Central limit Theorem:

$g(x)$ = distribution

$g(x)dx$ = probability on any particular trial to get $x$ between $x$ and $x+dx$.

$$\langle x \rangle_N = \frac{1}{N}\sum_{i=1}^{N} x_i \quad \text{with}$$

$$p(\langle x \rangle_N) = \frac{1}{\sqrt{\sigma_1^2/N}\sqrt{2\pi}} \exp\left\{\frac{-(\langle x \rangle_N^2 - \bar{x}^2)}{2\sigma_1^2/N}\right\} \quad \text{for } N \to \infty$$

where
$$\bar{x} = \int dx\, g(x)\, x$$
$$\sigma_1^2 = \int dx\, (x-\bar{x})^2 g(x)$$
$$\sigma_N^2 = \frac{\sigma_1^2}{N} \Rightarrow \sigma_N = \frac{\sigma_1}{\sqrt{N}}$$

Consider an ensemble of systems in different microstates corresponding to the same macro (i.e. thermo) variables, i.e. $(N, V, E)$

$\boxed{N, V, E}$ . . . . . . . . . . $\boxed{N, V, E}$

State 1 . . . State $\Omega$

there are $\Omega$ # of systems.

$$\langle G \rangle = \frac{1}{\Omega} \sum_i G_i$$

some observable

## Ergodic Hypothesis:

time average of 1 system

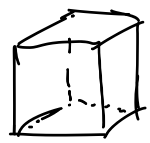
$$\langle G \rangle = \langle G \rangle_t$$

ensemble

$$\langle G \rangle_t = \frac{1}{\Omega} \sum_i G_i = \langle G \rangle$$

probability

1 particle in a box:



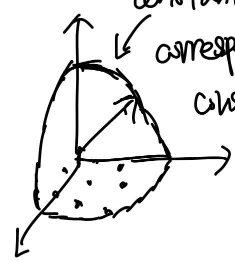
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$$

$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

$$\varepsilon = \frac{\hbar^2|\vec{k}|^2}{2m}$$

$$\vec{k} = \frac{n_x\pi}{L}\hat{e}_x + \frac{n_y\pi}{L}\hat{e}_y + \frac{n_z\pi}{L}\hat{e}_z$$

$$\varepsilon = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)$$




$$g(\varepsilon)d\varepsilon = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}d\varepsilon$$

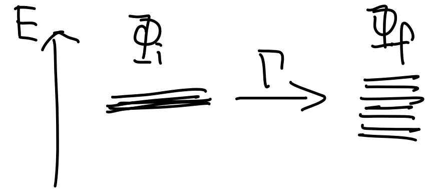
For N particles in box:

$$E = \varepsilon_1 + \cdots + \varepsilon_N$$

$$\overset{!}{=} \frac{\hbar^2}{2mV^{2/3}}\left(n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + \cdots n_{Nx}^2 + n_{Ny}^2 + n_{Nz}^2\right)$$

total DoS $= \bar{\Omega}(E) = \left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\Gamma\left(\frac{3N}{2}\right)}\right)^{3N/2} E^{\left(\frac{3N}{2}-1\right)}$

Fermi's Golden Rule:




$$W_{f\leftarrow i} = \frac{2\pi}{\hbar} \underbrace{\left|\langle \Phi_f | \hat{H} | \Phi_i \rangle\right|^2}_{\text{perturbation Matrix Element}} \bar{\Omega}(E)$$

DoF

For 1000 atoms in box

to stay $\Phi_i$ for 1 second (coherent)

$$\left|\langle \Phi_f | \hat{H} | \Phi_i \rangle\right|^2 \leq \frac{\hbar}{2\pi} \frac{1}{\Omega} \Gamma \approx 10^{-27,316} \text{ eV}$$

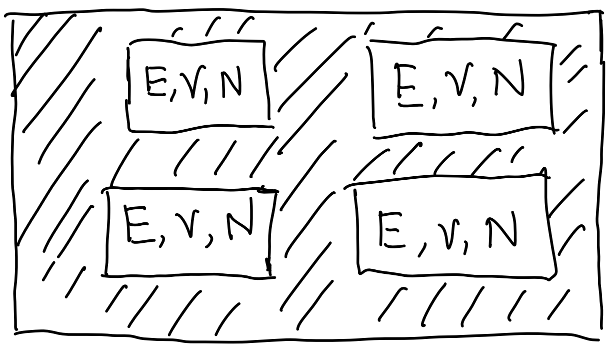
but $V_{grav} \cong 10^{-22}$ eV for two argon atoms far away.

which is greater than $\left|\langle \Phi_f | \hat{H} | \Phi_i \rangle\right|^2$. So it's impossible to stay in 1 state.

Ensembles: a collection of large # of microscopically but essential independent systems

Microcanonical Ensemble:

The microcanonical assemble is a collection of essentially independent assemblies having the same E, V, and N. Individual systems of microcanonical ensemble are separated by rigid, impermeable and insulated walls. So E, V, N are not affected by other system.

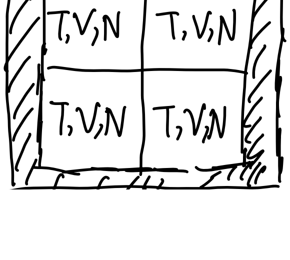



All microstates corresponding to a particular E, V, N are equal likely.

But all Macrostates are not equal likely and are well defined.

Canonical Ensemble: Assemblies with the same T, V, N. The disparate systems are separated by rigid, impermeable, but conducting walls.

Since energy can be exchanged, systems reach a common T.

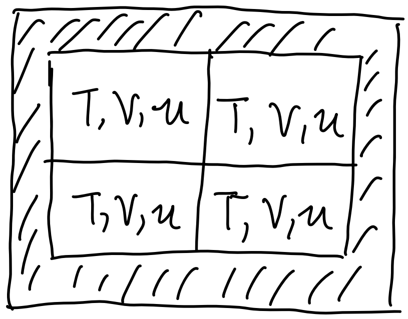



← Exchange energy but not particle.

## Grand Canonical Ensemble:

Independent Assemblies having the same $T, V, \mu$.

The individual system of grand canonical ensemble are separated by rigid, permeable, and conducting walls.



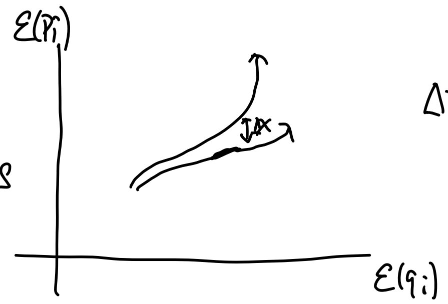

Exchange both energy and particle.

HW# 11-14.

Classical Argument:

Chaos:

A very close initial conditions lead to very different result.




$$\Delta X = \varepsilon e^{\lambda_i t}$$

$\lambda_i$ ← Lyapov Exponent

$\lambda_i < 10^{-12} s$

## Ergodic Principle:

$$\langle G \rangle_t = \sum_i P_i G_i$$

observable.

$\sum_i$: all states corresponding to constraint.

$P_i$: microstate probability

Consider a system with M degrees of freedom

each DoF:

$$g(\varepsilon) = \beta \varepsilon^{\alpha - 1}$$

$\alpha \sim 1$

single DoF

energy in DoF

# of states with energy less than $\varepsilon$

$$\Phi_1 = \int_0^{\varepsilon} \partial \varepsilon' \, g(\varepsilon') = C \varepsilon^{\alpha}$$

$$\Phi_M(E) \approx \left[\Phi_1(\varepsilon)\right]^M$$

# of states w/ energy less than E for M-DoF system

$E \approx M \varepsilon$

single DoF energy

$$\Omega_M(E) = \left(\frac{\partial \Phi_M}{\partial E}\right)_{\vec{x}} \delta E$$

$$= M(\Phi_1)^{M-1} \frac{\partial \Phi_1}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial E} \delta E$$

$$= M(\Phi_1)^{M-1} \left(\frac{\alpha \Phi_1}{\varepsilon}\right)\left(\frac{1}{M}\right) \delta E$$

$E = M\varepsilon$

$$= M(\Phi_1)^M \frac{\delta E}{E}$$

$$= C^M \left(\frac{E}{M}\right)^{\alpha M} \frac{M \delta E}{E}$$

$$\approx C^M \left(\frac{E}{M}\right)^{\alpha M}$$

$$\boxed{\Omega(E) = \bar{\Omega}_M(E)\,\delta E}$$

$\bar{\Omega}_M$: state density $\qquad$ $\Omega(E)$: total # of states

| $E_1$ | $E_2$ |
|---|---|

$$\Omega = \Omega(E_1)\,\Omega(E_2)$$

$$= \Omega(E_1)\,\Omega(E - E_1)$$

$E = E_1 + E_2$

$$= \Omega_{\frac{M}{2}}(E_1)\,\Omega_{\frac{M}{2}}(E - E_1)$$

since $S(E, \vec{x} | Y) < S(E, \vec{x})$ and $\Omega(E, \vec{x} | Y) < \Omega_{max}$.

implies: $\underline{S = f(\Omega)}$

2nd law:

1) $\left(\frac{\partial S}{\partial E}\right)_{\vec{x}} > 0$ $\qquad \Leftrightarrow \quad \frac{\partial \Omega}{\partial E} > 0$ and $\frac{\partial f}{\partial E} > 0$ so it matches.

2) $S$ is extensive $\qquad S = S_1 + S_2$

$\boxed{S_1}$ ($\Omega_1$) $\qquad \boxed{S_2}$ ($\Omega_2$) $\rightarrow$ $\boxed{S_1 + S_2}$ ($\Omega_1 \Omega_2$) $\Rightarrow f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$

this function can only be a log function.

So $f = C \ln \Omega$ $\qquad$ let $C = k_B$

$$\boxed{S = k_B \ln \Omega}$$

$$k_B = 1.380649 \times 10^{-23}\ \mathrm{J/K}$$

with $\Omega(E) = \bar{\Omega}(E)\,\delta E$ # of states between $E$ and $E + \delta E$

$$S = k_B \ln(\Omega(E)) + k_B \ln(\delta E)$$

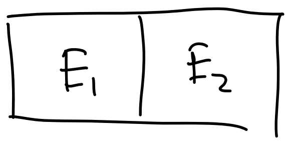
thermo potential

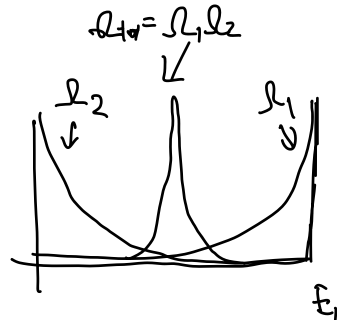
$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad dE = SdT - pdV.$$

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

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

$$\hookrightarrow \frac{1}{k_B T} = \beta = \left(\frac{\partial}{\partial E} \ln \Omega\right)_{N,V}$$

for 


Find the E such that $\Omega$ is max?

$$\frac{\partial}{\partial E_1}\Omega = 0$$

$$\frac{\partial}{\partial E_1}(\Omega_1\Omega_2) = 0$$

$$E_2 = E - E_1$$

$$\frac{\partial}{\partial E_1} = -\frac{\partial}{\partial E_2}$$

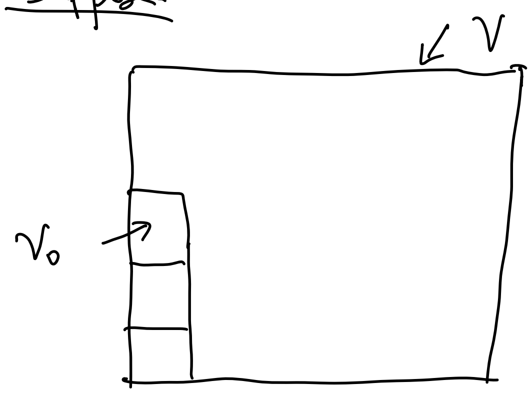
$$\hookrightarrow \frac{\partial}{\partial E_1}(\Omega_1)\Omega_2 + \frac{\partial}{\partial E_1}(\Omega_2)\Omega_1$$

$$\frac{1}{\Omega_1\Omega_2}\left[\Omega_2 \frac{\partial\Omega_1}{\partial E_1} - \Omega_1 \frac{\partial\Omega_2}{\partial E_2}\right] = 0$$

$$\frac{1}{\Omega_1}\frac{\partial\Omega_1}{\partial E_1} = \frac{1}{\Omega_2}\frac{\partial\Omega_2}{\partial E_2}$$

$$\boxed{\frac{\partial}{\partial E_1}\ln\Omega_1 = \frac{\partial}{\partial E_2}\ln\Omega_2} \Rightarrow \frac{1}{k_B T_1} = \frac{1}{k_B T_2}$$

Suppose:




For 1 particle, $\frac{V}{V_0}$ choices in each box.

For N particles: assume no correlation between ideal gas laws

$$\Omega \propto \left(\frac{V}{V_0}\right)^N$$

$$\Omega = C\left(\frac{V}{V_0}\right)^N = C' V^N$$

$$\partial S = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

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

$$\frac{P}{T} = \frac{\partial}{\partial V}\left(k_B \ln\Omega\right)_{E,N}$$

$$\stackrel{!}{=} \left(\frac{\partial}{\partial V} k_B \ln(C' V^N)\right)_{E,N}$$

$$\stackrel{!}{=} \frac{\partial}{\partial V}\left(N k_B \ln V + \underbrace{\cancel{k_B \ln C'}}_{\text{const}}\right)_{E,N}$$

$$\frac{P}{T} \stackrel{!}{=} \frac{N k_B}{V}$$

$$\hookrightarrow \boxed{PV = N k_B T}$$ ideal gas law.