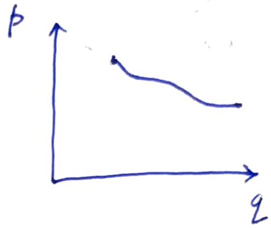
Ensemble average: As opporsed to varying time with 'one' system, we take many mental copies of the same system at one time. Essentially all these copies are in the same macrostate, but ~~one~~ different microstate!

Phase space: $(q_i; p_i)$: 6N dimension for N particles

Time varying description

$$\dot{q}_i = \frac{\partial H(q_i; p_i)}{\partial p_i}$$



$$\dot{p}_i = -\frac{\partial H(q_i; p_i)}{\partial q_i}$$

With time this point in the phase space changes in the direction of the velocity vector $\vec{v}(\dot{q}_i, \dot{p}_i)$.

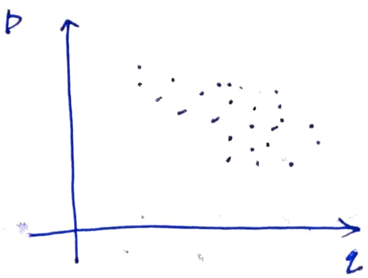
The region ~~in~~ phase-space is restricted.

$q_i \rightarrow$ restricted by V

The trajectory will be restricted to the 'hypersurface' $H(q_i; p_i) = E$.

Ensemble treatment

For the ensemble case, we have many points in the 'allowed space'.



density function: $\rho(q, p, t)$ such that the no of points in the phase space is given by $\int \rho(q, p, t)\, d^{3N}q\, d^{3N}p$

Ensemble average: $$\langle f \rangle = \frac{\int f(q,p)\, \rho(q, p; t)\, d^{3N}q\, d^{3N}p}{\int \rho(q, p; t)\, d^{3N}q\, d^{3N}p}$$

physical quantity

Stationary ensemble: $\frac{\partial \rho}{\partial t} = 0$

In this case, $\langle f \rangle$ is also independent of time!

Liouville's theorem:

continuity of representative points →

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \underbrace{[\rho, H]}_{\sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right)} = 0$$

$\frac{\partial \rho}{\partial t} = 0$ can come from $[\rho, H] = 0$

↓

ρ is independent of t, q, p

So, the points are 'uniformly' distributed in the allowed region of phase space. → PEAP (Postulate of equal apriori probability)

$$\langle f \rangle = \frac{1}{\omega} \int_{\omega} f(p,q)\, d\omega$$

↓

Property of microcanonical ensemble!

Another way of making $\frac{\partial \rho}{\partial t} = 0$ is $\rho(q,p) = \rho[H(q,p)]$
(explicit dependence of ρ on H) ⇒ $[\rho, H] = 0$

$$\rho(q,p) \propto \exp\left[-H(q,p)/kT\right]$$ (one choice)

↓

Canonical ensemble.

Microcanonical Ensemble:

Macrostate is defined by : $N, V, E \longrightarrow$ b/w $E \pm \frac{1}{2}\Delta$

Volume of the phase space : $\omega = \int d\omega = \int (d^{3N}q\, d^{3N}p)$

The density function: $\rho(q,p) = \text{constant}$ if $H \in (E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$

$= 0$ elsewhere

$\langle f \rangle =$ expectation value of f

$\Gamma = \omega / \omega_0$

multiplicities of the microstates accessible to the system

$\omega_0 \longrightarrow$ fundamental volume (vol^m equivalent to one microstate)

$S = k \ln \Gamma = k \ln (\omega / \omega_0)$ [But what is ω_0?]

Eg. Classical ideal gas : monoatomic particles

$$\omega = \underbrace{\int \cdots \int}_{} (d^{3N}q\, d^{3N}p)$$

(i) Within volume V.

(ii) E is within $(E - \frac{1}{2}\Delta)$ and $(E + \frac{1}{2}\Delta)$

In this case $H = H(p_i)$. (independent of q)

So, $\int \cdots \int d^{3N}q = V^N$

The remaining integral →

$$\underset{(E-\frac{1}{2}\Delta) \le \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m}\right) \le (E+\frac{1}{2}\Delta)}{\int \cdots \int} d^{3N}p \;=\; \underset{2m(E-\frac{1}{2}\Delta) \le \sum_{i=1}^{3N} y_i^2 \le 2m(E+\frac{1}{2}\Delta)}{\int \cdots \int} d^{3N}y$$

"hypershell of dim 3N bounded by hyperspheres of radius $\sqrt{2m(E-\frac{1}{2}\Delta)}$ and $\sqrt{2m(E+\frac{1}{2}\Delta)}$"

Under the condition $\Delta \ll E$, the integral takes the form:

$$\Delta \left(\frac{m}{2E}\right)^{1/2} \left\{ \frac{2\pi^{3N/2}}{\left[\frac{3N}{2}-1\right]!} (2mE)^{(3N-1)/2} \right\}$$

So, $$\omega = \frac{\Delta}{E} V^N \frac{(2\pi m E)^{3N/2}}{[(3N/2)-1]!}$$

In the asymptotic limit →

$$\Sigma(N,V,E) = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}$$

$$\Gamma'(N,V,E;\Delta) = \frac{3N}{2}\frac{\Delta}{E}\,\Sigma(N,V,E)$$

→ ~~[illegible]~~ chapter 1.4 ~~[illegible]~~

We get $(\omega/\Gamma)_{asym} = \omega_0 = h^{3N}$

For a system with $\mathcal{N}$ dof $\omega_0 = h^{\mathcal{N}}$

For the case of SHO →

$$H(q,p) = \frac{1}{2}Kq^2 + \frac{1}{2m}p^2$$

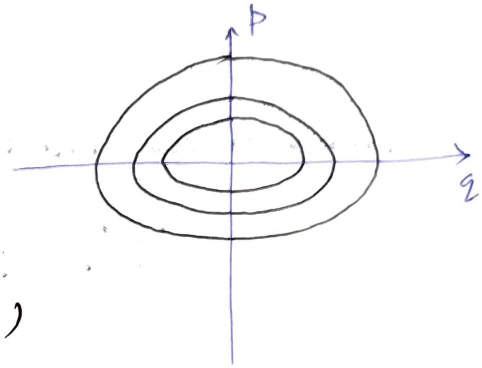
K → spring constant

m → mass

$H(q,p)$ → Function of both q and p.

$$q = A\cos(\omega t + \phi) \qquad p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

$$\omega = \sqrt{\frac{K}{m}}$$



$$E = \frac{1}{2}m\omega^2 A^2$$

A → amplitude

E → energy (constant of motion)

$$\frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{(2mE)} = 1$$

→ phase-space trajectory for energy E.

→ Ellipse with area $\frac{2\pi E}{\omega}$

For the condition $E - \frac{1}{2}\Delta \leq H(q,p) \leq E + \frac{1}{2}\Delta$ →

$$\iint dp\,dq = \frac{2\pi(E + \frac{1}{2}\Delta)}{\omega} - \frac{2\pi(E - \frac{1}{2}\Delta)}{\omega} = \underbrace{\frac{2\pi\Delta}{\omega}}_{\text{The allowed volume in the phase-space.}}$$

In quantum mechanics, the energy →

$$E_n = (n + \tfrac{1}{2})\hbar\omega \;;\; n = 0, 1, 2 \ldots$$

The area b/w two consequtive trajectories ($\Delta = \hbar\omega$) is $2\pi\hbar$.

For arbitrary case $E \gg \Delta \gg \hbar\omega \Rightarrow$

# of eigenstates with Δ is $\frac{\Delta}{\hbar\omega}$.

So, $$\omega_0 = \frac{(2\pi\Delta/\omega)}{\left(\frac{\Delta}{\hbar\omega}\right)} = 2\pi\hbar = h \quad (= h^N \text{ for } N \text{ SHOs})$$

↳ volume of equivalent to one eigenstate!

Quantum states and Phase space:

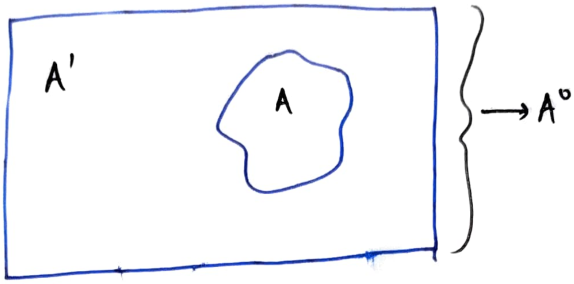
$(\Delta q\, \Delta p)_{min} \sim \hbar$ ↦ dividing the ~~cells~~ phase-space in cells of size $\hbar$ for 2D case.

Canonical Ensemble:

Macrostate: defined by N, V, T

$\hookrightarrow$ maintained constantly by a 'reservoir'.

System and Reservoir $\rightarrow$ (Not ensemble yet)



Total energy = $E^{(0)}$

At any particular time t $\rightarrow$ $\underbrace{E_r}_{\text{system}} + \overbrace{E_r'}^{\text{Reservoir}} = E^{(0)}$

Also, $$\frac{E_r}{E^{(0)}} = \left(1 - \frac{E_r'}{E^{(0)}}\right) \ll 1$$

Fix system energy $\rightarrow E_r \longrightarrow$ The reservoir energy $\rightarrow E_r'$

The number of microstates that allows the reservoir to have E_r' $\rightarrow \Omega'(E_r')$

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

Expanding around $E_r' = E^{(0)}$

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

$$= \text{const} - \beta' E_r$$

$$\longrightarrow \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \beta$$

In equilibrium, $\beta' = \beta = \frac{1}{kT}$

So, $P_r \propto \exp(-\beta E_r)$

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

System in canonical ensemble →

N identical systems shares a total energy E.

E_r → the energy eigenstates ($r = 0, 1, 2 \ldots$)

Conditions →

$$\sum_r n_r = N$$

n_r → # of systems with energy E_r

$$\sum_r n_r E_r = E = NU$$

U → average energy per system in ensemble.

we can reshuffle and make distinct ways to satisfy the condition.

# of ways → $W\{n_r\} = \frac{N!}{n_0! n_1! n_2! \cdots}$

→ # of times one set $\{n_r\}$ can occur!

so, 'most probable' mode is the one where W is max.

we call this n_r^* → this is the important one.

Expectation value of n_r → $\langle n_r \rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}}$

$\sum'$ → only the sets which follows the condition.

Showing $\frac{\langle n_r \rangle}{N}$ and $\frac{n_r^*}{N}$ are identical.

Now we get P_r from ensemble perspective!

$$\ln W = \ln(N!) - \sum_r \ln(n_r!)$$

As we take very large N ($\to \infty$), we take Stirling's formula,

$$\ln W = N \ln N - \sum_r n_r \ln(n_r)$$

So, we shift to a slightly different set from $\{n_r\} \to \{n_r + \delta n_r\}$

So, $$\underbrace{\delta(\ln W)}_{\text{This should vanish if } n_r \text{ is maximal}} = -\sum (\ln n_r + 1)\,\delta n_r$$

Also, δn_r should also follow $\to$

$$\sum_r \delta n_r = 0$$

$$\sum_r E_r \delta n_r = 0$$

Now using Lagrange's undetermined multiplier $\to$

$$\sum_r \underbrace{\{-(\ln n_r^* + 1) - \alpha - \beta E_r\}}_{\text{This should vanish}} \underbrace{\delta n_r}_{\text{arbitrary}} = 0$$

$$\ln n_r^* = -(\alpha + 1) - \beta E_r$$

$$\Rightarrow n_r^* = \underbrace{c}_{\exp(-\alpha - 1)} \exp(-\beta E_r)$$

$$N = \sum_r n_r^* = c \sum_r \exp(-\beta E_r)$$

So, $$\frac{n_r^*}{N} = \frac{\exp(-\beta E_r)}{\sum \exp(-\beta E_r)}$$

β is the solⁿ of the eqⁿ: $\dfrac{E}{N} = U = \dfrac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$

Connecting macroscopic with microscopic:

$$P_r = \frac{\langle n_r \rangle}{N} = \frac{n_r^*}{N} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$$ → Canonical distribution

β is determined by →

$$U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = -\frac{\partial}{\partial \beta} \ln \left[\sum_r \exp(-\beta E_r) \right]$$

Helmholtz free energy → $A = U - TS$

$$dA = dU - TdS - SdT = -SdT - PdV + \mu dN$$

Compare!

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}, \quad P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$$

$$= \left(\frac{\partial (A/T)}{\partial (1/T)}\right)_{N,V}$$

$$= \frac{\partial}{\partial (1/kT)} \left(\frac{A}{kT}\right)_{N,V}$$

$$\beta = \frac{1}{kT} \quad , \quad \ln\left[\sum_r \exp(-\beta E_r)\right] = -\frac{A}{kT}$$

→ matches with the A + A′ thing

Can express → $A(N,V,T) = -kT \ln \underbrace{Q_N(V,T)}$

→ $\sum_r \exp(-E_r/kT)$ → partition function

Once we know A, S, P and μ can be calculated from previous relations.

specific heat at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}$$

Gibbs free energy

$$G = A + PV = \underbrace{A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu}$$

⊛ will come to this later.

Expression of pressure:

$$P = -\frac{\sum_r \frac{dE_r}{dV}\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$$

↓

Can happen through change in Vol^n

$$P\,dV = -\sum P_r\,dE_r = -dU$$

driving force

Probability change in is unchanged energy eigen value

change in average energy of a system.

Entropy of a system:

$$P_r = q^{-1} \exp(-\beta E_r)$$

$$\underbrace{\langle \ln P_r \rangle}_{\text{ensemble average}} = -\ln q - \beta \langle E_r \rangle = \beta(A-U) = -S/k$$

$$S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r$$ → entropy depends only on probabilities.

→ (1) At ground state ($T=0$), if the ground state is unique, then $P_0 = 1$, $P_{\neq 0} = 0$.
∴ $S = 0$

→ (2) As # of states become large, $P_r \ll 1$.
So $\ln P_r$ is large -ve values, so $S \uparrow\uparrow$.

Connection with microcanonical ensemble →

For each member system of enesemble, a group of equally likely Ω states are there. So $P_r = \frac{1}{\Omega}$ for these states, 0 for all other states.

$$S = -k \sum_{r=1}^{\Omega} \left\{ \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) \right\} = k \ln \Omega$$

Alternative (Continuous) expression for partition function:

If there ~~are~~ is any degeneracy, i.e, there are g_i number of states belonging to the same energy level E_i then

$$Q_N(V,T) = \sum_i g_i \exp(-E_i/kT)$$

weight factor

Probability

$$P_i = \frac{g_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)}$$

If there are a large # of energy states, then,

$$P(E)\,dE \propto \exp(-\beta E)\, g(E)\, dE$$

density of states around the energy E.

$$\Rightarrow P(E)\,dE = \frac{\exp(-\beta E)\, g(E)\, dE}{\int_0^\infty \exp(-\beta E)\, g(E)\, dE}$$

probability that a given system of an ensemble has energy b/w E and E+dE

another expression for partition function.

Expectation value of a physical parameter f,

$$\langle f\rangle = \sum_i f_i P_i = \frac{\sum_i f_i \cancel{\exp}(E_i)\, g_i \exp(-\beta E_i)}{\sum_i g_i \exp(-\beta E_i)} = \frac{\int_0^\infty f(E)\, e^{-\beta E}\, g(E)\, dE}{\int_0^\infty e^{-\beta E}\, g(E)\, dE}.$$

The Classical Systems:

From the phase-space perspective.

$$\langle f \rangle = \frac{\int f(p,q)\, \rho(p,q)\, d^{3N}q\, d^{3N}p}{\int \underbrace{\rho(q,p)}_{} d^{3N}q\, d^{3N}p}$$

density of the representative points in the phase-space!

In canonical ensemble,

$$\rho(q,p) \propto \exp\left[-\beta H(q,p)\right]$$

$d^{3N}q\, d^{3N}p$

$$\langle f \rangle = \frac{\int f(q,p) \exp(-\beta H)\, d\omega}{\underbrace{\int \exp(-\beta H)\, d\omega}_{}}$$

has some relation with partition function

$$d\omega \rightarrow \frac{d\omega}{N!\, h^{3N}}$$

$d\omega$ vol^n is phase space corresponds to $\frac{d\omega}{N!\, h^{3N}}$ distinct quantum states.

partition function $\rightarrow$ $Q_N(V,T) = \frac{1}{N!\, h^{3N}} \int e^{-\beta H(q,p)}\, d\omega$

The next ~~st~~ step is to apply this formalism to a classical system!

Eg → ideal gas → monoatomic, contained in Vol^n V, equilibrium temp T.

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

Partition function →

$$Q_N(V,T) = \frac{1}{N!\, h^{3N}} \int e^{-(\beta/2m)\sum_i p_i^2} \prod_{i=1}^{N} (d^3q_i\, d^3p_i)$$

This integration just gives us V^N.

$$Q_N(V,T) = \frac{V^N}{N!\, h^{3N}} \left[\int_0^\infty e^{-p^2/2mkT} (4\pi p^2 dp) \right]^N$$

$$Q_N(V,T) = \frac{1}{N!} \left[\frac{V}{h^3} (2\pi mkT)^{3/2} \right]^N$$

Helmholtz free energy →

$$A(N,V,T) = -kT \ln Q_N(V,T) = NkT \left[\ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right] - 1 \right]$$

↳ Once we have this, it's open game!

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T} = kT \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right]$$

$$P = -\left(\frac{\partial A}{\partial V} \right)_{N,T} = \frac{NkT}{V}$$

equating this to PV = nRT, one can obtain the value of k as well!

$$S = -\left(\frac{\partial A}{\partial T} \right)_{N,V} = Nk \left[\ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right]$$

Also,

$$U = -\left[\frac{\partial}{\partial\beta}(\ln Q)\right]_{E_r}$$

$$= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$$

$$= A + TS = \frac{3}{2}NKT$$

How to get the density of states?

So we know,

$$Q_N(V,T) = \int_0^\infty e^{-\beta E} g(E)\, dE$$

For $\beta > 0$, $Q(\beta)$ is just a Laplace transformation of $g(E)$.

$$g(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E} Q(\beta)\, d\beta \qquad (\beta' > 0)$$

$$\beta = \beta' + i\beta''$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{(\beta'+i\beta'')E}\, Q(\beta'+i\beta'')\, d\beta''$$

In this case,

$$g(E) = \frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{3N/2} \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}}{\beta^{3N/2}}\, d\beta \qquad (\beta' > 0)$$

Now for all positive n values →

$$\frac{1}{2\pi i}\int_{s'-i\infty}^{s'+i\infty} \frac{e^{sx}}{s^{n+1}}\, ds = \begin{cases} \dfrac{x^n}{n!} & \text{for } x \geq 0 \\ 0 & \text{for } x \leq 0 \end{cases}$$

So,

$$g(E) = \begin{cases} \dfrac{V^N}{N!}\left(\dfrac{2\pi m}{h^2}\right)^{3N/2} \dfrac{E^{(3N/2)-1}}{[(3N/2)-1]!} & E \geq 0 \\ 0 & E \leq 0 \end{cases}$$

A good way of getting the density of states.

⊛ Later if possible will make a comparison b/w the three ensembles. (Probably Not Today :))

A system of Harmonic Oscillators :

Classical first → $H(q_i, p_i) = \frac{1}{2} m\omega^2 q_i^2 + \frac{1}{2m} p_i^2 \qquad (i = 1, \dots N)$

one oscillator partition function

$$Q_1(\beta) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-\beta\left(\tfrac{1}{2} m\omega^2 q^2 + \tfrac{1}{2m} p^2\right)\right] \frac{dq\,dp}{h}$$

$$= \frac{1}{h}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{1}{\beta\hbar\omega} = \frac{kT}{\hbar\omega}$$

N-oscillator partition function

$$Q_N(\beta) = [Q_1(\beta)]^N = (\beta\hbar\omega)^{-N} = \left(\frac{kT}{\hbar\omega}\right)^N ;$$

Thermodynamic properties

$$A = -kT \ln Q_N = NkT \ln\left(\frac{\hbar\omega}{kT}\right)$$

This whole thing can be derived from CE considerations

$$\mu = kT \ln\left(\frac{\hbar\omega}{kT}\right)$$

$$P = 0$$

$$S = Nk\left[\ln\left(\frac{kT}{\hbar\omega}\right) + 1\right]$$

$$U = NkT$$

$$C_p = C_v = Nk$$

Density of states:

$$g(E) = \frac{1}{(\hbar\omega)^N}\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}}{\beta^N}\, d\beta \quad (\beta' > 0)$$

$$\Rightarrow \quad g(E) = \begin{cases} \dfrac{1}{(\hbar\omega)^N}\dfrac{E^{N-1}}{(N-1)!} & \text{for } E \geq 0 \\ 0 & \text{for } E \leq 0 \end{cases}$$

~~[illegible]~~ Quantum HO →

$$\varepsilon_n = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2 \ldots$$

Single Oscillator partition function

$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = \frac{\exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - \exp(-\beta\hbar\omega)}$$

$$= \left\{2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right\}^{-1}$$

N-oscillator partition function

$$\mathcal{Q}_N(\beta) = [\mathcal{Q}_1(\beta)]^N$$

$$= \left[2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right]^{-N}$$

$$= e^{-(N/2)\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

Other thermodynamic quantities →

These things can be obtained using thermodynamic relations.

$$A = NkT\ln\left[2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right]$$

$$= N\left[\tfrac{1}{2}\hbar\omega + kT\ln\left[1-e^{-\beta\hbar\omega}\right]\right]$$

$$\mu = \frac{A}{N}$$

$$P = 0$$

For $kT \gg \hbar\omega$, all these go back to the usual one.

$$S = Nk\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

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

$$C_P = C_V = Nk(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

[redacted], [redacted], [redacted].

Grand Partition function →

$$\mathcal{Z}(\mu, V, T) = \sum_{i} \exp\left(\frac{N_i \mu - E_i}{k_B T}\right)$$

$$= \sum_{N_i} \underbrace{z^{N_i}}_{\text{Fugacity / activity.}} \underbrace{Z(N_i, V, T)}_{\text{Canonical Partition function.}}$$