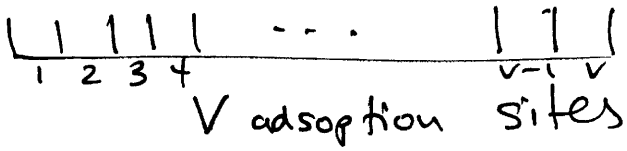
Counting States

Useful to review combinatorial relationships - e.g.

N particles



How many states Ω?

(a) Only one particle allowed on a site, particles are identical [must have $V \geq N$)

$$\Omega_a = \binom{V}{N} = \frac{V!}{(V-N)!\,N!}$$

(b) Only one particle per site, particles have unique labels (colors) ; 1, 2, .. N -
There are N! possible orderings of N particles,
So that $\Omega_b = N!\,\Omega_a = \frac{V!}{(V-N)!}$

(c) Any number of particles can go on a site, particles have unique labels (colors)

$$\Omega_c = V^N$$

(d) Any number of particles can go on a site, particles are identical

$$\Omega_d = \frac{(N+V-1)!}{N!\,(V-1)!}$$ [Proof: Problem 2.2]

MICROSCOPIC VIEW OF ENERGY

Time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + u(\vec{r})\psi(\vec{r}) = \epsilon\psi(\vec{r})$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$ Laplacian in Cartesian Coordinates

$\hbar = h/2\pi$ reduced Planck's constant

$\psi^*\psi$ gives the probability of finding particles (electrons, nuclei, etc) at $\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N$

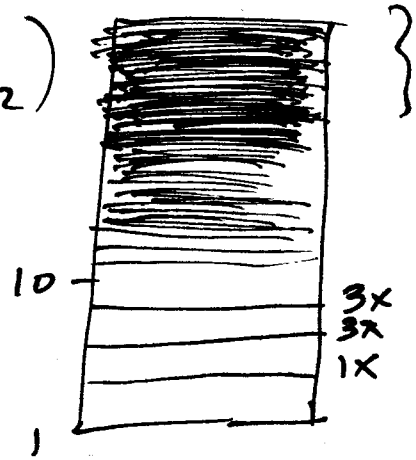
In compact notation: $\boxed{H\psi(\vec{r}) = E\psi(\vec{r})}$

where $H = -\frac{\hbar^2}{2m}\nabla^2 + u(\vec{r})$

E takes on discrete values (eigenvalues) $E_1, E_2, \ldots$

e.g. Particle-in-box between 0 and L,

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \quad n_i = 1, 2, \ldots \infty$$

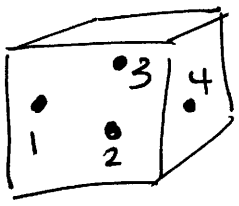


} more closely spaced at higher energies

Quantum effects important for
- low T
- low m (e.g., H)
- Chemistry

Classical picture

Particles (atoms) have well-defined positions + velocities (momenta)



$\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N$

$\vec{p}_1, \vec{p}_2 \ldots \vec{p}_N$ $\quad \vec{p}_i = m_i \vec{v}_i$

$\vec{p}_i$: momentum; $\vec{v}_i$: velocity

Potential energy function $U(\vec{r}^N)$

$$\vec{f}_i = -\nabla_i U(\vec{r}^N) = -\frac{\partial U(\vec{r}^N)}{\partial \vec{r}_i} \quad \text{(forces)}$$

$$\frac{\partial \vec{p}_i}{\partial t} = -\frac{\partial U(\vec{r}^N)}{\partial \vec{r}_i} \quad \text{(Newton's Law)}$$

Classical Hamiltonian is a constant of motion

$$H(\vec{p}^N, \vec{r}^N) = U(\vec{r}^N) + K(\vec{p}^N)$$
$$= U(\vec{r}^N) + \sum_i \frac{\vec{p}_i^2}{2m_i}$$

$U(\vec{r}^N)$

- non-bonded (intermolecular) interactions
  - Coulombic $u_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$
  - dispersion + repulsion $u_{ij} = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)$
- bonded (intramolecular)
  - bond stretching $u = a(d-d_0)^2$
  - bond bending $u = b(\theta-\theta_0)^2$
  - bond torsions $u = \sum_n C_n \cos\omega^n$

Intermolecular forces are short-ranged - a requirement for the existence of extensive properties

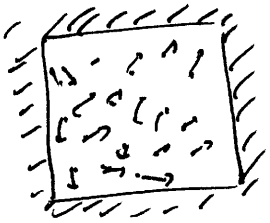
Microstates, Ensembles

Microscopic State (classical) — $3N$ positions $\vec{r}^N$: $x_1, y_1, z_1, \ldots x_N, y_N, z_N$

$6N$ degrees of freedom — $3N$ momenta $\vec{p}^N$: $p_{x_1}, p_{y_1}, p_{z_1}, \ldots p_{x_N}, p_{y_N}, p_{z_N}$

A "microstate" is a configuration of the system, with positions and velocities within a small range

"Ensembles" are collections of microstates compatible with the external constraints imposed on a system - e.g. given E, V, N



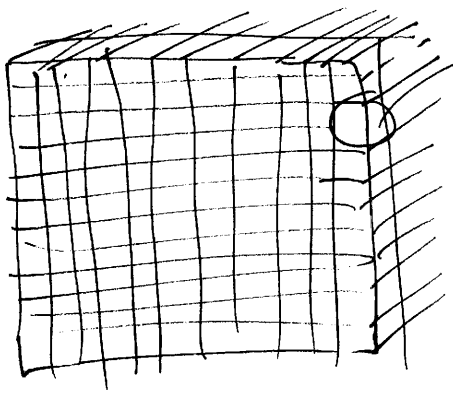
← Isolated system, rigid, impermeable walls → many microstates, only a single "macrostate"

Counting of microstates: ideal gas

for an ideal gas, $\mathcal{U}(\vec{r}^N) = 0$ (no interactions)

$$E = K(\vec{p}^N)$$

$$\Omega(E,V,N) = \Omega_{\text{momenta}}(E,N) \times \Omega_{\text{positions}}(V,N)$$



volume elements for discretizing positions $v \to 0$ so that at most 1 molecule in any of them ($\rho \to 0$)

$$\Omega_{\text{positions}}(V,N) = \left(\frac{V}{v}\right)^N \cdot \frac{1}{N!}$$

molecules are not distinguishable

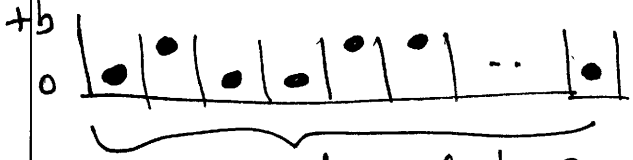
Stirling's approx: $N! \simeq \left(\frac{N}{e}\right)^N$

$$S = k_B \ln \Omega = k_B \ln \Omega_{\text{momenta}} + N k_B \ln\left(\frac{V}{N}\right) + N k_B \ln\left(\frac{e}{\nu}\right)$$

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

$$\boxed{PV = N k_B T}$$

Counting of microstates: 2-state model



$\varepsilon_i = 0$ or b $\qquad E = \sum_i \varepsilon_i = Mb$

M = # of particles in excited state

$$\Omega(E,N) = \frac{N!}{M!(N-M)!}$$

$$S = k_B \ln \Omega = N \ln N - \cancel{N} - M \ln M + \cancel{M} - (N-M)\ln(N-M) + \cancel{N-M}$$

$$= -N \ln \frac{N-M}{N} + M \ln \frac{N-M}{M} \quad \left[\text{set } M/N = x = \frac{E}{Nb}\right]$$

$$= N\left[-\ln(1-x) + x \ln \frac{1-x}{x}\right]$$

Note that entropy is extensive:

$S(\lambda E, \lambda N) = \lambda S(E,N)$ [x does not change]