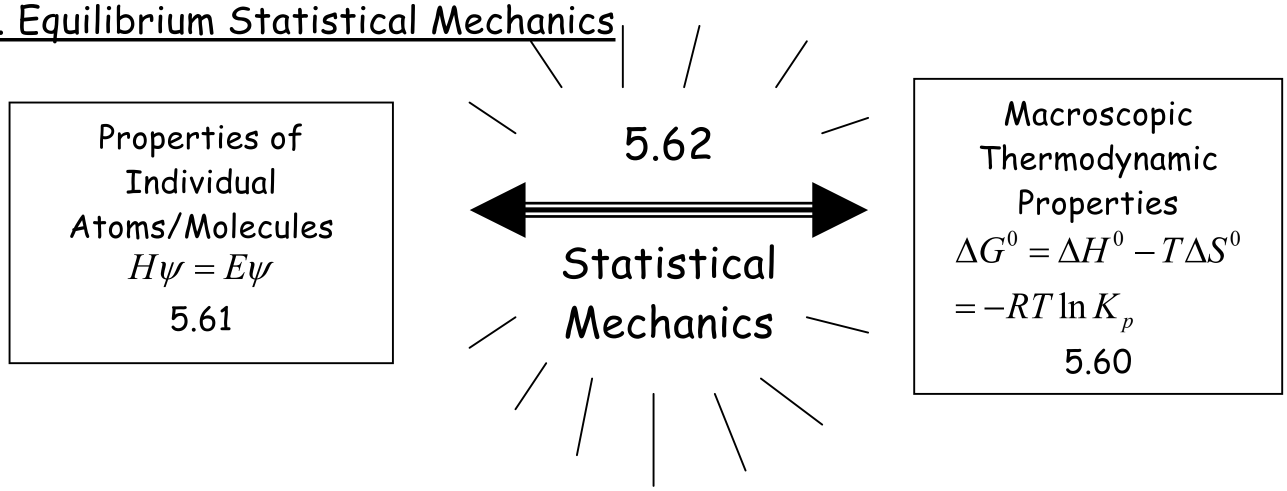
STATISTICAL MECHANICS

Topics covered in 5.62……

I. Equilibrium Statistical Mechanics



II. Intermolecular Forces & Condensed Phases

Modifications of "ideal" results

Properties of solids

III. Kinetic Theory of Gases

Bulk properties from averages over speed distributions

Transport processes, relaxation kinetics

IV. Theory of Reaction Rates

Microscopic properties $\rightarrow$ macroscopic rxn rate

Collision theory - based on kinetic theory

Transition state theory - based on statistical mechanics

Reaction dynamics & potential energy surfaces

<u>Goal of Statistical Mechanics</u>: to describe macroscopic, thermodynamic properties in terms of microscopic atomic & molecular properties

<u>Properties of a gas</u> can be described at two levels:

1) <u>Macroscopic</u> thermodynamic description e.g. *p, V, n,* C_V, *H, A, G*,.....

2) <u>Microscopic</u> description
Specify the state of each molecule!
Use classical or quantum mechanics

a) <u>Classical mechanics</u>: momentum $\vec{\mathbf{p}}$
position $\vec{\mathbf{q}}$ - for *N* particles in the gas

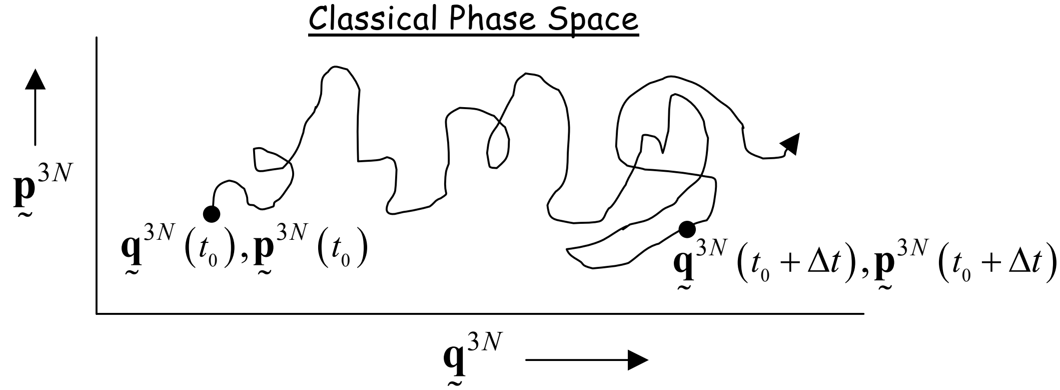
particle 1:	q_{1x}, q_{1y}, q_{1z}	p_{1x}, p_{1y}, p_{1z}
particle 2:	q_{2x}, q_{2y}, q_{2z}	p_{2x}, p_{2y}, p_{2z}
⋮	⋮	⋮
particle *N*:	q_{Nx}, q_{Ny}, q_{Nz}	p_{Nx}, p_{Ny}, p_{Nz}
total *N* particles	total 6*N* degrees of freedom	

Could define $\underset{\sim}{\mathbf{q}}^{3N}, \underset{\sim}{\mathbf{p}}^{3N}$ - generalized coordinate & momentum vectors
Each vector has 3*N* components for *all* the particle positions or momenta
Macroscopic sample: <u>$N \sim 10^{23}$</u>

We need 6*N* values at any time t_0! New values needed ~ 10^{-14} sec later!

Can represent changing microscopic configuration of the gas by

<u>Classical Phase Space</u>



Each point represents a macroscopic state of the entire system, specified by all $6N$ values of position & momentum coordinates.

As long as energy is conserved, *any* $\underset{\sim}{\mathbf{q}}^{3N}, \underset{\sim}{\mathbf{p}}^{3N}$ is accessible.

<u>"Ergodic"</u> system ≡ has access to all of phase space, all possible configurations

b) <u>Quantum mechanical</u> description – quantum number *n*

$$\begin{array}{ll} \text{particle 1:} & n_{1x}, n_{1y}, n_{1z} \\ \text{particle 2:} & n_{2x}, n_{2y}, n_{2z} \\ \vdots & \quad\vdots \qquad \vdots \\ \text{particle } N\text{:} & n_{Nx}, n_{Ny}, n_{Nz} \end{array}$$

total N particles	total $3N$ degrees of freedom

Either classical or quantum description is impractical. <u>Statistical mechanics</u> describes macroscopic mechanics in <u>statistical</u> terms, i.e. in terms of "average" or "most probable" results.

<u>Development of the statistical mechanics formalism</u>

ASSEMBLY ≡ Collection of a large number (N) of particles

STATE of an assembly ≡ A fully specified set of coordinates of every particle in the assembly – $3N$ values (QM) or $6N$ values (CM)

<u>Quantum description</u>

State is specified by the complete list of quantum numbers, e.g. for two states:

<u>State</u>	n_{1x}	n_{1y}	n_{1z}	n_{2x}	n_{2y}	n_{2z}	$\cdots$	n_{Nx}	n_{Ny}	n_{Nz}
"α"	1	2	1	1	2	1	$\cdots$	1	1	1
"β"	2	1	2	1	1	1	$\cdots$	1	1	1

Note these are <u>assembly</u> states (N particles), *not* molecular states!

E_α ≡ energy of assembly state α

$E_\alpha = \sum_{i=1}^{N} \varepsilon_i$ ≡ energy of assembly state α ε_i ≡ energy of *i*th particle

For translational energy, free particles: $\varepsilon_i = \frac{h^2}{8ma^2}\left(n_{ix}^2 + n_{iy}^2 + n_{iz}^2\right)$

DEGENERACY ≡ $\Omega(E,N)$ ≡ number of distinguishable assembly states whose energy is *E* and # particles is *N*.

Classical description

State is specified by the complete list of position & momentum components

e.g. "α" state has coordinate values $\begin{matrix} p_{1x}\ p_{1y}\ p_{1z}\ p_{2x}\ p_{2y}\ p_{2z}\ \cdots\ p_{Nx}\ p_{Ny}\ p_{Nz} \\ q_{1x}\ q_{1y}\ q_{1z}\ q_{2x}\ q_{2y}\ q_{2z}\ \cdots\ q_{Nx}\ q_{Ny}\ q_{Nz} \end{matrix}$

all specified (continuous variables).

$$E_\alpha = \sum_{i=1}^{N} \varepsilon_i \qquad \varepsilon_i = \left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2\right)/2m$$

System is dynamic! The values are always changing in QM or CM description

Classical: $\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$

Hamiltonian equations of motion (or Lagrangian, or Newton's,....)

Quantum: $i\hbar\frac{\partial}{\partial t}\Psi\left(x_i, y_i, z_i, t\right) = H\Psi\left(x_i, y_i, z_i, t\right)$

Time-dependent Schrödinger equation

Macroscopic properties given by a time average over the microscopic properties

ERGODIC HYPOTHESIS ≡ Time average of the microscopic quantities gives the same macroscopic result as an "ensemble" average!

ENSEMBLE ≡ a collection of all possible states of an assembly – all the states that the assembly would ever reach even in an infinite amount of time.