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5.62 Physical Chemistry II
Spring 2008

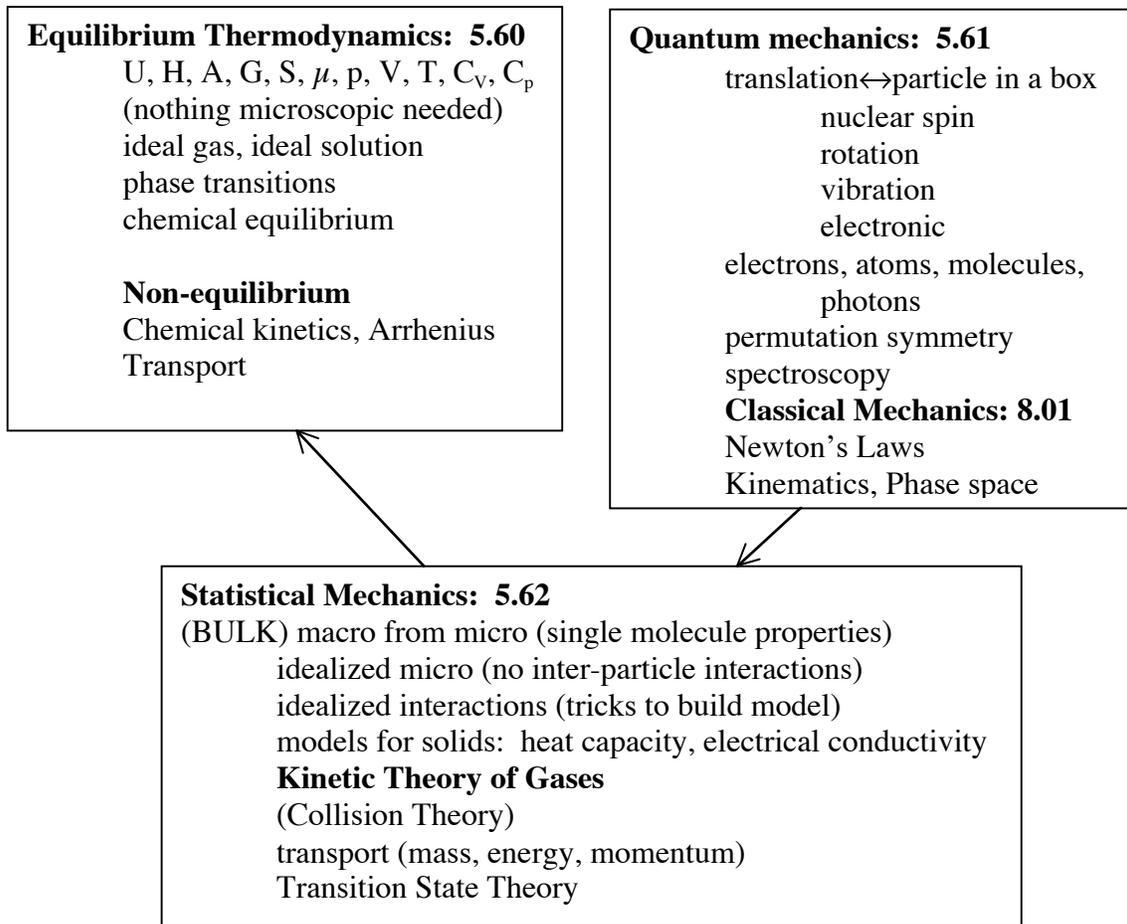
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Lecture 1: Assemblies⇒Ensembles, the Ergodic Hypothesis

TOPICS COVERED

This is a course in building *microscopic* models for *macroscopic* phenomena. Most of first half involves idealized systems, where inter-particle interactions can be ignored and where individual particles are adequately described by simple energy level formulas (from Quantum Mechanics 5.61 or Classical Mechanics). The second half deals with non-ideality, interacting atoms, as in solids and, in gas phase collisions and chemical reactions.

I. Equilibrium Statistical Mechanics (J. W. Gibbs) microscopic basis for macroscopic properties



II. Solid-State Chemistry

models for solids

prediction of macroscopic properties from microscopic interactions

III. Kinetics Models

- Kinetic Theory of Gases (Boltzmann)

- bulk properties obtained from averages over speed distributions

- less powerful than stat. mech., but simpler to apply in everyday circumstances

- transport properties — relaxation to equilibrium

IV. Theories of Reaction Rates

bridge between microscopic properties and macroscopic reaction rate:
result of many microscopic collisions

Collision Theory — based on kinetic theory — fraction of collisions that are effective in causing reaction

Transition-State Theory — based on stat. mech. probability that a special state (transition state) is occupied)

reaction dynamics, potential energy surfaces

Non-Lecture

Review of Thermodynamics

First Law: $dU = dq + dw$
 $\oint dU = 0$

Find complete set of functions of state and their natural variables:

$$U(S, V, \{n_i\})$$

$$dU = TdS - pdV + \sum_i \mu_i dn_i \quad (T_{\text{surr}}, p_{\text{ext}})$$

$$H = U + pV$$

$$H(S, p, \{n_i\})$$

$$dH = TdS + Vdp + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$A(T, V, \{n_i\})$$

$$dA = -SdT - pdV + \sum_i \mu_i dn_i$$

$$G = H - TS = A + pV$$

$$G(T, p, \{n_i\})$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

Many quantities are defined in terms of partial derivatives.

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, \{n_i\}} = \left(\frac{\partial H}{\partial S} \right)_{p, \{n_i\}}$$

$$p = - \left(\frac{\partial U}{\partial V} \right)_{S, \{n_i\}} = - \left(\frac{\partial A}{\partial V} \right)_{T, \{n_i\}}$$

$$V = \left(\frac{\partial H}{\partial p} \right)_{S, \{n_i\}} = \left(\frac{\partial G}{\partial p} \right)_{T, \{n_i\}}$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V, \{n_i\}} = - \left(\frac{\partial G}{\partial T} \right)_{p, \{n_i\}}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, \{n_j = n_i\}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, p, \{n_j \neq n_i\}} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, \{n_j \neq n_i\}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, \{n_j \neq n_i\}}$$

Maxwell relationships (mixed second derivatives), e.g.

$$\left(\frac{\partial^2 U}{\partial S \partial V} \right)_{\{n_i\}} = \left(\frac{\partial^2 U}{\partial V \partial S} \right)_{\{n_i\}} \Rightarrow - \left(\frac{\partial p}{\partial S} \right)_{V, \{n_i\}} = \left(\frac{\partial T}{\partial V} \right)_{S, \{n_i\}}$$

$$\left(\frac{\partial^2 G}{\partial p \partial n_i} \right)_{T, \{n_j \neq n_i\}} = \left(\frac{\partial^2 G}{\partial n_i \partial p} \right)_{T, \{n_j \neq n_i\}} \Rightarrow \left(\frac{\partial \mu_i}{\partial p} \right)_{T, \{n_j \neq n_i\}} = \left(\frac{\partial V}{\partial n_i} \right)_{T, \{n_j \neq n_i\}} = \bar{V}_i$$

$$\left(\frac{\partial^2 G}{\partial T \partial n_i} \right)_{p, \{n_j \neq n_i\}} = \left(\frac{\partial^2 G}{\partial n_i \partial T} \right)_{p, \{n_j \neq n_i\}} \Rightarrow \left(\frac{\partial \mu_i}{\partial T} \right)_{p, \{n_j \neq n_i\}} = -\bar{S}_i.$$

This allows us to express all Thermodynamic quantities in terms of G and to express G in terms of measurable quantities T, V, p, C_V , C_p .

Suppose we know $G(T, p)$

$$S = - \left(\frac{\partial G}{\partial T} \right)_p$$

$$V = \left(\frac{\partial G}{\partial p} \right)_T$$

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_p$$

$$U = G - T \left(\frac{\partial G}{\partial T} \right)_p - p \left(\frac{\partial G}{\partial p} \right)_T$$

$$A = G - p \left(\frac{\partial G}{\partial p} \right)_T$$

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

So we can derive all thermodynamic quantities from $G(T,p)$. If we can derive a Statistical Mechanical expression for $G(T,p)$, then we will have all other thermodynamic functions of state.

It is also possible to show how all Thermodynamic quantities maybe derived from measurements of p, V, T, C_p, C_v .

From the natural variables we know the conditions for equilibrium. (Actually this is how we discovered in 5.60 all of the state functions and their natural variables.)

Quantities Held <u>Constant</u>	Condition for <u>Equilibrium</u>	
N, p, T	G minimized	
N, V, T	A minimized	
N, p, S	H minimized	
N, V, S	U minimized	
$\underbrace{N, U, V}_{\text{closed, isolated system}} \text{ or } N, H, p$	S maximized	(2 nd Law)

We are going to talk about two kinds of “partition functions” in 5.62.

Microcanonical	$\Omega(N, E, V) \Leftrightarrow S(N, E, V)$
Canonical	$Q(N, T, V) \Leftrightarrow A(N, T, V)$

Let's begin!

Goal of Statistical Mechanics: describe macroscopic bulk Thermodynamic properties in terms of microscopic atomic and molecular properties. These microscopic properties are generally measured by spectroscopy.

Macroscopic: $U, H, A, G, S, \mu, p, V, T, C_V, C_p$

complete intensive description of a **bulk** system: $N \approx 10^{23}$ particles

e.g. $p\bar{V} = RT$

only two intensive variables are needed!

Gibbs Phase Law

$$F = C - P + 2$$

There are only a few things about a bulk system that we can (or need to) measure!

Microscopic: N particle monatomic gas

If we assume non-interacting particles, we must describe the “state” of each particle in the system.

Two ways we might do this.

Classical Mechanics: p_x, p_y, p_z, x, y, z for each particle ($\underline{p}^{3N}, \underline{q}^{3N}$)

Quantum Mechanics: quantum state (n_x, n_y, n_z) for each particle.

Classical Mechanics: N particles, $6N$ degrees of freedom

Quantum Mechanics: N particles, $3N$ degrees of freedom

$N \approx 10^{23}$ ridiculous amount of information needed.

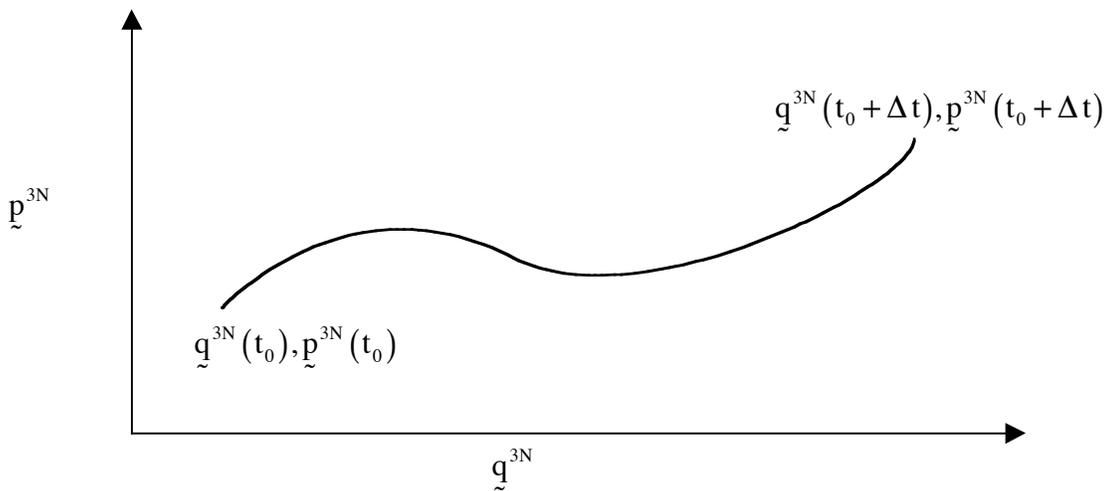
Suppose we had all this information, every time there is a collision, we need to do a complicated calculation.

(How long does a collision take?

$v_{\text{relative}} \approx 10^5 \text{ cm/s}$, size of molecule, $D \approx 2 \times 10^{-8} \text{ cm}$,
collision duration is $\delta t = D/v \approx 2 \times 10^{-13} \text{ s} = 0.2 \text{ ps.}$)

Cartoon description

Classical Phase Space



We would need to solve a lot of kinematic (8.01) equations to compute the path of a phase point for given initial conditions. Even if we could do it, we would be throwing away a huge amount of information to reduce it to the small number of knowable bulk properties.

Quantum Mechanics

$$\Psi \left(\underbrace{\{n_{ix}, n_{iy}, n_{iz}\}}_{3N \text{ quantum numbers}} \right) \left(\tilde{q}^{3N} \right)$$

Should we use Classical or Quantum Mechanics? Either or both, as convenient! Statistical Mechanics will tell us how to vastly reduce the amount of information needed to “completely” describe a bulk system.

- * idealizations (initially)
- * amazing properties of average over very large numbers of degrees of freedom
- * combinatorics
- * average and most probable behaviors

Formalism: How do we describe the “state” of a system consisting of many particles: an “assembly”?

Each quantum state of an assembly consisting of N non-interacting particles is described by 3N quantum numbers.

state	n_{1x}	n_{1y}	n_{1z}	n_{2x}	...	n_{Nz}
α	1	2	1	1		1
β	1	1	1	2		1

$E_\alpha = \sum_{i=1}^N \epsilon_i$ (energy of i-th particle in α state of assembly). For one particle in an infinite 3-D cube of length L

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} \left[n_x^2 + n_y^2 + n_z^2 \right]$$

Since the α and β states have different sets of occupation numbers they are in principle distinguishable, but they do have the same E. Degenerate state.

Degeneracy $\equiv \Omega(E, N)$ number of (in principle) distinguishable assemblies with the *same* total E and N

But collisions cause the quantum state to change rapidly and unpredictably with time.

What do we do?

Make the ERGODIC HYPOTHESIS

Replace **time average** over microscopic description by **ensemble average**

ENSEMBLE \equiv collection of an enormous number of replicas of the assembly. In a sense this includes *all* microscopic states that the time evolving state would pass through after an infinite amount of time. WE CAN DO THIS!