5.60 Thermodynamics & Kinetics
Spring 2008

STATISTICAL MECHANICS
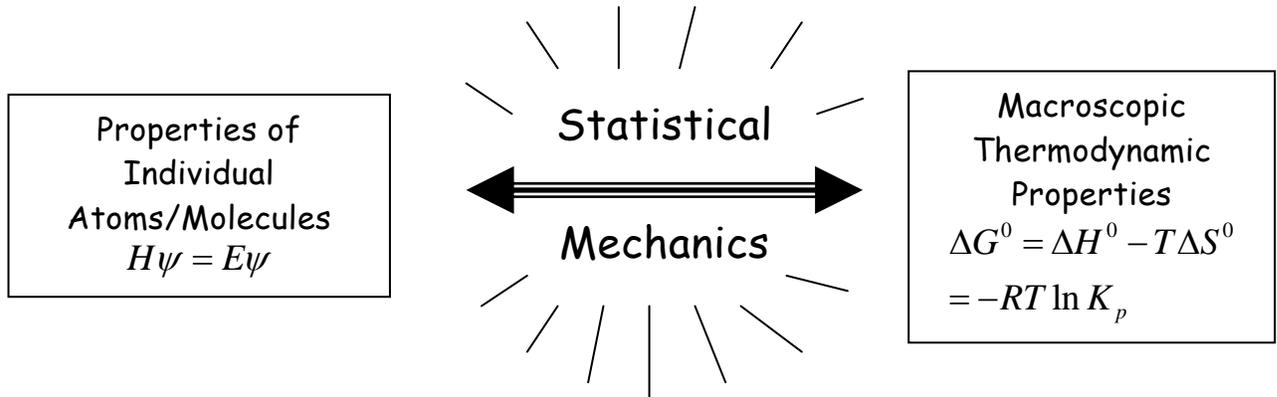
Goal of Statistical Mechanics: to describe macroscopic, thermodynamic properties in terms of microscopic atomic & molecular properties

Properties of a system can be described at two levels:

1) Macroscopic thermodynamic description e.g. p, V, n, C_V, H, A, G,.....

2) Microscopic description
Specify the state of each molecule!
Use classical or quantum mechanics
More than 10^{23} variables! And need to update them every 10^{-15} s or so!

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

Probability of system in a state with given energy

What is functional form?

For independent energies ε_i and ε_j the joint probability should be the product:

   $P_{ij}(\varepsilon_i + \varepsilon_j) = P_i(\varepsilon_i)P_j(\varepsilon_j)$

Suggests exponential form $P_{ij}\left(\varepsilon_i + \varepsilon_j\right)e^{C\left(\varepsilon_i+\varepsilon_j\right)} = e^{C\varepsilon_i}e^{C\varepsilon_j}$ ($C \equiv$ constant)

We expect high-energy states to be less probable than low-energy states, and that they become more probable at high T, i.e. ratio of ε_i to T is what matters.

Suggests form　　$P_i(\varepsilon_i) \sim e^{-C\varepsilon_i/T}$　　($C \equiv$ constant > 0)

Or more conventionally　$\boxed{P_i(\varepsilon_i) \propto e^{-\varepsilon_i/kT}}$　Boltzmann probability distribution

where k = R/N_A = 1.38 x 10^{-16} erg/K is the Boltzmann constant

For two states i and j with energies ε_i and ε_j, the relative probability is

$$\frac{P_i}{P_j} = \frac{e^{-\varepsilon_i/kT}}{e^{-\varepsilon_j/kT}} = e^{-(\varepsilon_i - \varepsilon_j)/kT}$$

To get absolute probabilities (not just relative), write
$$P_i(\varepsilon_i) \propto e^{-\varepsilon_i/kT} = ae^{-\varepsilon_i/kT}$$

Sum of probabilities for all the states must equal 1:
$$\sum_i P_i = 1 = a\sum_i e^{-\varepsilon_i/kT} \qquad \Rightarrow \qquad a = \frac{1}{\sum_i e^{-\varepsilon_i/kT}}$$

$$\Rightarrow \qquad \boxed{P_i = \frac{e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}} \qquad \text{probability of being in state i}$$

For a whole system or assembly of molecules, in a particular system state i (specified by indicating the state of each and every molecule) with energy E_i:

$$\boxed{P_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}}$$

Partition functions

The sums　　$\sum_i e^{-\varepsilon_i/kT} \equiv q$　　　*Molecular partition function*

$\sum_i e^{-E_i/kT} \equiv Q$　　　*Canonical partition function*

measure how probabilities are partitioned among different available states. They are unitless numbers.

Example: perfect atomic crystal lattice at T ≈ 0 K
Set ground state energy $E_0 = 0$
All other state energies $\gg kT \Rightarrow Q \approx 1$

$$P_0 = \frac{e^{-E_0/kT}}{\left(e^{-E_0/kT} + e^{-E_1/kT} + \cdots\right)} \approx \frac{e^{-E_0/kT}}{e^{-E_0/kT}} = 1$$

Example: mole of atoms in the gas phase at room T
Could be treated quantum mechanically (particle in a box states) or classically (continuum of states of different kinetic energy).
Or use "lattice" model: divide available volume into atomic size volume elements
$\sim 1 \text{ Å}^3 = 10^{-30} \text{ m}^3$
If total volume $\sim 1 \text{ m}^3$, then each atom has 10^{30} possible locations
Molecular "translational" partition function is

$$\sum_i e^{-\varepsilon_{i,trans}/kT} = q_{trans} \approx 10^{30}$$

For a system of $N = 10^{24}$ atoms, how many microscopic states?
How many ways to assign atoms to selected locations:
$$\left(10^{30}\right)\left(10^{30}\right)\left(10^{30}\right)\cdots\left(10^{30}\right) = \left(10^{30}\right)^{10^{24}} = 10^{\left(30 \times 10^{24}\right)} = q_{trans}^N$$

Huge number! Number of distinguishable states is less if the particles are indistinguishable: Have to divide by $N! = 10^{24}!$

$$Q_{trans} = q_{trans}^N \qquad \text{distinguishable particles}$$
$$Q_{trans} = q_{trans}^N / N! \qquad \text{indistinguishable particles}$$

Stirling's approximation: $\ln N! \approx N \ln N - N$ or $N! \approx e^{-N} N^N$
So

$$Q_{trans} = \frac{q_{trans}^N}{N!} = \frac{q_{trans}^N}{N^N e^{-N}} = \frac{\left(10^{30}\right)^{10^{24}}}{\left(10^{24}\right)^{10^{24}} e^{-10^{24}}} = \left(10^6\right)^{10^{24}} e^{10^{24}} = \left(10^6\right)^{10^{24}} \left(10^{0.4}\right)^{10^{24}} = 10^{6.4 \times 10^{24}}$$

Smaller, but still huge! So probability for any one system state is incredibly small. The probability is partitioned among a huge number of states.

Example: polymer configurations including protein folding.
e.g. just 4 polymer subunits with some favorable interaction energy $-\varepsilon_{int}$ (e.g. due to H bonding) if non-covalently bonded subunits are in neighboring "lattice" sites:

Molecular state i:

Energy ε_i: $-\varepsilon_{int}$ 0 0 0

Degeneracy g_i: 1 3
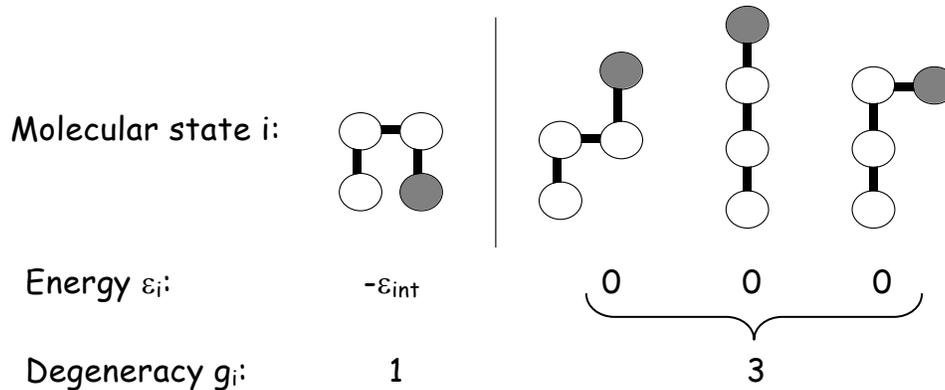
In this simple example, the "configurational" molecular partition function is

$$q_{conf} = \sum_{\substack{microstates \\ i}} e^{-\varepsilon_{i,conf}/kT} = e^{\varepsilon_{int}/kT} + e^{0/kT} + e^{0/kT} + e^{0/kT} = e^{\varepsilon_{int}/kT} + 3e^{0/kT} = e^{\varepsilon_{int}/kT} + 3$$

The last expression suggests writing the partition function as a sum over energy levels ε_i instead of individual states, if we account for their degeneracies g_i:

$$q_{conf} = \sum_{\substack{energies \\ \varepsilon_i}} g_i e^{-\varepsilon_i/kT} = e^{\varepsilon_{int}/kT} + 3e^{0/kT} = e^{\varepsilon_{int}/kT} + 3$$

This can be done for the canonical partition function too, if we account for the degeneracies Ω_i of system energies E_i:

$$Q = \sum_{\substack{states \\ i}} e^{-E_i/kT} = \sum_{\substack{energies \\ E_i}} \Omega_i e^{-E_i/kT}$$

All the thermodynamic functions can be calculated from Q!!