5.62 Physical Chemistry II
Spring 2008

<u>5.62 Lecture #2</u>: E, A, and S: Macroscopic Properties from Microscopic $\{P_i\}$ Probabilities

Problem:	How do we calculate a macroscopic property, which is constant in time, from a microscopic property that fluctuates in time?

Example: Pressure, which is a macroscopic property that arises from the microscopic impulses of each molecule impacting the vessel's walls. The positions and velocities of each molecule change on a 10^{-13}s time scale (the duration of a collision)!

Possible Solution: TIME AVERAGE the microscopic variable

f_{obs} is the observed macroscopic property

$f(\underset{\sim}{q}^{3N},\underset{\sim}{p}^{3N})$ is the instantaneous value of the sum over all microscopic contributions to the macroscopic property

$$f_{obs} = \lim_{\tau\to\infty} \tfrac{1}{\tau}\int_0^\tau f\left(\underset{\sim}{q}^{3N},\underset{\sim}{p}^{3N}\right)d\tau'$$ this is how a classical mechanical time average is defined

But this calculation is impossible because it requires knowledge of the time dependence of a very large number, N, of $\underset{\sim}{q}_i,\underset{\sim}{p}_i$.

Instead, we make use of ENSEMBLE THEORY, developed by J. Willard Gibbs (1839-1903) (founder of Stat. Mech.)

ENSEMBLE $\equiv$ A COLLECTION OF ALL "POSSIBLE" STATES OF AN ASSEMBLY
system (e.g. a molecule) $\rightarrow$ assembly of systems $\rightarrow$ ensemble

In thermodynamics, the word "system" is used to specify the macroscopic object under construction.

Example:

(1) Quantum – assembly consisting of 2 particles only

state	n_{1x}	n_{1y}	n_{1z}	n_{2x}	n_{2y}	n_{2z}
α	2	1	1	1	1	1
β	1	2	1	1	1	1
γ	1	1	2	1	1	1
δ	1	1	1	2	1	1
ε	1	1	1	1	2	1
η	1	1	1	1	1	2

Constant E ensemble with $E = 9\varepsilon_0$

$$E = \sum_{i=1}^{N} \varepsilon_i$$

$$\varepsilon_i = \frac{h^2}{8m_i a^2}\left[n_{ix}^2 + n_{iy}^2 + n_{iz}^2\right]$$

$$\varepsilon_0 = \frac{h^2}{8m_i a^2}$$

For a 2 particle assembly there are only 6 ways $E = 9\varepsilon_0$ can be achieved.

(2) Classical – 1 particle

In general $\quad E = \sum_{i=1}^{N} \varepsilon_i$

$$\varepsilon_i = \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m}$$

In this case $\quad E = \frac{p^2}{2m} = \text{ constant}$

For a 2 particle assembly there are an infinite number of ways $E = 9\varepsilon_0$ can be achieved.

Note that the quantum ensemble is a set of *discrete* states, whereas the classical ensemble is a set of infinitely many states described by *continuous* variables.

ENSEMBLE THEORY: SOMEHOW, WE CAN KNOW ALL POSSIBLE STATES OF AN ASSEMBLY WITHOUT WATCHING IN REAL TIME WHAT STATES THE ASSEMBLY VISITS. SO, INSTEAD OF THE INFEASIBLE TIME AVERAGE, WE COMPUTE AN AVERAGE OVER ALL FEASIBLE STATES OF AN ASSEMBLY.

It is frequently feasible to list (enumerate) the states possible for the assembly without "watching in real time". This is where combinatorics and statistics enter.

A FUNDAMENTAL POSTULATE OF STATISTICAL MECHANICS

THE ERGODIC HYPOTHESIS
TIME AVERAGE ≡ ENSEMBLE AVERAGE

(actually it is also an average over cells in phase space, each of volume h^{3N} where N is the number of particles)

ENSEMBLE AVERAGE

Discrete case — Quantum

macroscopic observable quantity $\equiv \bar{f} = \sum_j P_j f_j$

$f_j \equiv$ a microscopic property of j^{th} distinguishable state of assembly

sum over distinguishable assembly states in ensemble

$P_j \equiv$ probability that assembly is in state *j*.

so macroscopic energy $\bar{E} = \sum_j P_j E_j$ = ensemble average energy

Continuous case — classical

$$\bar{f} = \int \cdots \int \; P\left(\underset{\sim}{q}^{3N}, \underset{\sim}{p}^{3N}\right) f\left(\underset{\sim}{q}^{3N}, \underset{\sim}{p}^{3N}\right) d\underset{\sim}{q}^{3N} d\underset{\sim}{p}^{3N}$$

where $P\left(\underset{\sim}{q}^{3N}, \underset{\sim}{p}^{3N}\right) d\underset{\sim}{q}^{3N} d\underset{\sim}{p}^{3N} \equiv$ prob. of finding the assembly in the phase space volume element $d\underset{\sim}{q}^{3N} d\underset{\sim}{p}^{3N}$ centered at $\underset{\sim}{q}^{3N}, \underset{\sim}{p}^{3N}$.

NOTE: To calculate an ensemble average, you need values for P_j $\left(\text{or } P\left(\mathbf{q}^{3N}, \mathbf{p}^{3N}\right)\right)$

PROBLEM: How do we determine P_j?

SOLUTION: Minimize the Helmholtz free energy, $A = \bar{E} - TS$, holding the natural variables of A, (N, T, and V), constant.

DETERMINATION OF P_j

Our ensemble is a

CANONICAL ENSEMBLE ≡ ensemble subject to constraints that N,V,T are constant. A closed, thermodynamically stable system.

Condition for thermodynamic stability (equilibrium) for N, V, T constant is

$$A_{N,V,T} \equiv \text{MINIMUM}$$

The states of the assembly present in the ensemble, as given by $\{P_j\}$, must minimize A.

Must write A in terms of $\{P_j\}$.

$$A = \bar{E} - TS \quad \text{and} \quad \bar{E} = \sum_j P_j E_j = \sum_j (\Gamma_j/\Gamma) E_j$$

where Γ_j is the number of replicas of the j-th assembly in the ensemble, Γ is the total number of assemblies in the ensemble

$\dfrac{\Gamma_j}{\Gamma}$ is the probability of j-th assembly in the ensemble

$$\text{so } A = \sum_j P_j E_j - TS$$

Now connect S and $\{P_j\}$...

An *isolated* system at *equilibrium* is one of *maximum entropy*, S - 2nd Law. If the system is perturbed, it will relax to maximum entropy, a macro property. On a microscopic scale, it relaxes by going from a less probable state to a more probable state. So, there must be a connection between entropy (a macro property) and P_j (a micro property). That connection is *assumed* to be…

$$\boxed{S = -k\sum_j P_j \ln P_j}$$

A CRUCIAL ASSUMPTION!

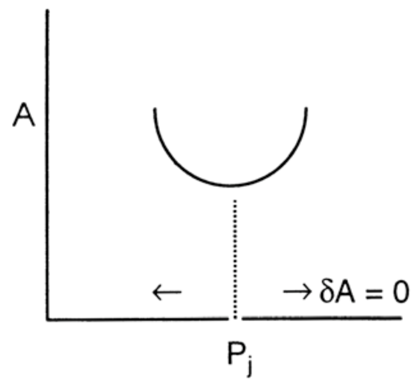
Boltzmann wrote this down in a slightly different form. No derivation. Only plausibility arguments. It is an assumption on which statistical mechanics is built. It works!!!

So now, $A = \bar{E} - TS$

$$A = \sum_j P_j E_j + kT \sum_j P_j \ln P_j$$

$$A = \sum_j P_j (E_j + kT \ln P_j)$$

Finding those P_j's that make A a minimum ...



Replace P_j by $P_j + \delta P_j$, then $A \to A + \delta A$. The "correct" set of $\{P_j\text{'s}\}$ gives $\delta A = 0$, which corresponds to the minimum of A

$$\delta A = \delta\left[\sum_j P_j (E_j + kT \ln P_j\right] \quad \text{(N, V, T constant)}$$

$$= \sum_j \left[E_j \delta P_j + P_j \delta E_j + kT\left(\ln P_j\right)\delta P_j + kTP_j \frac{1}{P_j}\delta P_j\right] \qquad \left(\delta E_j = 0\right)$$

$$= \sum_j \delta P_j\left[E_j + kT\left(\ln P_j + 1\right)\right] \text{ set to 0 for extremum}$$

Introduce Constraint

$$\sum_j P_j = 1 = \sum_j (P_j + \delta P_j)$$

This implies $$\sum_j \delta P_j = 0$$

$$\text{or } \delta P_{j=1} = -\sum_{j=2}^{N} \delta P_j \qquad \text{the trick!}$$

Remove the first term from the summation:

Now $$\delta A = \delta P_1\left[E_1 + kT(\ln P_1 + 1)\right] + \sum_{j=2}^{N} \delta P_j\left[E_j + kT(\ln P_j + 1)\right]$$

employ the trick

$$\delta A = -\sum_{j=2}^{N} \delta P_j\left[E_1 + kT(\ln P_1 + 1)\right] + \sum_{j=2}^{N} \delta P_j\left[E_j + kT(\ln P_j + 1)\right]$$

$$\delta A = +\sum_{j=2}^{N} \delta P_j\left[(E_j - E_1) + kT(\ln P_j - \ln P_1)\right] = 0$$

δP_j's are completely independent of each other for arbitrary δP_j; j = 2,3 ..., thus each coefficient of each δP_j must separately be zero.

$$\therefore \quad E_j - E_1 + kT(\ln P_j - \ln P_1) = 0$$

$$\frac{E_j - E_1}{kT} = \ln(P_1/P_j)$$

$$e^{\frac{E_j - E_1}{kT}} = P_1/P_j$$

$$\therefore \quad P_j = P_1 e^{E_1/kT} e^{-E_j/kT} \qquad *$$

Need to normalize P_j $$\sum_j P_j = 1$$

$$\sum_j P_j = P_1 e^{E_1/kT} \sum_j e^{-E_j/kT} = 1$$

Solve for P_1

$$P_l = \frac{1}{e^{E_l/kT}\sum_j e^{-E_j/kT}}$$

Use * equation: $P_l = P_j e^{E_j/kT} e^{-E_l/kT}$

$$\therefore \qquad P_j = \frac{1}{e^{E_l/kT}\sum_m e^{-E_m/kT}}\left[e^{E_l/kT}e^{-E_j/kT}\right]$$

$$\boxed{P_j = \frac{e^{-E_j/kT}}{\sum_m e^{-E_m/kT}}}$$ Canonical Distribution Function!

Probability of finding an assembly with energy E_j among all of the assemblies in the ensemble.

These are the probabilities of states of an assembly that make the ensemble thermodynamically stable

$\Rightarrow$ minimized A

$\Rightarrow$ needed probalistic assumption for $S = -k\sum_j P_j \ln P_j$

Since we now know Pj, we can calculate ensemble averages. Thus we can calculate macroscopic properties from microscopic properties using ensemble average instead of time average.