Physics 301: Thermodynamics and Statistical Mechanics

Reading assignment due by next class:

1) Handout on "The Nature of Thermodynamics", available on the class web site
2) Stowe Chapter 5: "Internal Energy and Equipartition."

Don't confuse "parts" with "chapters."

It will be assumed that you are familiar with the material in Stowe Chapter 2, Sections A, B, C, E, F, G, and H. These will not be explicitly covered in the lectures. But if you have questions about these sections, do not hesitate to ask!

Outline of Lecture 1:

I. The subject matter of thermodynamics
II. Thermodynamics variables
III. Internal energy

I. The subject matter of thermodynamics

In physics we study 3 core subjects:

	Subject Matter	New Law
1) Mechanics (classical or QM)	the dynamics of particles acted on by forces	Newton/Lagrange/Hamilton, Schroedinger
2) E&M (classical or QM)	the dynamics of fields that mediate the forces	Maxwell
3) Thermo and Stat Mech	any system that is macroscopic i.e., involves a large number of objects	No new law

Note Thermo and Stat Mech differs from (1) and (2) in that it

(i) often does not predict specific numerical values for observable quantities

(ii) frequently sets limits (inequalities) on physical processes

II. Thermodynamic variables

Recall from Physics 160 that thermodynamics investigates relationships among quantities such as energy, volume, temperature, entropy, and so forth.

Why those?

Typically we study systems that may have 10^{23} particle coordinates. That's the number of particles in a liter of water.

Thermodynamics considers things that we want to measure, that occur in groups, for example:

atmospheres
stellar interiors
refrigerant particles
plasmas

The particles under consideration are in motion. The physical size of our instruments leads to inertia, resistivity, etc, that $\underbrace{\text{limit the characteristic time and characteristic distance}}_{\Downarrow \atop \textit{precision}}$ of measurements.

Contemporary standard for short timescale measurements: 10^{-12} seconds

Typical timescale for observable changes due to thermal motion of particles: 10^{-15} seconds

So, compared to the timescale of motion of the system we want to observe, our measurement is approximately *static*.

Static does NOT mean "motionless."

Static means: "averaged over a time that is long, compared to characteristic times in the system being measured.

That is: we measure properties that change over times and distance scales that are large relative to atomic oscillation periods and distances.

Properties whose changes are not zeroed out by averaging are called **thermodynamic variables.**

Thermodynamics uses the thermodynamic variables to study the consequences of changes in the atomic coordinates that are not explicitly in the macroscopic description of the system.

"Atomic coordinates" includes angular momenta, position, linear momenta, etc., of the individual atoms.

III. Internal energy

Recall the definition of energy --- not just internal energy:
A system (or object) has energy if it has the capacity to cause change.

Energy transfer via a macroscopic ("thermodynamic") variable is called Work.
(Remember $dW = -P \cdot dV$ for work done on a system by pressure and volume change)

Energy transfer via a change in hidden atomic coordinates is Heat.

Notice that the thermo variable (Work) reflects the *consequences* of changes to the microscopic variable (Heat). Heat is only measurable by converting a sample of it into work...for example, making a column of mercury rise (dV) in a thermometer.

Definition of **internal energy**: the sum of the energies of the individual elements of a system...*as opposed to the energy associated with the center of mass*.

Facts about internal energy:

1) Internal energy can include kinetic

- for example, translational motion of electrons in a metal, or rotational motion of molecules in a liquid

and it can include potential energy.

- for example, stored energy of "stretched spring" electric forces between nuclei in a lattice.

2) On average, 1/2 of a system's internal energy is kinetic, and 1/2 is potential.

This is a special case of the Virial Theorem, $2\langle T \rangle = -\sum_{i=1}^{N} \langle \vec{F}_i \cdot \vec{r}_i \rangle$.

Demonstrate this:

Consider a solid made of N particles.

Each particle is connected by a spring-like potential U, so its $U = \frac{1}{2} k r_i^2$.

Each particle has momentum p_i.

Notice that both p_i and r_i are bounded: they cannot become arbitrarily large.

Define a function $S \equiv \sum_i \vec{p}_i \cdot \vec{r}_i$.

Calculate $\frac{dS}{dt} = \sum_i (p_i \cdot \dot{r}_i + \dot{p} \cdot r_i)$ [leaving vector arrows off, for simplicity]

Time-average $\langle \quad \rangle$ this over some interval τ:

$$\underbrace{\left\langle \frac{dS}{dt} \right\rangle}_{\Downarrow} = \left\langle \sum_i p_i \cdot \dot{r}_i \right\rangle + \left\langle \sum_i \dot{p}_i \cdot r_i \right\rangle \qquad \text{"Eq 1"}$$

$$\underbrace{\frac{1}{\tau}\int_0^\tau \frac{dS}{dt} dt}_{\Downarrow}$$

$$\frac{S(\tau) - S(0)}{\tau}$$

Because p_i and r_i are bounded, S is bounded, so we can choose a long enough interval τ that $\frac{S(\tau) - S(0)}{\tau} \rightarrow 0$.

Because the LHS of Eq 1 equals zero, the RHS must equal zero. Then:

$$\left\langle \sum_i p_i \cdot \dot{r}_i \right\rangle = -\left\langle \sum_i \dot{p}_i \cdot r_i \right\rangle$$

Use kinetic energy $T = \dfrac{m\dot{r}^2}{2} = \dfrac{p_i \cdot \dot{r}_i}{2}$

and $F = ma = \dot{p}$

$$\left\langle 2\sum_i T_i \right\rangle = -\left\langle \sum_i F_i \cdot r_i \right\rangle$$

Recall $F_i = -\vec{\nabla} U_i = -\vec{\nabla}\left(\dfrac{kr_i^2}{2}\right) = -kr_i$

$$-\left\langle \sum_i \left(-kr_i\right) \cdot r_i \right\rangle$$

But $kr_i \cdot r_i = 2U_i$

$$\left\langle 2\sum_i T_i \right\rangle = \left\langle 2\sum_i U_i \right\rangle$$

$$\langle Total\ \ T \rangle = \langle Total\ \ U \rangle$$

I. Degrees of freedom
II. A general way to count degrees of freedom
III. Some facts about degrees of freedom
IV. Changing a system's internal energy
V. Work

Please read Stowe Chapter 6.

I. Degrees of freedom ("DOF")

"Degrees" means "kinds" of freedom, not thermal degrees Celsius.

Several equivalent definitions of DOF for a system:

1) (Stowe's definition) The number of ways that the system can store energy, including information about the number of components (particles) it has and the number of dimensions each is free to move in.

2) The number of independent variables needed to describe the energy of the system.

Why DOF are important:

they affect the internal energy, heat capacity, and thermal properties (for example conduction, insulation of solids).

II. A general way to count degrees of freedom

Consider first, free molecules (no lattice). Each molecule has N component atoms (N>2).

$$\left.\begin{array}{l}\text{\# position coordinates: 3N}\\ \text{\# linear momentum coordinates: 3N}\end{array}\right\}\text{These are the 6N phase space coordinates of the system.}$$

Transform from this arbitrary coordinate system into the center of mass system.
The # of position and momentum coordinates does not change, but now it can be separated cleanly between coordinates of the center-of-mass and internal coordinates.

# position coordinates x_i = 3N	**# momentum coordinates p_i = 3N**
3 are due to COM location	3 are due to COM momentum
3 are due to COM angular orientation	3 are due to COM angular momentum
To make everything in this column sum to 3N, there must be (3N-6) vibrational separations.	Similarly, there must be (3N-6) vibrational momenta.

Thermodynamics counts degrees of freedom to be those x_i and p_i that contribute to the internal energy with terms $\propto q_i^2$.

So not all of these contribute in every situation.

For example: consider the case of a molecule in a region free of external fields.

In that case the COM location makes no difference nor does the COM angular orientation. So the total # of DOF (= total number of contributors to internal energy) is:

3 due to COM $\vec{p}$

3 due to COM $\vec{L}$

(3N-6) due to vibrational p_i

(3N-6) due to vibrational x_i

total : **6N - 6 degrees of freedom when there is no external field.**

Modifications for special cases:

(i) When the molecule is in an external field: add 6 DOF

(ii) When N=2 ("dumbbell"), and an external field is present:

total #x_i = 3N

3: COM location

2: COM angular coord.

Total for this column must sum to 3N, so conclude:

(3N-5) vibrational separations

total #p_i = 3N

3: COM momentum

2: COM angular momentum

Similarly, 3N-5 vibrational momenta.

DO NOT CONTRIBUTE IN FIELD-FREE CASE.

Thus total #DOF when N=2, in an external field is:

3+3+2+2+(3N-5)+(3N-5)=3+3+2+2+1+1=12

Total #DOF when N=2, in NO external field is:

3(COM mom)+2(COM ang mom)+(3N-5, vib mom)+(3N-5, vib sep)

=3+2+1+1=7

(iii) When N=1, and an external field is present:

total $x_i = 3N$	total $p_i = 3N$
3 : COM location	3: COM momentum
0: COM angular orientation	0: COM angular momentum
Conclude: 3N-3 vibrational separation, but this is 0 for N=1.	Similarly, 3N-3=0 vibrational momenta.

DOES NOT CONTRIBUTE IN FIELD-FREE CASE

Total #DOF for N=1, in an external field:
3+3=6

Total #DOF for N=1, with no external field:
3

(iv) When atoms are locked into a lattice, there is no contribution from the COM at all. Then $\# DOF = 2(3N - 6) = 6N - 12$.

III. Previews of coming attractions: some facts about degrees of freedom

1) The Equipartition Theorem

Every degree of freedom whose energy takes the form bq^2

constant generalized coordinate
like x or p

contributes on average an energy $E = \frac{1}{2}kT$ to the total internal energy of the system.

k = Boltzmann's constant=1.381×10^{-23} J/K

T = temperature in Kelvin K

We will prove this in Chapter 12.

2) Temperature is a measure of the average internal energy stored in each particle, averaged over all degrees of freedom (not just those related to kinetic energy!) whose energy has the form bq^2.

$$\text{i.e., T} \propto \frac{\text{Average energy per particle}}{\text{\#DOF per particle}}$$

If a DOF provides energy that is potential, the energy must be measured relative to the bottom of that *particle's own potential well*.

3) Sometimes energy is added to a system but the temperature does not change.
This is due to 2 phenomena:

(i) new degrees of freedom are opening up, and the energy is flowing into them while maintaining the average energy per DOF unchanged.

Example of this from classical physics phase changes:

Begin with N rigid diatomic molecules in a potential.

Add enough energy to break every bond. Now there are 2N monatomic molecules.

#DOF before: 3N(kinetic energy modes)+3N(potential energy modes)=6N

#DOF after: $3 \cdot 2$N(kinetic energy modes)+$3 \cdot 2$N(potential energy modes)=12N

So even if the amount of internal energy doubles, the temperature will not change.

We will examine a QM example in Chapter 27.

(ii) particles that were at the bottoms of their personal potential wells (i.e., U=0) receive so much energy that they are completely unbound, so relative to their new reference point (KE=0) they are still at zero. This is also a phase change.

IV. Changing a system's internal energy

3 ways:

1) work done on or by the system

2) heat transferred into or out of the system

3) particles transferred into or out of the system

The next sections explain each of these.

V. Work

Recall the definition: $W \equiv \int_{s_1}^{s_2} \vec{F} \cdot d\vec{s}$

Force displacement of some parts of the system

The displacement can be

i) a macroscopic displacement ("piston compressing gas")

ii) a microscopic displacement ("electrostatic force shifting electrons in a metal)

We schematically represent *all* types of work with piston drawings just for simplified illustration.

When an external force does work ON a system, (e.g. compresses a gas), the system's energy INCREASES.

(e.g. the gas molecules hit walls that are moving toward them, and so gain some of the walls' energy)

I. Heat

II. Particle transfer

III. Exothermic effects and the chemical potential μ

IV. The First Law of Thermodynamics

Please read Stowe Chapter 7.

I. Heat

When a system's internal energy changes but its external parameters (volume, pressure, etc) do not change, we say it has *exchanged heat* ("undergone a thermal interaction").

So heat is observed indirectly as

"ΔE of a system when there is no ΔWork" or "internal energy in transit".

Mechanisms for heat transfer:

1) conduction: collisions between individual particles. *Microscopic* motion of particles. On average, in each collision, the more energetic particle transfers energy to the less energetic one.

2) convection: *macroscopic* exchange of particles in a way that causes no net work.

3) radiation: emission of energy waves ($E = h\nu$) or emission of particles (photons) that convey energy ($E = pc$)

The probability of radiating is proportional to the radiator's acceleration (which is proportional to its internal energy).

So on average, a more energetic body will radiate more than a less energetic one, so their energies will equalize.

II. Particle transfer

Why mixing 2 systems --- a chemical reaction --- can be exothermic.

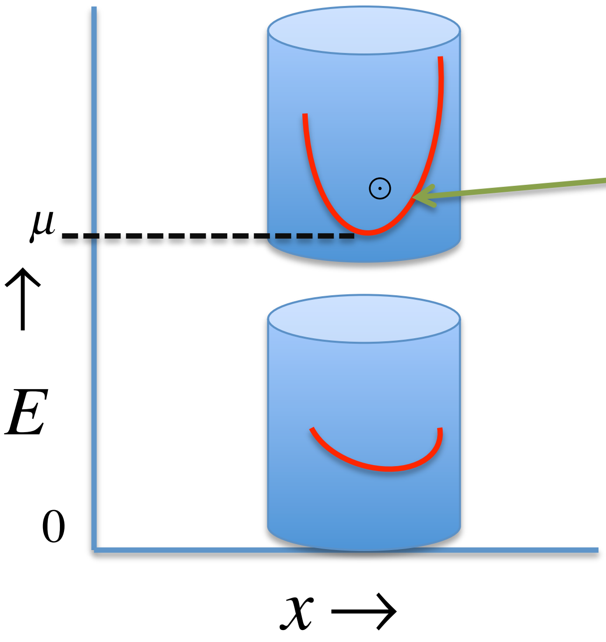
For every element of a system (i.e. for every particle):

Stored energy = kinetic + potential

Its PE is measured relative to the bottom of its own potential well (i.e. the potential that it feels due to interaction with its neighbors). This well is defined by the other particles in its system.

The universal zero-energy reference for all systems is conventionally the PE of a particle that is not interacting with any other particles ("it is located at infinity and there is nothing else out there").

So the potential wells of 2 particles in different systems ("chemistry beakers") can be very different, because they depend on the local environments.



Two substances. Typical particles in each experience very different local potentials.

Consider this particle. Its total energy is

$$E = \underbrace{KE} + \underbrace{PE}$$

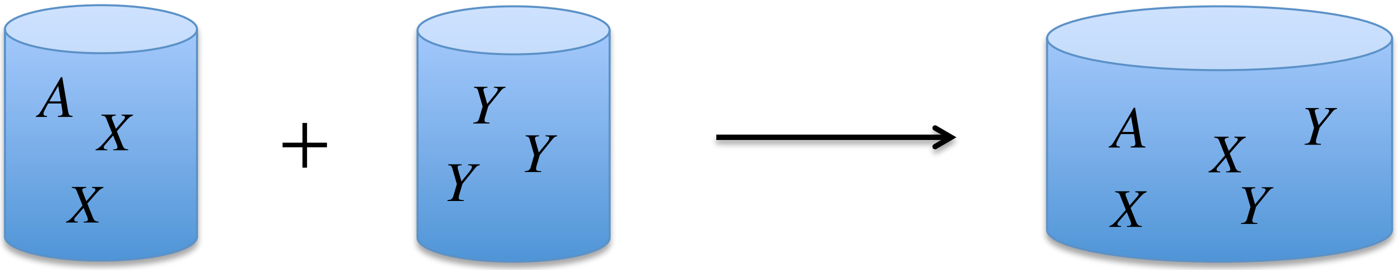
$$\boxed{\overbrace{\frac{1}{2}mv^2}+\overbrace{\frac{1}{2}kx^2}}\overbrace{+\boxed{\mu}}$$

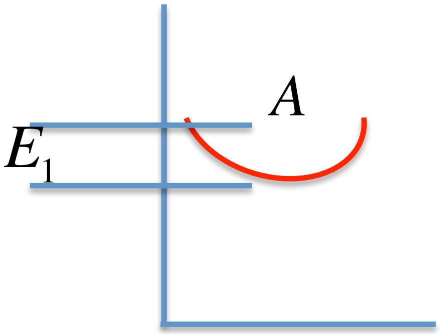
Call this $\varepsilon_{thermal}$, the only part of the total E that is reflected in the temperature.

Call this the chemical potential of the species, the *average* value of its $PE = 0$ point above the reference $E = 0$ point. *Average* because the environment that generates the potential is in motion, so the exact shape of the well fluctuates.

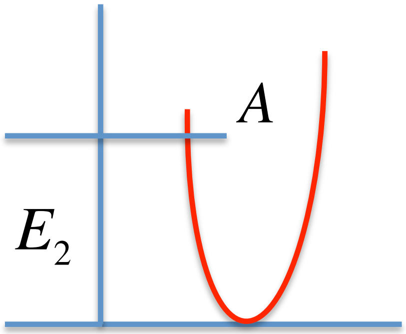
Suppose we mix 2 previously isolated systems to produce a "diffusive interaction."

Watch particle "A":





A's $\varepsilon_{thermal} = E_1$ here,
where the well shape is
generated by attraction/repulsion
between A and the X's.



A's $\varepsilon_{thermal} = E_2$ here,
where the well shape is
generated by attraction/repulsion
between A and the X's and Y's.

$E_2 - E_1 =$ energy released or absorbed and could be chemical, nuclear, electrostatic...

Facts about the chemical potential μ:

1) The Equipartition Theorem only really concerns the partition of $\varepsilon_{thermal}$, not μ.

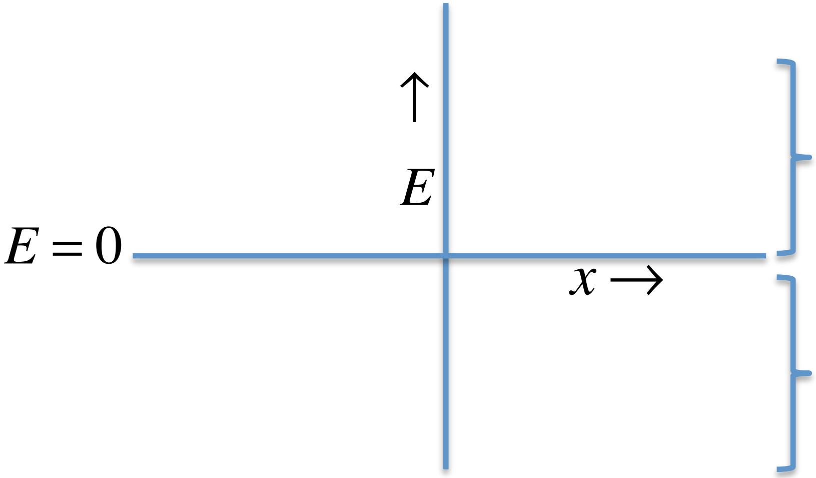
2) If you are considering an *isolated* system, you can let μ=0.

"Isolated" means no exchanging particles with any other system.

3) If the particle interactions that form the well are:

- attractive, then the μ is negative
- repulsive, then the μ is positive

To see this, recall:



free particles (experiencing no force) or particles experiencing repulsive force

bound particles (experiencing attractive force

and μ is defined as $\mu \equiv (\text{well minimum E}) - (\text{reference E})$

4) μ depends on anything that can shape the well, i.e, affect the force between particles, including:

Temperature T

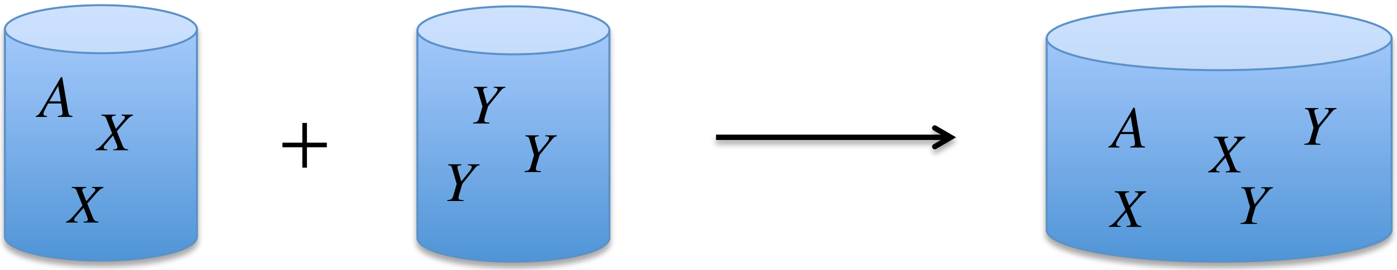
Volume V

Number of each type of particle present, N_i

5) For nuclear reactions, $\mu \sim$ MeV

For chemical reactions, $\mu \sim$ eV

III. More about exothermic effects and μ



$E_2 - E_1 =$ energy absorbed in general

$\mu_2 - \mu_1 =$ a negative number, so energy is actually liberated in this case.

The energy can be ascribed to the kinetic energy of the environment atoms as they squeeze closer together to create the stronger bonds.

IV. The First Law of Thermodynamics

We will do this carefully to get *sign conventions* right.

Recall the ways to increase the internal energy E of a system:

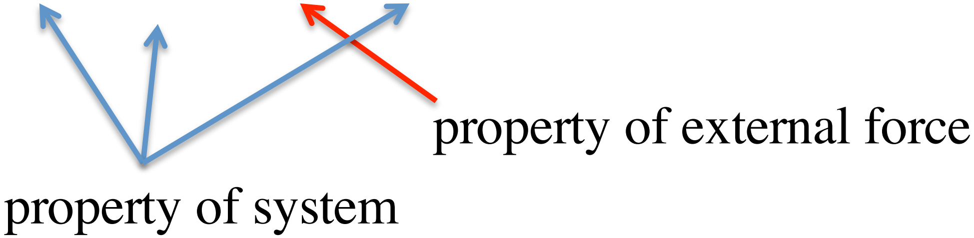
1) Add heat $+Q$ *to* the system

2) Do work $+W'$ *on* the system (W' is work done *by* an external force, *on* a system)

3) Change #particles N *in* system

The change in energy E is:

$$dE = dQ + dW' + \mu dN$$



property of external force

property of system

To convert this equation so all the variables refer to the system, define W (no prime) as "work that the system does on an external object: $W \equiv -W'$.

Then

$$dE = dQ - dW + \mu dN$$

If there are N species of particles involved, and if the system is able to do M different kinds of work (due to different forces), then:

$$dE = dQ - \sum_{j=1}^{M} dW_j + \sum_{i=1}^{N} \mu_i dN_i$$

This is the First Law of Thermodynamics

I. Exact and inexact differentials

II. State variables, processes, and differentials

III. Introduction to Chapter 7: "The States of a System"

Please read Stowe Chapter 2, Section D only.

I. Exact and inexact differentials

Overview:

(1) Physics Goal: to identify quantities that are conserved.

These are quantities whose integrals are path-independent.

(2) Math trick: it turns out that you can identify these quantities

by the properties of their derivatives.

$g(x,y)dx + h(x,y)dy$ is conserved if $\dfrac{dg}{dy} = \dfrac{dh}{dx}$.

A quantity with this property is called "an exact differential."

Otherwise it is an "inexact differential."

Next we demonstrate this...

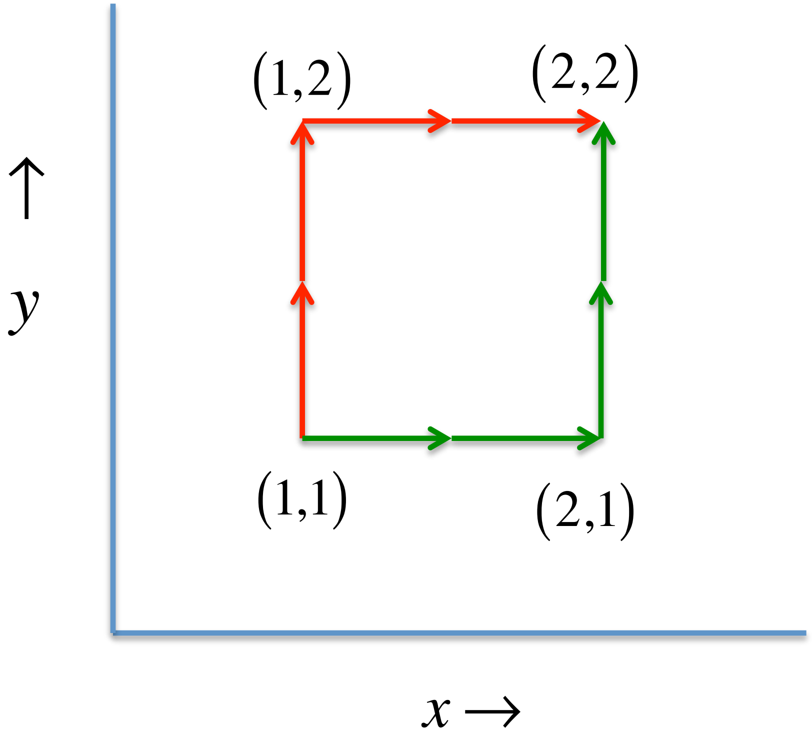
Consider a quantity $dF = g(x,y)dx + h(x,y)dy$.

Note that there may not necessarily be an F that is the integral of this.

In general, $\int dF$ is path dependent.

That means: there is no associated conserved quantity F.

Example of path-dependent and path-independent cases:



Path 1 is green.

Path 2 is red.

Path dependent case:

Suppose $dF = \alpha dx + \beta \frac{x}{y} dy = \alpha dx + \beta x d(\ln y)$

$$\int_{path1} dF = \int_{\substack{x_1=1\\ y=1, fixed}}^{x_2=2} \alpha\, dx + \int_{\substack{y_1=1\\ x=2, fixed}}^{y_2=2} \beta x d(\ln y) = \alpha(2-1) + \beta\cdot 2\cdot(\ln 2 - \ln 1) = \alpha + 2\beta \ln 2$$

$$\int_{path2} dF = \int_{\substack{y_1=1\\ x=1, fixed}}^{y_2=2} \beta x d(\ln y) + \int_{\substack{x_1=1\\ y=2, fixed}}^{x_2=2} \alpha\, dx = \beta\cdot 1\cdot(\ln 2 - \ln 1) + \alpha(2-1) = \alpha + \beta \ln 2$$

If dF were replaced by $dG = \frac{dF}{x} = \frac{\alpha}{x} dx + \frac{\beta}{y} dy$, the integral would be path independent.

That is, the conclusion would be that "G is conserved."

The way to guarantee path independence is to insist that the order of traversing x and y does not matter. This is equivalent to requiring:

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$$

To get an alternative, equivalent form of this requirement, note:

If F exists, then $dF = \underbrace{\frac{\partial F}{\partial x}}_{\text{call this "}g\text{"}} dx + \underbrace{\frac{\partial F}{\partial y}}_{\text{call this "}h\text{"}} dy$

Then require $\frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$

A quantity that produces this condition is called "an exact differential."

Otherwise, it is an "inexact differential."

The Stowe book uses the notation đQ (with a bar through the d)

to indicate inexact differentials.

II. State variables, processes, and differentials

Recall that thermodynamics describes systems that are macroscopic, and measurements of macroscopic features naturally require time intervals that are long relative to the period of fluctuations of the system.

"Long time observations" imply that the systems under observation are static, in equilibrium.

Some of the variables that can characterize a macroscopic state:

N	#particles
μ'	chemical potential per particle
V, L, A	volume, length, area
P	pressure
$\vec{M}$	magnetization
$\vec{H}$	magnetic field strength
τ,σ	tension, surface tension
$\vec{P}$	electric polarization
$\vec{E}$	electric field
T	temperature
S	entropy

and more..........enthalpy, Gibbs Free Energy, Helmholtz Free Energy......

By definition, the state variables contain no information about the history ("path") of a system.

Other variables characterize a process rather than a state, for example:

Work: energy transferred through application of a force

Heat: energy transferred in the absence of work

They may be combined in different ways ("paths") to produce the same final state.

Exact differentials refer to quantities that can be determined unambiguously (no path dependence) by examining the state (for example, dE or dN)

Inexact differentials refer to quantities that cannot be determined unambiguously for a state. For example:

more than one combination of Work and Heat can be used to produce a particular Energy state. Given some E, you cannot know what the Q and W were that produced it. So dW and dQ are inexact and we should call them đW and đQ.

III. Preparing for Chapter 7: the states of a system

We're aiming to introduce the Fundamental Postulate of Statistical Mechanics, which is:

"An isolated system in equilibrium is equally likely to be in any of its accessible states."

To understand that, we need to know:

1) what is a quantum state?
2) how do we calculate the probability of being in a particular quantum state, so that we know whether two are "equally likely"?
3) what is equilibrium?

Those are the next 3 topics.

I. Phase space and quantum states

II. Multiparticle states

Please read Stowe Chapter 3.

I. Phase space and quantum states

Recall the Uncertainty Principle from QM:

$$\Delta \mathrm{x} \cdot \Delta \mathrm{p}_x \geq \frac{\hbar}{2}$$

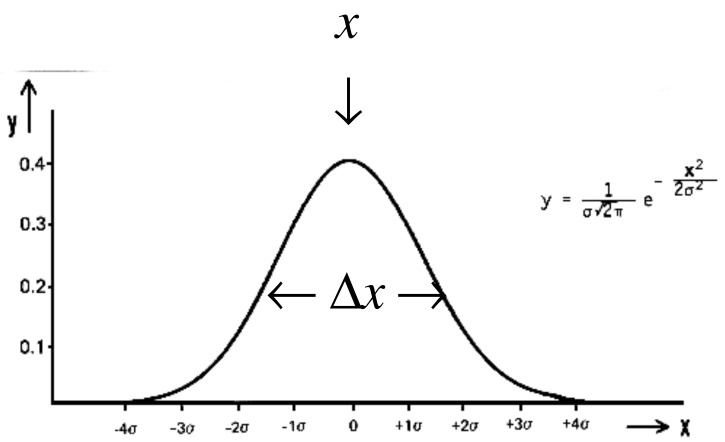
$$\hbar = 1.06 \times 10^{-34}\,\mathrm{Joule-sec}$$

$\Delta \mathrm{p}_x$ is the precision to which one can know a specific particle's momentum p

Δx is the precision to which one can know its position x

This is not due to failure of measurement tools. It results from the fact that the "particle" is also a "wave," and a wave does not have a precisely defined position.

To see where the Δx comes from, recall that the position of the particle is spread over its wavelength:

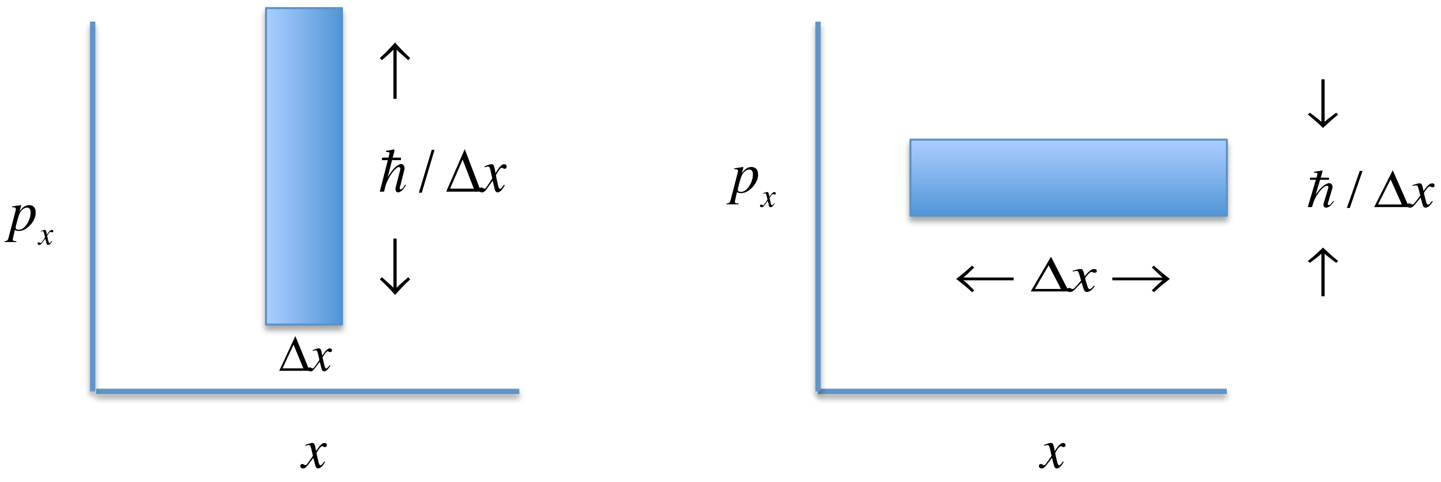


The Δp also comes from the wave property of the particle but is a little harder to see directly. The wave is a packet made of a superposition of wave trains, each with a different value of "p" (think Fourier composition).

So the packet does not have one unique p, but a combination of them that spans the range "Δp."

If we plot x versus p_x for the particle, the region of uncertain product $\Delta x \cdot \Delta p_x$ has constant area: the better you measure one, the worse you measure the other.

Example situations: both rectangles have the same area.



Similar relationships hold for $\Delta y \cdot \Delta p_y \geq \frac{\hbar}{2}$ and $\Delta z \cdot \Delta p_z \geq \frac{\hbar}{2}$.

Generalize from 2D-space (x, p_x) to 6D-space (x, y, z, p_x, p_y, p_z).

-This is called "phase space"

-In phase space, the minimum size 6-dimensional box specifying a particle's position and momentum is given by

$$\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \geq \frac{\hbar^3}{8}.$$

Note, $\frac{\hbar^3}{8} = 1.5 \times 10^{-103}$. Stowe approximates this as h^3, which is 2910×10^{-103}.

So we will also use h^3 as the volume of 1 cell in phase space.

So if a particle is known to be in some region defined by:

$0 \leq x \leq x_0$

$0 \leq y \leq y_0$

$0 \leq z \leq z_0$

$0 \leq p_x \leq p_{x0}$

$0 \leq p_y \leq p_{y0}$

$0 \leq p_z \leq p_{z0}$

Then there is a finite number of cells ("quantum states") available to it:

A quantum state is the minimum volume in phase space that can be occupied by a particle.

The number of distinct quantum states available to that particle is given by:

$$\frac{\text{total 6D volume}}{\text{volume of 1 quantum state}} = \frac{\underbrace{\boxed{x_0 y_0 z_0}}_{\text{Call this } V_r} \cdot \underbrace{\boxed{p_{x0} p_{y0} p_{z0}}}_{\text{Call this } V_p}}{h^3}$$

So #quantum states $\approx \dfrac{V_r \cdot V_p}{h^3}$

The "$\approx$" indicates the fact that we have used h *instead of* $\hbar/2$.

But for most physical systems, the # is huge, like 10^X where X is 24 digits long.

So the h-approximation is negligible, and we now replace $\approx$ with $=$.

If V_r and V_p are differentially small, let

$\mathrm{V}_r = d^3r = dxdydz$ and $\mathrm{V}_p = d^3p = dp_x dp_y dp_z$

Then the number of quantum states in a differentially small volume $dV_r dV_p$ is:

$$\frac{1}{h^3} dx \cdot dy \cdot dz \cdot dp_x \cdot dp_y \cdot dp_z$$

A conclusion: if "q" represents any phase space coordinate (x or p), then the # of quantum states scales linearly with dq. Thus

$$\left(\#\text{quantum states in interval } dq\right) \propto dq.$$

To find the total number of quantum states in a finite ($\vec{r}$,$\vec{p}$) volume, you technically should sum them (because they are discrete), but you can approximate that sum by an integral (as if they were continuous).

Then the #quantum states in a finite volume is $\displaystyle\iint_{\vec{r},\vec{p}} \frac{1}{h^3}\, dV_r\, dV_p$

$$= \frac{1}{h^3} \underbrace{\int_{\vec{r}} dV_r}_{V_r} \underbrace{\int_{\vec{p}} dV_p}_{\int_p p^2\, dp \underbrace{\int_{\theta,\phi} \sin\theta\, d\theta\, d\phi}_{4\pi}}$$

So the total number of quantum states in a finite volume is

$$\int_p \left(\frac{4\pi V_r}{h^3} \right) p^2\, dp \qquad \text{"Eq 1"}$$

Consider a special case: if the particle is NOT in a potential, then all of its energy ε is kinetic. If the particle also has $v \ll c$, we use the classical relationship between KE and momentum,

$$\varepsilon = \frac{p^2}{2m}$$

Then $d\varepsilon = \dfrac{2p}{2m}dp = \dfrac{pdp}{m}$

So $md\varepsilon = pdp$

Also $p = (2m\varepsilon)^{1/2}$

Recall Eq. 1, and substitute these in:

$$\# \text{ of quantum states in a finite volume } (r,p) = \int_p \left(\frac{4\pi V_r}{h^3}\right) \underset{\overset{\uparrow}{(2m\varepsilon)^{1/2}}}{p} \cdot \underset{\overset{\nwarrow}{md\varepsilon}}{pdp}$$

$$= \int_\varepsilon \left(\frac{4\pi V_r}{h^3}\right)(2m\varepsilon)^{1/2}\, md\varepsilon$$

# of quantum states of a free, non-relativistic particle confined to volume V_r, and carrying energy $\varepsilon = \displaystyle\int_\varepsilon \left[\frac{2\pi V_r}{h^3}(2m)^{3/2}\right]\varepsilon^{1/2} d\varepsilon$

That was for a special case. More generally, the particle could be relativistic or may be confined by a potential. Then the integral is still over dε but the integrand could be different:

# of quantum states for a general particle $= \int_{\varepsilon} g(\varepsilon)\, d\varepsilon$.

$g(\varepsilon)$ is called the "density of states." It is the # of accessible quantum states per unit energy range $d\varepsilon$ centered on ε.

The density of states function encodes information about the environment (constraints, potential) of the particle, so it essentially characterizes the material (for example, the orbital structure). It will be used later on to find things like total # of electrons in a system, their total energy, and the heat capacity of their material.

II. Multi-particle states

Thus far we have referred only to the states of 1 particle.
If the system has >1 particle, each state is a unique permutation of the particles within 6-dimensional phase space.

Example: Consider 2 particles, each of which can have 3 states. The total number of states of the 2-particle system is $3 \times 3 = 9$. Specifically these are:

Particle 1, individual states	1	1	1	2	2	2	3	3	3
Particle 2, individual states	1	2	3	1	2	3	1	2	3
Combined two-particle system	1	2	3	4	5	6	7	8	9