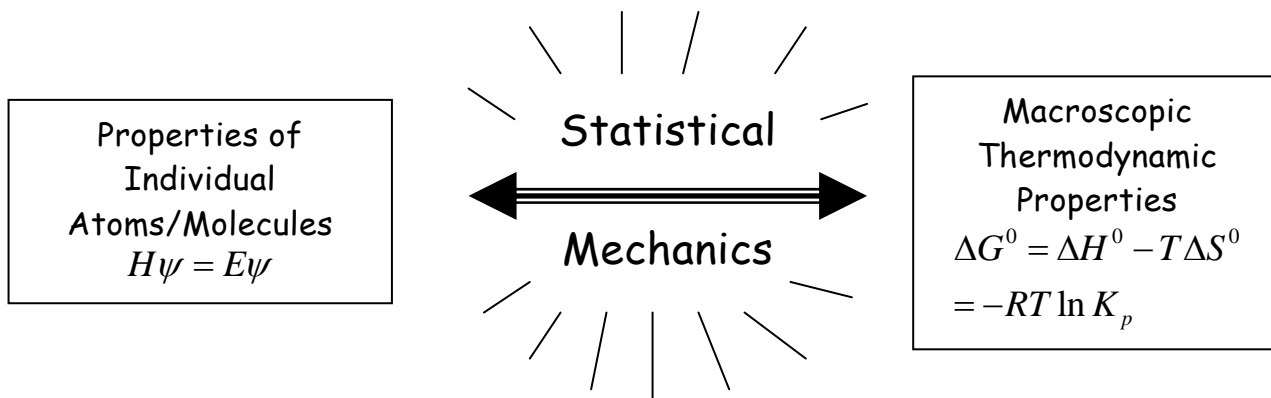


## STATISTICAL MECHANICS



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.  $p, V, n, C_v, H, A, G, \dots$
- 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  $\epsilon_i$  and  $\epsilon_j$  (e.g. energies of two different molecules or  $x$  and  $y$  components of kinetic energy in a single molecule, etc.) the joint probability should be the product:

$$P_{ij}(\epsilon_i + \epsilon_j) = P_i(\epsilon_i)P_j(\epsilon_j)$$

Suggests exponential form  $e^{C(\varepsilon_i + \varepsilon_j)} = e^{C\varepsilon_i} e^{C\varepsilon_j}$

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  $\varepsilon_i$  to T is what matters.

$$\Rightarrow P_i(\varepsilon_i) \sim e^{-C\varepsilon_i/T}$$

Or more conventionally

$$P_i(\varepsilon_i) \propto e^{-\varepsilon_i/kT} \quad \text{where } k = R/N_A = 1.38 \times 10^{-16} \text{ erg/K is the Boltzmann constant}$$

For two states i and j with energies  $\varepsilon_i$  and  $\varepsilon_j$ , the relative probability is

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

To get absolute probabilities (not just relative), write

$$P_i(\varepsilon_i) \propto e^{-\varepsilon_i/kT} = a e^{-\varepsilon_i/kT}$$

Sum of probabilities for all the states

$$\sum_i P_i = 1 = a \sum_i e^{-\varepsilon_i/kT} \quad \Rightarrow \quad a = \frac{1}{\sum_i e^{-\varepsilon_i/kT}}$$

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

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  $E_i$ :

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

## Partition functions

The sums

$$\sum_i e^{-\varepsilon_i/kT} \equiv q \quad \text{Molecular partition function}$$

and

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

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

Example: perfect atomic crystal lattice at  $T \approx 0$  K

Set ground state energy  $E_0 = 0$

All other state energies  $\gg kT \Rightarrow Q \approx 1$

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

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

$\sim 1 \text{ \AA}^3 = 10^{-30} \text{ m}^3$

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:

$$(10^{30})(10^{30})(10^{30}) \dots (10^{30}) = (10^{30})^{10^{24}} = 10^{(30 \times 10^{24})} = q_{trans}^N$$

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

$$Q_{trans} = q_{trans}^N \quad \text{distinguishable particles}$$

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

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

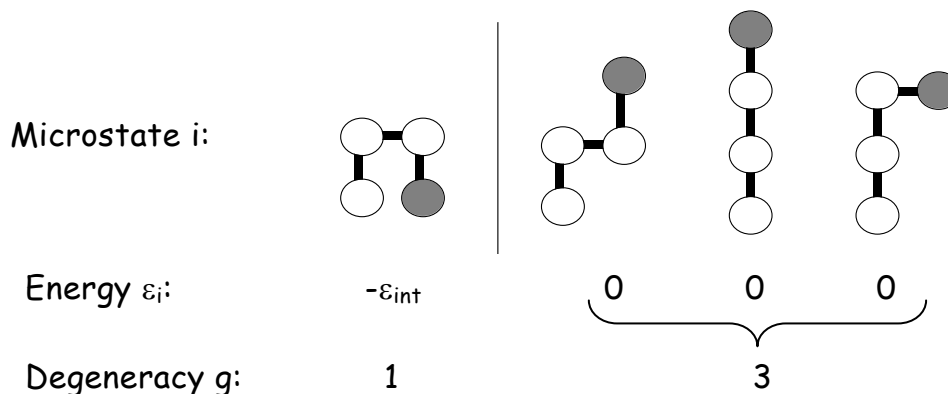
So

$$Q_{trans} = \frac{q_{trans}^N}{N!} = \frac{q_{trans}^N}{N^N e^{-N}} = \frac{(10^{30})^{10^{24}}}{(10^{24})^{10^{24}} e^{-10^{24}}} = (10^6)^{10^{24}} e^{10^{24}} = (10^6)^{10^{24}} (10^{0.4})^{10^{24}} = (10^{5.6})^{10^{24}}$$

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:



In this simple example, the "configurational" molecular partition function is

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

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

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

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

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

### Thermodynamic properties from partition functions

All the macroscopic thermodynamic properties can be derived from the microscopically based partition functions!

Start with energy  $U = \langle E \rangle$ , the average system energy. Use  $\beta = 1/kT$ .

$$U = \langle E \rangle = \sum_i p_i E_i = \frac{1}{Q} \sum_i E_i e^{-\beta E_i}$$

Use the following result:

$$\left( \frac{\partial Q}{\partial \beta} \right)_{V,N} = \left( \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} \right)_{V,N} = - \sum_i E_i e^{-\beta E_i}$$

Then

$$\langle E \rangle = \frac{1}{Q} \sum_i E_i e^{-\beta E_i} = - \frac{1}{Q} \left( \frac{\partial Q}{\partial \beta} \right)_{V,N} = - \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = - \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} \left( \frac{\partial T}{\partial \beta} \right)_{V,N}$$

$$\left( \frac{\partial \beta}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{1}{kT} \right) = - \frac{1}{kT^2}$$

$$\boxed{U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}}$$

Generally  $U$  is a function of  $(N, V, T)$ .

This leads naturally to the Helmholtz free energy  $A(N, T, V)$ .

Derive  $A$  based on analogy with the Gibbs-Helmholtz relation.

$$A = U - TS \quad A/T = U/T - S \quad U = \left( \frac{\partial (A/T)}{\partial (1/T)} \right)_{V,N}$$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = -k\left(\frac{\partial \ln Q}{\partial (1/T)}\right)_{V,N} \Rightarrow \boxed{A = -kT \ln Q}$$

(constant of integration can be shown to be zero)

$$S = -\frac{A}{T} + \frac{U}{T} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

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

### Entropy in terms of probabilities and degeneracies

$$\frac{S}{k} = \frac{U - A}{kT} = \frac{1}{kT} \frac{\sum_i E_i e^{-E_i/kT}}{Q} + \ln Q$$

But  $E_i = -kT \ln e^{-E_i/kT}$  so  $\frac{S}{k} = -\sum_i \frac{e^{-E_i/kT}}{Q} (\ln e^{-E_i/kT}) + \ln Q$

Since  $\sum_i p_i = \frac{\sum_i e^{-E_i/kT}}{Q} = 1$ , we can multiply  $\ln Q$  by 1 and combine terms to get

$$\frac{S}{k} = -\sum_i \frac{e^{-E_i/kT}}{Q} (\ln e^{-E_i/kT}) + \sum_i \frac{e^{-E_i/kT}}{Q} \ln Q = -\sum_i \frac{e^{-E_i/kT}}{Q} \ln \left(\frac{e^{-E_i/kT}}{Q}\right)$$

This is just

$$\boxed{S = -k \sum_i p_i \ln p_i} \quad \text{Gibbs eq for entropy in terms of state probabilities}$$

If the system is isolated, then all states have the same energy and the same probability  $p = 1/\Omega$  where  $\Omega$  is the number of degenerate states. Then

$$\boxed{S = k \ln \Omega} \quad \text{Boltzmann expression for entropy (on his tombstone!)}$$

Can understand entropy in terms of number of different available states. This microscopic picture of entropy is at the heart of statistical mechanics.