Why Statistical Physics.

In this class we will study the physics of <u>macroscopic</u> systems. That is, the physics of systems with a <u>large</u> <u>number of equivalent</u> particles (or subsystems). There are two key concepts here:

① <u>large numbers</u>: Typically the # of particles N is extremely big, $\sim 10^{23}$, as in bulk solids, liquids, gases, stars, etc.

② <u>Equivalent</u>: unlike biological systems, in physics we deal with large collections of objects which for all purposes are <u>strictly identical</u>.

→ Reference to Thermodynamics.

As you know, at the <u>microscopic level</u>, the laws of physics are governed by Quantum Mechanics and, at high energies, Relativity plays a dominant role. At length scales large compared to the de Broglie wavelength of a particle, the ~~description is g~~ physics is described by Classical Physics.

In classical physics we can describe the state of a system completely by giving, at a given time t, the coordinates and velocities of all the particles. Since each particle

require 6 numbers (3 coordinates and 3 components of
the velocity ~~speed~~) we need 6N numbers to describe the
state. That is 6×10^{23} numbers! Suppose we know these all
numbers at a given time, to describe the system we need
to solve Newton's equations for some length of Time.
Suppose
~~If~~ we know these 6N numbers with some precision
given by some uncertainty Δx for the coordinates and
Δp for the velocities ~~momenta~~. As time goes by the particle's
coordinates and velocities will change. The problem is
that, for generic mechanical systems, the uncertainties
also grow and, in fact, they grow exponentially
fast. Thus, after some time, which depends on
the system, the uncertainty will become large $\Delta x \sim x$
and the system will have forgotten the initial

"mixing"

state!

For a generic isolated mechanical system, there are at least seven
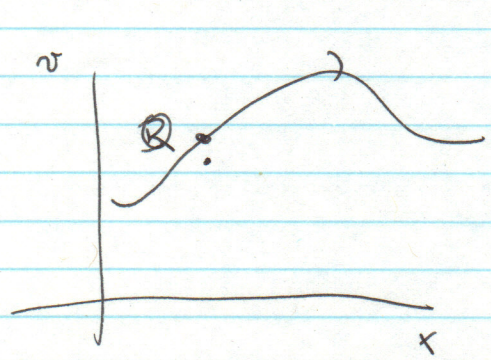conserved quantities: Energy (1), Momentum (3)
Symmetry
and Angular Momentum (3). There are simple
systems (i.e. two body problem with central forces)
for which these 7 conserved quantities are enough to

describe the system. In some exceptional cases more conservation laws are found and, very rarely, there are enough conservation laws to specify in full the state (integrable system).

Thus, for $N \gg 1$, even though at the microscopic level we may know "everything", at the macroscopic level the situation is quite different. We must conclude that even a perfect knowledge of the state of the system at the microscopic level is not sufficient to determine the state of a macroscopic system.

We can put these statements more formally. Let us define the state of the system by a point Q in the $6N$ dimensional space of coordinates and velocities (or momenta) ("phase space"). As the system evolves, the point Q will trace out a trajectory in phase space. Let us Suppose we choose a coord. system in which the total momentum $\vec{P}$ and angular momentum $\vec{L}$ are zero. Then the trajectory is characterized by the total energy E.

However, there is a large number of trajectories in phase space (i.e. histories of the system) ~~compatible with~~ for a given ~~total energy~~ total energy, momentum and angular momentum. Suppose now that we start the system a large number of times, always with the same values of E, $\vec{P}$ and $\vec{L}$. Obviously, the system will ~~occupy~~ be in one of the many possible histories compatible with these very few conditions. Alternatively, we can imagine a collection ~~of~~ or ensemble, of systems all with the same values of E, $\vec{P}$, and $\vec{L}$. If the system is ~~very~~ to complex ~~so~~ that it ~~does~~ forgets about the detailed initial conditions very rapidly, it is natural to assume that each one of these trajectories (or histories) is just as likely to happen and in very that many trials (or for a large ensemble) all ~~possible~~ possible trajectories are equally likely. In other words, we assume that very large systems with very complex dynamics behave effectively as if they were governed by simple statistical or probabilistic laws. This assumption that all possible states compatible

with the requirements of E, $\vec{P}$ and $\vec{L}$ fixed, are equally likely is known as the <u>Postulate</u> of <u>Equal a Priory Probabilities</u>. It was first stated by <u>Ludwig Boltzmann</u> ($\sim$1870). The <u>ensemble</u> of systems governed by this probability law is known as the <u>Micro canonical Ensemble</u>.

Another way to think about this problem is to use the <u>Axiom of Ergodicity</u> of a complex mechanical system which states that if one waits long enough the system will get arbitrarily close to any given state in phase space. If we pick a small volume in phase space around a given state, the <u>fraction of time</u> $\frac{\Delta t}{T}$ the system spends in that volume (where T is the total time evolution of the system), ~~then it follows that~~ is independent of the particular state (with a given energy).

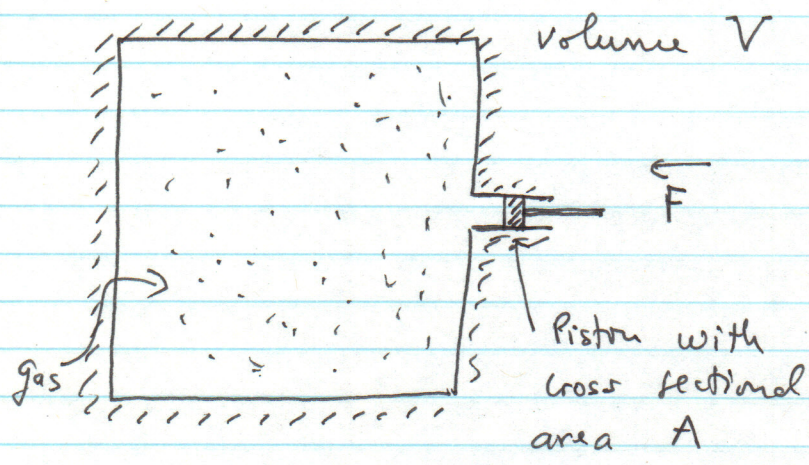Here too, the fraction $\frac{\Delta t}{T}$ can be regarded as the probability of that state.

with the requirements on E, $\vec{P}$, and $\vec{L}$, are equally likely is known as the Postulate of Equal a Priori Probabilities and it was first stated by Ludwig Boltzmann. The ensemble of systems governed by this probability law is known as the Microcanonical Ensemble.

Can Quantum Mechanics help to overcome this situation? The answer is actually no. QM in fact implies that even at the microscopic level the our knowledge of a physical system is always incomplete. The state of the system is determined by the wave function Ψ whose $|\Psi|^2$ is the probability density to find the system in a given state. Moreover only certain possible wave functions are allowed (each for a given allowed state with a fixed energy). But the state (or its wave function) is completely determined. However For a large system this is no longer possible. The level spacing (in general) becomes very small and, once again, you can give only the probability of a state with given total energy. In QM this state is said to be a mixed

~~only~~
~~state since the wave function is~~

state since only the probability of the state is known.

~~HW~~

<u>Simple Example of Statistical Physics</u>: <u>Elementary Kinetic Theory</u>

volume V

Pressure: $\dfrac{|\vec{F}|}{A} = P$

here $\vec{F}$ is the force that we must apply on the piston to keep the gas from expanding.
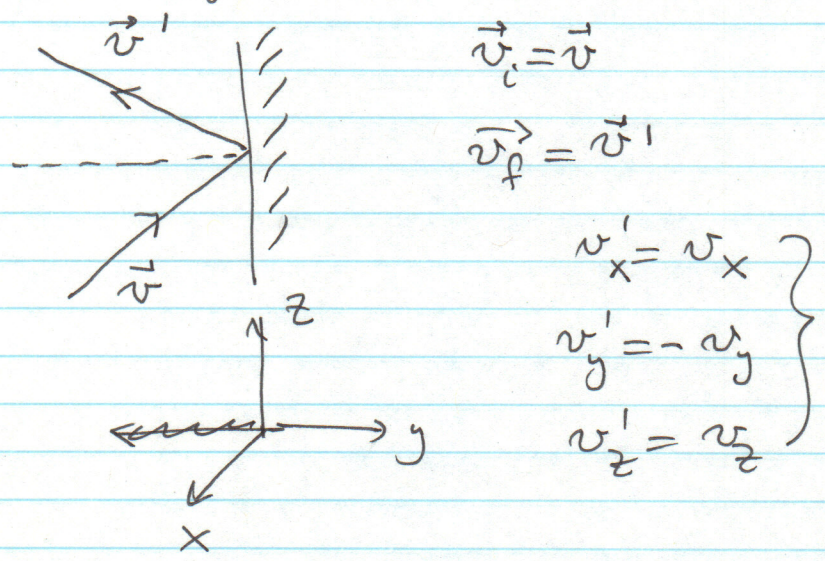
Piston with cross sectional area A

gas

Thus, from a macroscopic stand point (~~thermodynamics~~) the pressure P is a parameter (or variable) that characterizes the state of the gas. Another variable is the volume V occupied by the gas.

Microscopically, the gas has N atoms (or molecules) (i=1, ..., N) each with mass m (monoatomic gas) and each atom has velocity $\vec{v}_i$ at time t.

The velocities are in general very different

but there will be an average speed and the speed of most atoms will ~~be~~ be close to the average speed.

Let's assume for simplicity that the atoms do not collide with each other but only with the right walls of the container (this is what we call an Ideal Gas). Between two collisions with the wall (or the piston) the velocity of each atom remains unchanged. Upon a collision we find

$$\vec{v}_i = \vec{v}$$

$$\vec{v}_f = \vec{v}\,'$$

$$\left.\begin{array}{l} v'_x = v_x \\ v'_y = - v_y \\ v'_z = v_z \end{array}\right\}$$

Change in momentum:

$$\Delta \vec{p} = m \vec{v}_f - m \vec{v}\,' = m (\vec{v}_f - \vec{v}\,')$$

$$= 2m\, v_y\, \hat{y}$$

(Here $\hat{y}$ is the unit vector in the y direction.)

Force : rate of change of momentum: $\dfrac{d\vec{p}}{dt}$ (Newton's)

There is a force exerted against the wall (and piston) by the atoms that collide with the wall.

How many collisions in Δt ? Only by those atoms

that can hit the wall between t and $t + \Delta t$.

Say that an atom (A) is at a distance d from the wall and has velocity $v_y = v$. If $d < v \Delta t$ the atom will hit the wall in the interval Δt and it won't if $d > \ell = v \Delta t$

How many atoms ~~know~~ hit the wall?

There are N atoms in V. Thus the density is

$$\rho = \frac{N}{V} \quad (\# \text{ atoms per unit volume}).$$

The piston has area A. The atoms that hit the piston in Δt occupy a volume $A \, v_x \Delta t$

and there are

$$\rho \, A \, v_y \Delta t$$

atoms in that volume

(total)

The change in momentum is

$$\Delta \vec{P} = (\rho \, A \, v_y \Delta t) \; 2m v_y \, \hat{y}$$

$$\Rightarrow \vec{F} = \frac{\Delta \vec{P}}{\Delta t} = \hat{y} \; \rho \, A \; 2m v_y^2$$

Pressure:

$$\underline{P = 2m \, v_y^2 \, \rho}$$

But all atoms have $\neq$ velocity

$$\Rightarrow \quad P = 2 \rho m \langle v_y^2 \rangle \tfrac{1}{2} \qquad \text{(since, on average, } \tfrac{1}{2}$$
$$\text{of the atoms move forwards}$$
$$\langle v_y^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} v_{iy}^2 \qquad \text{and } \tfrac{1}{2} \text{ backwards)}$$

$$\Rightarrow \quad p = \rho m \langle v_y^2 \rangle$$

But the gas is $\underline{isotropic}$ (i.e. no preferred direction)

$$\Rightarrow \quad \langle v_y^2 \rangle = \langle v_x^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle \vec{v}^2 \rangle$$

$$\Rightarrow \quad p = \frac{1}{3} \rho m \langle v^2 \rangle$$

$$\langle \vec{v}^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\Rightarrow \quad p = \frac{2}{3} \rho \left\langle \frac{1}{2} m \vec{v}^2 \right\rangle$$

We recognize $\frac{1}{2} m \vec{v}^2$ as the kinetic energy ^{K} of one atom $\Rightarrow$

$$p = \frac{2}{3} \langle K \rangle \frac{N}{V}$$

For this case (no potential energy), the total energy $U = N \langle K \rangle + V \equiv NK$

$$\Rightarrow \quad p = \frac{2}{3} \frac{U}{V} \quad \Rightarrow \quad \boxed{pV = \frac{2}{3} U} \qquad \text{(Boyle)}$$

In your undergraduate class you showed...

What did we do: ① we made a microscopic model of the gas whose behavior we predicted using Classical Mechanics (Newton's laws). (calculated changes in momenta due to collisions, estimated the # of collisions and the total momentum change) ② we used statistical arguments to relate the pressure to the ~~average~~ total energy. The result is a relationship between the pressure P, the volume V and the total energy U which we derived from a microscopic kinetic consideration.

The relation

$$pV = \frac{2}{3} U \qquad\qquad (1)$$

is a thermodynamic relation which connects the thermodynamic variables P, V, and U for a gas in equilibrium (i.e. the averages do not change with time). This equation states that all not thermodynamic variables can be independent if the system is in equilibrium. This is also known as an equation of state.

Eqn. (1) relates macroscopic variables without reference to a microscopic parameter.

Statistical Ensembles

More formally, let us consider a macroscopic body or system of bodies, and assume that this system is closed: i.e. it does not interact with any other bodies. A small part of the system, small but large enough to be considered macroscopic, can be regarded as being separate from the rest. Such part will be called a subsystem. However a subsystem by definition is not closed since it interacts with other subsystems in complex ways. We will represent a subsystem by the coordinate and momentum of its center of mass. Let $\Delta p \Delta q$ be the volume of phase space occupied by the subsystem. After some long time T the trajectory of the subsystem in phase space will pass many times through each such possible volume. The postulate of equal a-priori probabilities is equivalent to the statement that the fraction of time a subsystem

speeds in some volume $\Delta p \Delta q$ is the same for all
such volumes accessible for a certain total
energy, total momentum and total angular
momentum. Thus we can ~~the~~ define the
probability of the state as the fraction of
time the system spends there.

$$w = \lim_{T \to \infty} \frac{\Delta t}{T}$$

This limit is constant in time.

$$\Rightarrow \quad dw = \mathcal{S}(\{q_i\}, \{p_i\}) \; dp \wedge dq$$

$$\underbrace{\qquad\qquad}_{\text{volume of phase space.}}$$

$\mathcal{S}(p, q)$ is the statistical distribution function.
It is normalized

$$\int dp \wedge dq \; \mathcal{S}(q, p) = 1$$

Notice that since this distribution function is
time-independent, it is independent of the initial
conditions! This is an equilibrium state.

If we know $\mathcal{S}(q, p)$ we can compute

averages of any physical observable $f(q,p)$

$$\langle f \rangle = \int dq \wedge dp \quad f(q,p) \; S(q,p)$$

From the assumption that the distribution is time independent (and from the definition of the distribution itself) that it follows that $\langle f \rangle$ is also equal to

$$\langle f \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt \; f(t)$$

Thus a complex deterministic system behaves (under these hypotheses) as a probabilistic system.

We have assumed above that the subsystems are not closed but interact very weakly with each other. By weakly we mean that the interactions are of sufficiently short range that their effects grow in proportion to the surface of the subsystem and not its volume. From this condition it follows that if A and B are two subsystems they can be regarded as being statistically independent. Hence the

Joint probability distribution factorizes

$$\boxed{P_{AB} = P_A \, P_B}$$

In practice this condition is much too restrictive but what will matter is that if a system is composed of N subsystems $\Rightarrow$ P

$$\ln P \leq \sum_{i=1}^{N} \ln P_i \leq N \, max(\ln P_i)$$

$$\Rightarrow \boxed{\ln P} \text{ is an } \boxed{\text{extensive}} \text{ quantity as } N \to \infty$$

For statistically independent quantities the following results follow. Let f be a physical additive quantity and f_i its value for a subsystem $\Rightarrow$

$$\sum_{i=1}^{N} f_i = N \langle f \rangle$$

Likewise $\Delta f_i = f_i - \langle f \rangle$

$$\langle (\Delta f)^2 \rangle = \langle (\Sigma_i \, \Delta f_i)^2 \rangle =$$

statistical independence.

$$= \Sigma_{i,j} \langle \Delta f_i \, \Delta f_j \rangle$$

$$= \Sigma_i \langle (\Delta f_i)^2 \rangle$$
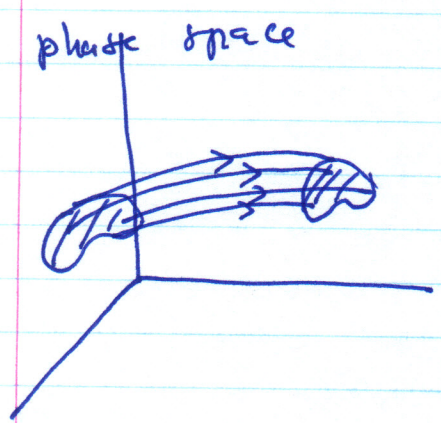
$$\Rightarrow \frac{\sqrt{\langle (\Delta f)^2 \rangle}}{\langle f \rangle} \sim \frac{1}{\sqrt{N}}$$

In the theory of probabilities is proven that the sum of weakly correlated random variables obey the <u>central limit theorem</u> which implies that the conditions stated above are true.

Liouville's Theorem

Let us discuss the general properties of the distribution function $f(q,p)$. We can brew the evolution of the system by

phase space

saying that of we observe it at times $t_1, ..., t_N$, then, at each time the subsystem will be found at a set of points $P_1, ..., P_N$ of phase space. Alternatively, $P_1, ..., P_N$ can be regarded as the places in phase space in which an <u>ensemble</u> of identically prepared but independent subsystems are found at the same time t. Then the distribution function will tell us what is the probability to find a subsystem of the ensemble at a particular

state $\Gamma \equiv (\{q_i\}, \{p_i\})$ of phase space. Each subsystem is then one point in phase space, which is a $2N$-dimensional Euclidean space (for N coordinates). We can think of this as a gas of particles (each particle being $\overleftrightarrow{a}$ subsystem). Since the # of subsystems is fixed (and conserved) $\cancel{the}$ the __density__ ρ obeys a continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

$\vec{v}$: "velocity"

Steady state: $\frac{\partial \rho}{\partial t} = 0$

$$\Rightarrow \quad \cancel{\vec{\nabla}} \vec{\nabla} \cdot (\rho \vec{v}) = 0 \Rightarrow \sum_{i=1}^{N} \left[\frac{\partial}{\partial q_i} \left(\rho \frac{dq_i}{dt} \right) + \frac{\partial}{\partial p_i} \left(\rho \frac{dp_i}{dt} \right) \right]$$

$$= 0$$

$$\sum_{i=1}^{N} \left(\frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} \right) + \rho \sum_{i=1}^{N} \left[\frac{\partial}{\partial q_i} \left(\frac{dq_i}{dt} \right) + \frac{\partial}{\partial p_v} \left(\frac{dp_i}{dt} \right) \right] = 0$$

Hamilton's Eqns: $\quad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \qquad \frac{dp_i}{dt} = - \frac{\partial H}{\partial q_i}$

$$\Rightarrow \quad \frac{\partial}{\partial q_i}\left(\frac{dq_i}{dt}\right) = \frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}$$

$$\frac{\partial}{\partial p_i}\left(\frac{dp_i}{dt}\right) = -\frac{\partial}{\partial p_i}\frac{\partial H}{\partial q_i} = -\frac{\partial^2 H}{\partial q_i \partial p_i}$$

$$\Rightarrow \boxed{\frac{d\rho}{dt} = \sum_{i=1}^{N}\left(\frac{\partial \rho}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial \rho}{\partial p_i}\frac{dp_i}{dt}\right) = 0}$$

Liouville's Theorem

$$\Rightarrow \quad \rho \text{ is constant along a classical trajectory.}$$

of the subsystem.

A consequence of Liouville's Thm is that ρ depends only on the constants of motion. In addition we saw before that $\ln\rho$ must be an additive ~~~~~~~~ function $\Rightarrow$ only additive integrals of motion are allowed.

In a generic mechanical system there are only $\underline{7}$ additive integrals of motion (there are exceptional systems that have more): the total

Energy $\underline{E}$, the total linear momentum $\vec{P}$ and the total angular momentum $\vec{M}$. For a subsystem α

$$\Rightarrow \quad \ln g_\alpha = C_\alpha + \beta \, E_\alpha [q, P] + \vec{\gamma} \cdot \vec{P}[q, P] + \vec{\delta} \cdot \vec{M}[q, P]$$

$$\uparrow \qquad \uparrow \qquad\qquad\qquad \uparrow \qquad\qquad \uparrow$$

normalization
constant

$\hspace{3cm}$ independent of the subsystem!

If we go to the center of mass frame ($\vec{P} = 0$)

and the system is not rotating ($\vec{M} = 0$)

$\Rightarrow$ $\ln g$ depends only on the energy, E.

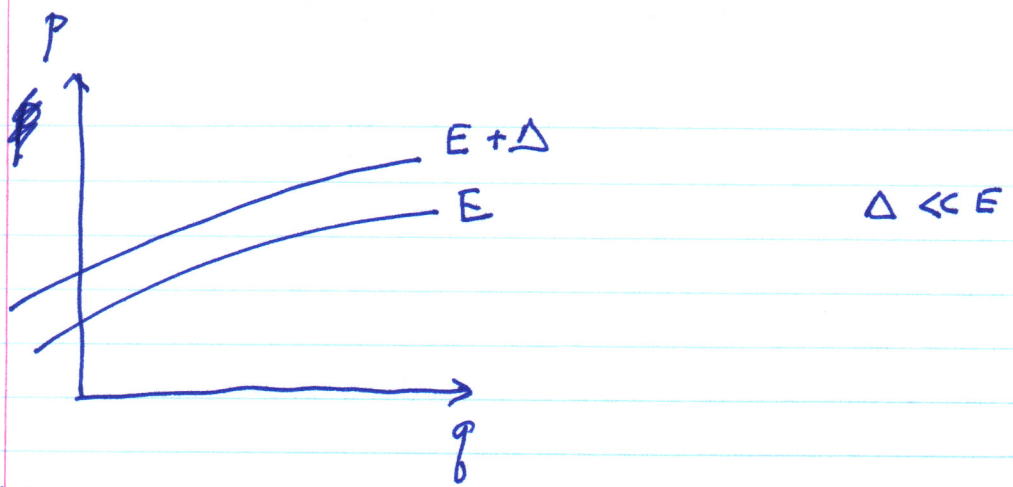$\Rightarrow$ This is almost (but not quite) correct. The manifold of points accessible to any subsystem is the phase space restricted by the conditions that E, $\vec{P}$ and $\vec{M}$ are fixed. This is a $6N-7$ -dimensional space. $\Rightarrow$ if $\int \int \rho \, dp \, dq \neq 0 \Rightarrow$ ρ must diverge on the allowed manifold and vanish outside. $\Rightarrow$

$$\boxed{\begin{array}{c} \rho = \text{constant} \times \delta(E - E_0) \times \delta^{(3)}(\vec{P} - \vec{P}_0) \, \delta^{(3)}(\vec{M} - \vec{M}_0) \\[4pt] \text{This is the Microcanonical Ensemble.} \end{array}}$$

Thus, the Postulate of equal a-priori probability implies that in equilibrium, the system is a member of the Microcanonical Ensemble whose density distribution function satisfies $(\Delta \ll E)$

$$\rho(p,q) = \begin{cases} \text{const.} & \text{if} \quad E < H(q,p) < E+\Delta \\ 0 & \text{otherwise} \end{cases}$$

All members of the ensemble have the same N, V.

Let $\Gamma(E)$ be the volume of phase space occupied by the Microcanonical Ensemble, i.e.

$$\Gamma(E) = \int_{E < H(q,p) < E+\Delta} d^{3N}q \; d^{3N}p = \text{# of states in the energy shell}$$

and let $\Sigma(E)$ be

$$\Sigma(E) = \int_{H(q,p) < E} d^{3N}q \; d^{3N}p$$

$$\Rightarrow \quad \Gamma(E) = \Sigma(E+\Delta) - \Sigma(E)$$

If $\quad \Delta \ll E \Rightarrow \quad \Gamma(E) = \omega(E)\Delta + O(\Delta^2)$

where $\quad \omega(E)$ is the density of thermodynamic states.

$$\omega(E) = \frac{\partial \Sigma(E)}{\partial E}$$

Let us consider the quantity

$$S(E,V) = k \log \Gamma(E)$$

which we will show it behaves like the

thermodynamic entropy. Let us prove 2 properties

ⓐ $\quad S(E,V)$ is extensive

ⓑ $\quad S(E,N)$ satisfies the properties of the

entropy ^{as} required by the Second Law of
Thermodynamics.

ⓐ <u>Extensivity</u>. let us divide the system into

two subsystems with N_1 particles and volume V_1

and N_2, V_2 respectively. We will assume

that the total energy (Hamiltonian) is

$$H(\vartheta, P) = H_1(\vartheta_1, P_1) + H_2(\vartheta_2, P_2)$$

We have ignored the interaction term. In practice

our conclusions will continue to hold provided the interactions do not grow with the volume of the system. We are also assuming that the particles are _distinguishable_. We will see that this will lead to problems which we will deal with later on. (Gibbs Paradox)

Thus if we have two separate subsystems we can write

$$S_1(E_1, V_1) = k \log \Gamma_1(E_1)$$

$$S_2(E_2, V_2) = k \log \Gamma_2(E_2)$$

For the composite system the total energy will lie between E and $E + 2\Delta$, s.t.

$$E < E_1 + E_2 < E + 2\Delta$$

What is the volume that of the composite system occupies in phase space? Obviously it is $\Gamma_1(E_1) \Gamma_2(E_2)$

However we will only specify the total energy E

$$\Rightarrow \quad \Gamma(E) = \sum_{intervals} \Gamma_1(E_i) \Gamma_2(E - E_i)$$

$\Rightarrow$ the entropy for a composite system with

$$N = N_1 + N_2 \quad \text{and} \quad V = V_1 + V_2$$

$$S(E,V) = k \log \left(\sum_{\nu=1}^{E/\Delta} \Gamma_1(E_i) \, \Gamma_2(E - E_i) \right)$$

However, as $N_1 \to \infty$ and $N_2 \to \infty$ there is a configuration with $\bar{E}_1, \bar{E}_2$, which makes the probability maximal. This term (one among many positive terms) dominates the sum in this limit.

Clearly we can bound $\Gamma(E)$ as follows

$$\Gamma_1(\bar{E}_1) \, \Gamma_2(\bar{E}_2) \leq \Gamma(E) \leq \frac{E}{\Delta} \, \Gamma_1(\bar{E}_1) \, \Gamma_2(\bar{E}_2)$$

$$\frac{E}{\Delta} \quad \text{\# of energy intervals}$$

$\Rightarrow$

$$k \log \left(\Gamma_1(\bar{E}_1) \, \Gamma_2(\bar{E}_2) \right) \leq S(E,V) \leq k \log \left(\Gamma_1(\bar{E}_1) \Gamma_2(\bar{E}_2) \right)$$
$$+ k \log \left(\frac{E}{\Delta} \right)$$

since $\Gamma_1(\bar{E}_1) \gg \frac{E}{\Delta}$ and $\Gamma_2(\bar{E}_2) \gg \frac{E}{\Delta}$

$$\Rightarrow S(E,V) \underset{N \to \infty}{=} k \log \Gamma_1(\bar{E}_1) + k \log \Gamma_2(\bar{E}_2)$$

$$= S_1(E_1, V_1) + S_2(E_2, V_2)$$

$\Rightarrow$ S is additive

Moreover, what we just proved is that two systems weakly coupled to each other will have energies $\bar{E}_1$ and $\bar{E}_2$, $E = \bar{E}_1 + \bar{E}_2$, ~~chosen~~ in ~~st~~ such a way that the <u>probability</u> us <u>largest</u> .

$$\Rightarrow \quad \delta(\Gamma_1(E_1) \, \Gamma_2(E_2)) = 0 \qquad \delta(E_1 + E_2) = 0$$

$$\frac{\partial}{\partial E_1} \log \Gamma_1(E_1) \Big|_{E_1 = \bar{E}_1} = \frac{\partial}{\partial E_2} \log \Gamma_2(E_2) \Big|_{E_2 = \bar{E}_2}$$

$\Rightarrow$ the <u>configuration</u> of <u>maximum probability</u>

is such that the quantity

$$\frac{\partial}{\partial E} \log \Gamma(E)$$

is the <u>same</u> for all systems in contact and in equilibrium.

We will define the <u>absolute temperature</u> T s.t.

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \qquad \Rightarrow \qquad T_1 = T_2 \qquad \text{This is the}$$

Zeroth law of thermo-

Thus in statistical mechanics there is a natural definition of Entropy. Entropy is the logarithm of the number of accessible states.

The pple. of maximum probability is the principle of maximum entropy. This also implies that for a closed system the ~~the~~ equilibrium state is the maximum entropy state $\Rightarrow$ entropy cannot decrease is a probabilistic law. This is the nature of the Second Law of Thermodynamics.

the pple. that

Properties of the Entropy

Consider two systems, I and II. Suppose we remove an amount of energy ΔU from system I and that we add it to system II.

$\Rightarrow \Delta E_I = - \Delta U$

$\Delta E_{II} = + \Delta U$

How does the entropy change?

Suppose that initially system I was at temperature T_I and system II at T_{II}.

$$\frac{1}{T_I} = \frac{\partial S_I}{\partial E_I} \qquad \frac{1}{T_{II}} = \frac{\partial S_{II}}{\partial E_{II}}$$

The entropy of the combined system is

$$S = S_I + S_{II} = S(E, V) = S(E_I, E_{II})$$

How does S change as $\Delta E_I = -\Delta U$

$$\Delta E_{II} = +\Delta U \quad ?$$

$$\Delta S = \left.\frac{\partial S}{\partial E_I}\right|_{E_{II}} \Delta E_I + \left.\frac{\partial S}{\partial E_{II}}\right|_{E_I} \Delta E_{II}$$

$$\Delta S = \left.\frac{\partial S_I}{\partial E_I}\right|_{E_{II}} + \left.\frac{\partial S_{II}}{\partial E_{II}}\right|_{E_I}$$

Since $\dfrac{\partial S_I}{\partial E_{II}} = \dfrac{\partial S_{II}}{\partial E_I} = 0$

$$\Rightarrow \Delta S = \frac{1}{T_I}\Delta E_I + \frac{1}{T_{II}}\Delta E_{II} = -\left(\frac{1}{T_I} - \frac{1}{T_{II}}\right)\Delta U$$

$\Rightarrow$ If $T_I > T_{II} \Rightarrow \Delta S > 0$

and $T_I < T_{II} \Rightarrow \Delta S < 0$

$\Rightarrow$ if we transfer energy from a <u>hotter</u> body

to a <u>colder</u> body the <u>entropy increases</u>.

Since the entropy is the log of the # of

accessible states, the <u>final state with more</u>

<u>more accessible states is more probable</u>. $\Rightarrow$

the physically allowed state is the one with

largest probability $\Rightarrow$ Second Law.

This stops in the equilibrium state where $T_I = T_{II}$

<u>Definition</u> :

<u>Heat</u>: is the <u>spontaneous</u> flow of energy between

two systems in thermal contact, and at different temperature.

In other words it is the exchange of energy <u>not</u>

due to the work of external forces. Let us

denote by Q this exchange of energy and

let W_I be the work done by external forces on system

I (W_{II} on System II) $\Rightarrow$

$$\Delta E_I = -Q + W_I$$

$$\Delta E_{II} = +Q + W_{II}$$

In general

$$\Delta E = Q + W$$

First Law of Thermodynamics

$Q > 0$ if heat flows <u>into</u> the system

$W > 0$ if work is done <u>on</u> the system.

Quantum Systems: The Density Matrix

In quantum mechanics, the physical states allowed to an isolated (finite) system are <u>pure states</u>.

Pure states are linear superpositions of a set of basis states $\{|\psi_n\rangle\}$. This set is linearly independent and complete, i.e.

$$\hat{1} = \sum_n |\psi_n\rangle\langle\psi_n|$$

$\uparrow$

Projection operator on the state $|\psi_n\rangle$

Thus a pure state is

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

$$c_n \in \mathbb{C}$$

Once this state is given at time t_0 ⟹ the ulterior evolution of the system is fully determined

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \qquad \text{Schrödinger's Equation.}$$

with $\quad |\psi(t_0)\rangle = |\psi\rangle$ ⟹ *phase coherence*

⟹ the functions $c_n(t)$ (complex) describe the evolution of the system (in the basis $\{|\psi_n\rangle\}$)

For a macroscopic (quantum) system this is as hard to do as it is for a classical system.

In practice systems are never completely isolated. The true "system" is the system + the "universe".

Let the Hilbert space of the combined system be spanned by states of the form $\quad |\varphi_i\rangle|\theta_j\rangle \equiv |\varphi_i, \theta_j\rangle$

$$\underset{\text{system}}{\uparrow} \qquad \underset{\text{universe}}{\uparrow}$$

$$\Rightarrow \quad |\psi\rangle = \sum_{i,J} C_{i,J} \, |\varphi_i\rangle |\theta_J\rangle$$

("Schmidt decompositions")

Let x be the "coordinates" of the system and $\underline{X}$ be the "coordinates" of the rest $\Rightarrow$

$$\varphi_i(x) = \langle x | \varphi_i \rangle$$

$$\theta_J(\underline{X}) = \langle \underline{X} | \theta_J \rangle$$

$$\Rightarrow \quad \psi(x, \underline{X}) = \langle x, \underline{X} | \psi \rangle$$

$$= \sum_{i,J} C_{i,J} \, \varphi_i(x) \, \theta_J(\underline{X})$$

$$= \sum_i \underbrace{\left(\sum_J C_{iJ} \, \theta_J(\underline{X}) \right)}_{C_i(\underline{X})} \varphi_i(x)$$

$$C_i(\underline{X}) = \sum_J C_{iJ} \, \theta_J(\underline{X})$$

Let $\hat{A}$ be a physical observable ~~which~~ that acts only on the states of the system ~~alone~~

$$\Rightarrow \quad \hat{A} = \sum_{i,i'} A_{0_{i,i'}} |\varphi_i\rangle \langle \varphi_{i'}|$$

$$= \sum_{i,i'} \sum_J A_{ii'} \, |\varphi_i\rangle |\theta_J\rangle \langle \theta_J| \langle \varphi_{i'}|$$

$$(\text{since} \quad \hat{I} = \sum_J |\theta_J\rangle \langle \theta_J| \, , \text{ completeness})$$

$$\Rightarrow \quad \langle \psi | \hat{A} | \psi \rangle =$$

$$= \sum_{\substack{i,i' \\ J,J'}} c_{iJ}^* c_{i'J'} \langle \varphi_i \theta_J | \hat{A} | \varphi_{i'} \theta_{J'} \rangle$$

$$= \sum_{\substack{i,i' \\ J,J'}} c_{iJ}^* c_{i'J} A_{ii'}$$

$$= \sum_{i,i'} \left(\sum_J c_{iJ}^* c_{i'J} \right) A_{ii'}$$

Density Matrix: $\quad \hat{\rho}_{ii'} = \sum_J c_{iJ}^* c_{i'J} = \langle i | \hat{\rho} | i' \rangle$

$$\langle \psi | \hat{A} | \psi \rangle = \sum_{i,i'} \hat{\rho}_{i'i} \hat{A}_{ii'}$$

$$= tr \left(\hat{\rho} \hat{A} \right) = tr \left(\hat{A} \hat{\rho} \right)$$

$$\rho_{ii'}^* = \sum_J c_{iJ}^* c_{i'J} = \rho_{i'i}$$

$$\Rightarrow \hat{\rho} = \hat{\rho}^\dagger \qquad \hat{\rho} \text{ is hermitean.}$$

and $\quad tr \hat{\rho} = \sum_i \rho_{0i} = \sum_i \sum_J c_{iJ} c_{iJ}^*$

$$= \sum_{i,J} |c_{iJ}|^2 = |\langle \psi | \psi \rangle|^2$$

If $|\langle \psi | \psi \rangle| = 1 \Rightarrow \boxed{tr \hat{\rho} = 1}$

Let $\{|w_i\rangle\}$ be a basis of eigenvectors of $\hat{\rho}$

$$\hat{\rho}|w_i\rangle = w_i |w_i\rangle$$

$$\hat{\rho} = \sum_i w_i |w_i\rangle\langle w_i|$$

$$\text{tr}\,\hat{\rho} = \sum_i w_i = 1$$

Consider $\hat{A} = |i'\rangle\langle i'| = \sum_J |i'J\rangle\langle Ji'|$

$$\Rightarrow \langle\hat{A}\rangle = \langle\Psi|\hat{A}|\Psi\rangle = \sum_J |\langle\Psi|i',J\rangle|^2 \geq 0$$

But $\langle\hat{A}\rangle = \text{tr}(\hat{A}\hat{\rho}) = \sum_j \langle j|i'\rangle\langle i'|\hat{\rho}|j\rangle$

$$= \rho_{i'i'} = w_i \geq 0$$

$$\Rightarrow \quad w_i \geq 0 \quad \text{and} \quad \sum_i w_i \gtrless 1 \quad \Rightarrow \text{probabilities}!$$

We can reformulate QM as follows

① Any system is describable by a density matrix

$$\hat{\rho} = \sum_i w_i |i\rangle\langle i|$$

where ① $\{|i\rangle\}$ is a complete set of orthonormal vectors

② $w_i \geq 0$

③ $\sum_i w_i = 1$

④ $\qquad \langle \hat{A} \rangle = tr(\hat{\rho}\hat{A}) = \sum_i w_i \langle i | \hat{A} | i \rangle$

$\langle i | \hat{A} | 0 \rangle$ is the expectation value of $\hat{A}$ in state $|i\rangle$ and w_i is the probability to find the system in state $|i\rangle$. We have an __ensemble__ of systems with the probability distribution $\{w_i\}$.

We will call this a __mixed state__. A pure __state__ is a state in which __only one__

$$w_i \neq 0$$

i.e. $\qquad w_i = 1$

$$w_j = 0 \qquad j \neq i$$

$$\Rightarrow \langle \hat{A} \rangle = \langle i | \hat{A} | i \rangle$$

(VII) Equation of Motion for $\hat{\rho}$

$$\hat{\rho}(t) = \sum_i w_U | \psi_i(t) \rangle \langle \psi_i(t) |$$

$$i\hbar \frac{\partial}{\partial t} | i(t) \rangle = \hat{H} | i(t) \rangle$$

$$-i\hbar \frac{\partial}{\partial t} \langle i(t)| = \langle i(t)| \hat{H}$$

$$\Rightarrow \quad \frac{\partial \hat{\rho}}{\partial t} \equiv \dot{\hat{\rho}} = \sum_i w_i \; \frac{1}{i\hbar} \hat{H} |i(t)\rangle \langle i(t)|$$

$$- \sum_i w_i \; \frac{1}{i\hbar} |i(t)\rangle \langle i(t)| \hat{H}$$

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

$$\Rightarrow \boxed{i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]}$$

quantum mechanical Liouville's theorem.

and

$$\frac{d}{dt} \langle \hat{A} \rangle = \frac{d}{dt} \mathrm{tr}(\hat{\rho}\hat{A}) = \mathrm{tr}\left(\frac{d\hat{\rho}}{dt} \hat{A}\right) + \mathrm{tr}\left(\hat{\rho} \frac{d\hat{A}}{dt}\right)$$

$$= \frac{1}{i\hbar} \mathrm{tr}\left([\hat{H}, \hat{\rho}] \hat{A}\right) + \mathrm{tr}\left(\hat{\rho} \frac{d\hat{A}}{dt}\right)$$

$$\boxed{\frac{d}{dt} \langle \hat{A} \rangle = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{1}{i\hbar} \mathrm{tr}\left([\hat{A}, \hat{H}] \hat{\rho}\right)}$$

Microcanonical Ensemble:

$$P_{ii'} = w_i \, \delta_{ii'} \qquad (\text{i.e. } \hat{P} \text{ is diagonal})$$

$$w_i = \begin{cases} \text{const} & \text{for } E \leq E_i \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

i.e. all accessible states have the same probability. (where $\hat{H}|E_n\rangle = E_n |E_n\rangle$)

$$\Rightarrow \hat{P} = \sum_{E \leq E_n \leq E + \Delta} |\psi_n\rangle \langle \psi_n| \qquad (\text{unnormalized})$$

(unnormalized!) $\text{Tr}\,\hat{P} = \sum_n P_{nn} = \Gamma(E)$ is the # of states with energy in the interval $[E, E+\Delta]$

$\Rightarrow$ Entropy

$$S(E,V) = k \log \Gamma(E) = \text{k log Tr } \hat{\rho}$$

$$= k \log (\text{Tr}\,\hat{\rho})$$

for $\hat{P}$ unnormalized

The Canonical Ensemble (the Gibbs Ensemble)

Consider a physical system in equilibrium at temperature T. Q: What is the probability to find the system in a state with energy E?

Q1: How do we maintain a system at fixed temperature

A: Let R be a very large system already in equilibrium at temperature T. Let S be the system we are interested in.

R: reservoir or heat bath

Let us assume that the joint system RUS is isolated. After R and S become in thermal contact they reach an equilibrium state with common temperature T'. In this process an amount ΔU of energy is exchanged between R and S.

$$\Delta T = T' - T = \frac{\Delta U}{C \, M_{reservoir}}$$

↑ Specific heat of the reservoir

Since $M_{reservoir} \to \infty \Rightarrow (\Delta T)_{reservoir} = 0 \Rightarrow T_{res} = const.$

Since $S' \cup R$ is isolated $\Rightarrow$

$$E = U_R + U_S$$

In state $|n\rangle$, the system has energy $U_S = E_n$

and $U_R = E - E_n$

The probability of being in state $|n\rangle$ is

proportional to the # quantum states of the joint

system when S' is in $|n\rangle$. This equal to

# of quantum states of R when S' is in $|n\rangle$ times

# of quantum states of S' when S' is in $|n\rangle$ $(=1)$

$\overset{\propto}{}$ (proportional to)

$\Rightarrow$ the probability is ~~given by~~ the # of quantum

states of R when S' is in state $|n\rangle = \Gamma'_{res}(E-E_n)$

Notice that $|E| \gg E_n|$

Since R is large $\Rightarrow T$ does not change for small

changes of the energy E_n

$$\Rightarrow \text{const.} = \frac{1}{k_B T} = \frac{\partial S_{reservoir}}{\partial E_R}$$

$$\frac{\partial \log \Gamma_{res}}{\partial E} = \frac{1}{kT} \Rightarrow \log \Gamma_{res} = \frac{E_{res}}{kT} + \text{const.}$$

$$\Gamma_{res}(E_{res}) = e^{\frac{E_{res}}{kT}} \times const.$$

$\Rightarrow$ Probability to found the system with energy E_n at temperature T is $\propto \Gamma_{res}(E_{res})$

$$P(E_n) = const \; e^{E_{res}/kT}$$

$$= const \times e^{(E-E_n)/kT}$$

$$\Rightarrow P(E_n) = const' \times e^{-E_n/kT}$$

Normalization

$$\sum_n P(E_n) = 1$$

$$1 = const' \times \sum_n e^{-\frac{E_n}{kT}}$$

Partition Function $\quad Z = \sum_n e^{-E_n/kT}$

$$\boxed{P(E_n) = \frac{1}{Z} e^{-\frac{E_n}{kT}}}$$

Gibbs ~~Boltzmann~~ Distribution

(Gibbs Ensemble)
or Canonical
Ensemble.

Entropy and the Canonical Ensemble

In the Microcanonical Ensemble the entropy is the logarithm of the # of available states at fixed energy. In the canonical ensemble the energy is not fixed but the probability to find the system at that energy is given by the Gibbs distribution. The entropy now is the expectation value of the log of the # of states at each energy $\Rightarrow$

$$S = - k \sum_n P_n \ln P_n = - k \langle \ln P \rangle$$
$$\equiv - k \, \text{tr}(\hat{\rho} \ln \hat{\rho})$$

when $\hat{\rho}$ is the density matrix for the Gibbs distribution. Here I used that $\text{tr}\hat{\rho} = \sum_n \rho_n = 1$

Using this definition we get the following result

$$S = - k \sum_n P_n \ln P_n = -\frac{k}{Z} \sum_n e^{-E_n/kT} \left[-\frac{E_n}{kT} - \ln Z \right]$$
$$= \frac{1}{T} \langle E \rangle + k \ln Z$$

If we now define the Free Energy F

$$F = -kT \ln Z$$

$$\Rightarrow \quad \frac{\partial F}{\partial T} = -S$$

we will shortly see that this relation holds in thermodynamic equilibrium.

Similarly, the internal energy $\mathcal{U} = \langle E \rangle$ is

$$\mathcal{U} = \langle E \rangle = \frac{1}{Z} \sum_n E_n \, e^{-E_n/kT}$$

If we now define $\beta = \frac{1}{kT} \Rightarrow \beta F = -\ln Z$

$$\Rightarrow \quad \langle E \rangle = \frac{\partial \ln Z}{\partial \beta} = \frac{\partial (\beta F)}{\partial \beta}$$

Thus we can compute the internal energy and the entropy once we know the partition function.