = \frac{\partial}{\partial \beta}\left[\ln \int_{-\infty}^{\infty} e^{-\beta \varepsilon_i}\, dp_i\right]$$

$$= \frac{\partial}{\partial \beta}\left(\ln \sqrt{\beta}\right)$$

$$= \frac{1}{\sqrt{\beta}} \, \frac{1}{2} \, \frac{1}{\sqrt{\beta}} = \frac{1}{2\beta}$$

$$\therefore \quad \langle \varepsilon_i \rangle = \frac{\tau}{2} = \frac{1}{2} kT$$

Thus, the mean of the quadratic energy term is $\frac{1}{2} kT$

A typical Situation.

→ Given the external parameters of a system, the quantum mechanical states are fixed with each quantum mechanical state r having some energy

$$E_r = E_r(x_1, x_2, \ldots x_n)$$

where x_i are the external parameters.

Example: Particle in a Box (Quantum Mechanical)

① (x, y, z) are the coordinates of the particle

② $0 \le x \le L_x, \quad 0 \le y \le L_y$ and $0 \le z \le L_z$;

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = E\psi.$$

Schrodinger's

$$\psi = \sin\left(\pi \frac{n_x x}{L_x}\right) \sin\left(\pi \frac{n_y y}{L_y}\right) \sin\left(\pi \frac{n_z z}{L_z}\right).$$

Energy associated with state

$$E_r = \frac{\hbar^2}{2m}\pi^2 \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right).$$

$$r \equiv (n_x, n_y, n_z).$$

a) The states are enumerated by

$r = (n_x, n_y, n_z)$; $n_x, n_y, n_z \in \{1, 2, \dots\}$,

Purely thermal Interaction.

Pure thermal Interaction

→ In a pure thermal interaction between two systems A and A', the quantum states of A and quantum states of A' do not change as the external parameters are all fixed

→ Pure thermal interaction changes the probability of system A being in state r (with energy E_r) and thus changes the mean energy at thermal equilibrium of A [similarly for A']

Explanation of A [similarity for ...

Purely Mechanical Interaction

→ In a purely mechanical Interaction the number of elements of an ensemble (pertaining to A) in a particular state r does not change

→ The external parameters are changed and thus, E_r the energy pertaining to the state is changed.

Work done

→ Suppose the external parameter is changed from x_α to $x_\alpha + dx_\alpha$ with the energy of state r, E_r changing by

$$\frac{\partial E_r}{\partial x_\alpha} dx_\alpha \quad \text{with}$$

$$\Delta E_r = \int_{x_{\alpha i}}^{x_{\alpha f}} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$; where x_α has changed from $x_{\alpha i}$ to $x_{\alpha f}$

$\therefore$ Net change in mean Energy $= \sum_r P_r \Delta E_r$

where in a pure Mechanical interaction P_r is

Pure mechanical work

→ unchanged from the initial probability distribution

→ $$\overline{\Delta W} \mathrel{\dot{=}} \sum_r P_r \, \Delta E_r$$

is the corresponding work done.

Typical Interaction

→ In a typical interaction both the external parameters are changed and the probability of being in any particular state are also altered.

→ Complex situation!

→ Still manageable for "Quasistatic Process".

Work and Heat in a General Interaction

→ Typically it is possible to find W work done through some other means (W is the work done by the system)

→ Suppose the change in mean energy $\overline{\Delta E}$ is also known then heat absorbed by the system is <u>defined</u> as

$$Q = \overline{\Delta E} + W.$$

Quasistatic Process

→ A process where the external parameters of the system are changed in a manner in which at every stage of the process the system is in thermal equilibrium.

Example: Particle in a Box (Quantum Mechanical)

① (x, y, z) are the coordinates of the particle

② $0 \le x \le L_x$, $0 \le y \le L_y$ and $0 \le z \le L_z$;

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = E\psi.$$

Schrodinger's

$$\psi = \sin\left(\pi \frac{n_x x}{L_x}\right)\sin\left(\pi \frac{n_y y}{L_y}\right)\sin\left(\pi \frac{n_z z}{L_z}\right).$$

Energy associated with state γ

$$E_\gamma = \frac{\hbar^2}{2m}\pi^2\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right).$$

$$\gamma \equiv (n_x, n_y, n_z).$$

a) The states are enumerated by

$r := (n_x, n_y, n_z)$; $n_x, n_y, n_z \in \{1, 2, \dots\}$,

Work done when length is changed

Question: If the length of the box in the x-direction is changed quasistatically from L_x to $L_x + dL_x$ what is the work done.

Assume initially $L_x = L_y = L_z$.

<u>Answer</u>: For each state r, the change in energy due to the change $L_x \mapsto L_x + dL_x$ is

$$dE_r = \frac{\partial E_r}{\partial L_x} dL_x = \frac{\partial}{\partial L_x}[M]\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] dL_x$$

$$\therefore dE_r = -2M L_x^{-3} n_x^2 \, dL_x.$$

$$\left[E_r = M\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad M = \hbar^2\pi^2/2m \right]$$

Work done by a particle in a box.

$$\Rightarrow \quad dE_r = -2M \frac{n_x^2}{L_x^3} dL_x.$$

⊛ The associate work done by the system is

$$đW_r = -dE_r = 2M \frac{n_x^2}{L_x^3} dL_x$$

⊛ Therefore

$$đW = \sum_r P_r(L_x, L_y, L_z)\, đW_r$$

with $P_r(L_x, L_y, L_z)$ determined by Equilibrium statistics

Work done by a particle in a box.

⊛ There is another means of evaluating dW.

Indeed by symmetry ($L_x = L_y = L_z$) we have

$$\langle n_x^2 \rangle = \langle n_y^2 \rangle = \langle n_z^2 \rangle .$$

Now,
$$\langle E \rangle = M \left[\frac{\langle n_x^2 \rangle}{L_x^2} + \frac{\langle n_y^2 \rangle}{L_y^2} + \frac{\langle n_z^2 \rangle}{L_z^2} \right]$$

and therefore
$$\langle n_x^2 \rangle = \frac{\langle E \rangle}{3M} L^2$$

$$\langle n_x^2 \rangle = \frac{\langle E \rangle L^2}{3M} \quad ; \; L = L_x = L_y = L_z$$

Work done by a particle in a box.

⊙ Thus,

$$dW = \sum_r P_r \, dW_r$$

$$= \sum_r P_r(L_x, L_y, L_z) \frac{2M}{L^3} n_x^2 \quad dL_x$$

$$\Rightarrow dW = \frac{2M}{L^3} dL_x \sum_r P_r(L_x, L_y, L_z) n_x^2$$

$$= \frac{2M}{L^3} dL_x \quad \langle n_x^2 \rangle$$

$$= \frac{2M}{L^3} dL_x \frac{\langle E \rangle}{3M} \frac{L^2}{L^3} = \frac{2}{3} \frac{\langle E \rangle}{L_x} dL_x$$

Work done by a particle in a box.

(*) Now, the partition function is given by (with dimensions L_x, L_y, L_z)

$$Z = \sum_r e^{-\beta E_r} = \sum_{n_x}\sum_{n_y}\sum_{n_z} e^{-\beta M\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)} \quad \text{--- (*)}$$

and $\langle E \rangle = -\frac{\partial}{\partial \beta}(\ln Z)$

(*) Note that (*) can be evaluated to find Z and therefore to find $\langle E \rangle (L_x, L_y, L_z)$. Thus $\langle E \rangle$ is known.

Work done by a particle in a box

* Therefore we have

$$dW = \frac{2}{3} \bar{E}(L_x, L_y, L_z) \frac{dL_x}{L_x}$$

where $\bar{E}$ is known

* Note that once Z is known its possible in principle to evaluate

$$\langle n_x^2 \rangle = \sum_{n_x n_y n_z} e^{-\beta E_r(n_x n_y n_z)} n_x \Big/ Z$$

Work done by a particle in a box

$$\langle n_x^2 \rangle = \sum_{n_x, n_y n_z} n_x^2 e^{-\beta E_r} \Big/ Z$$

$$\therefore \langle n_x^2 \rangle = \frac{\sum_{n_x n_y n_z} n_x^2 e^{-\beta(E_x + E_y + E_z)}}{Z}$$

Let $E = M\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$

$$= \frac{M n_x^2}{L_x^2} + \frac{M n_y^2}{L_y^2} + \frac{M n_z^2}{L_z^2}$$

$$= \colon E_x + E_y + E_z]$$

$$= \frac{\left(\sum_{n_x} n_x^2 e^{-\beta E_x}\right) \sum_{n_y n_z} e^{-\beta(E_y + E_z)}}{\left(\sum_{n_x} e^{-\beta E_x}\right) \sum_{n_y n_z} e^{-\beta(E_y + E_z)}}$$

$$= \frac{\sum_{n_x} n_x^2 e^{-\beta M n_x^2 / L_x^2}}{\sum_{n_x} e^{-\beta M n_x^2 / L_x^2}}$$

Work done by a particle

- Let $$Z_x = \sum_{n_x=1}^{\infty} e^{-\beta M n_x^2 / L_x^2}$$

Then $$\frac{\partial Z_x}{\partial \beta} = \sum_{n_x=1}^{\infty} (-n_x)(2) \frac{\beta M}{L_x^2} e^{-\beta M n_x^2 / L_x^2}$$

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_{n_x=1}^{\infty} \left(\frac{2\beta M n_x}{L_x^2}\right)^2 e^{-\beta M n_x^2 / L_x^2}$$

$$\langle n_x^2 \rangle (L_x) = \frac{\left(\frac{L_x^2}{2\beta M}\right)^2 \frac{\partial^2 Z}{\partial \beta^2}}{Z} = \frac{\sum_{n_x=1}^{\infty} n_x^2 e^{-\beta M n_x^2 / L_x^2}}{Z}$$

Work done by a particle

→ Thus, $\langle \Pi_x^2 \rangle$ can be evaluated as a function of L_x.

Thus, dW is known as a function of L_x and thus

$$W = \int_{L_{x_f}}^{L_{x_i}} dW$$

$$= \frac{2}{M} \int_{L_{x_f}}^{L_{x_i}} \langle \Pi_x^2 \rangle \, dL_x .$$

Heat during the process

(*) $$đQ \stackrel{\circ}{\underset{\circ}{:=}} \overline{dE} + đW$$

The heat during the process is

$$Q = \underbrace{\langle E \rangle}_{\text{calculated as before.}} + \underbrace{W}_{\text{calculated as before}}$$

Quasistatic Processes.

→ We will now generalize the discussion on work done.

⊛ $E_r = E_r(x_1, x_2, \dots x_n)$.

⊛ $$dE_r = \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha$$

is the change in energy of quantum state r when $x_\alpha \mapsto x_\alpha + dx_\alpha$.

⊛ dW_r = the work done by the system when it remains in the particular state r

Work done in a Quasistatic Process

→ $$đW_r = -dE_r = \sum X_{\alpha,r}\, dx_\alpha$$

where $$X_{\alpha,r} = -\frac{\partial E_r}{\partial x_\alpha}$$

→ Suppose the probability distribution over the states r when the external parameters are x_α ; $\alpha = 1 \ldots n$ is known

→ $$đW = \sum_{\alpha=1}^{n} \left(\sum_r P_r(x_1, \ldots x_n)\, X_{\alpha,r} \right) dx_\alpha$$
$$= \sum_{\alpha=1}^{n} \overline{X}_\alpha\, dx_\alpha$$

Work done during a Quasi-static Process

- $$\bar{X}_\alpha = \sum_r P_r X_{\alpha,r} = \sum_r P_r \left(-\frac{\partial E_r}{\partial x_\alpha}\right)$$

is the mean generalized force conjugate to x_α.

Generalized Force

$E_r(x_1, x_2, \cdots x_n)$.

Then, when the parameter changes

from $x_\alpha \mapsto x_\alpha + dx_\alpha$

$$dE_r = + \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha .$$

$$dW_r = - dE_r = - \sum_{\alpha=1}^{n} \frac{\partial E_r}{\partial x_\alpha} dx_\alpha .$$

→ quasistatic process is assumed

then

$$dW = - \sum_{\alpha=1}^{n} \overline{\frac{\partial E_r}{\partial x_\alpha}} dx_\alpha = \sum_{\alpha=1}^{n} \bar{X}_\alpha dx_\alpha .$$

Generalized force

$\rightarrow \quad \bar{X}_\alpha = -\overline{\dfrac{\partial E_r}{\partial x_\alpha}}$; the mean being calculated using the existing equilibrium statistics.

$\rightarrow$ X_α is the generalized force conjugate to the parameter x_α.

(*) Dependence of the density of states with respect to external parameters:

(i) how does $\Omega(E, x)$ change when $x \mapsto x + dx$.

$$\rightarrow \quad \frac{\partial \ln \Omega(E, x)}{\partial x} = \beta \bar{X}$$

(ii) If $x_1, x_2 \ldots, x_n$ are the parameters then

$$\rightarrow \quad \frac{\partial \ln \Omega(E, x_1, x_2 \ldots x_n)}{\partial x_\alpha} = \beta \bar{X}_\alpha \, . \quad ; \quad \beta = \frac{\partial \ln \Omega(E, x)}{\partial E} \, .$$