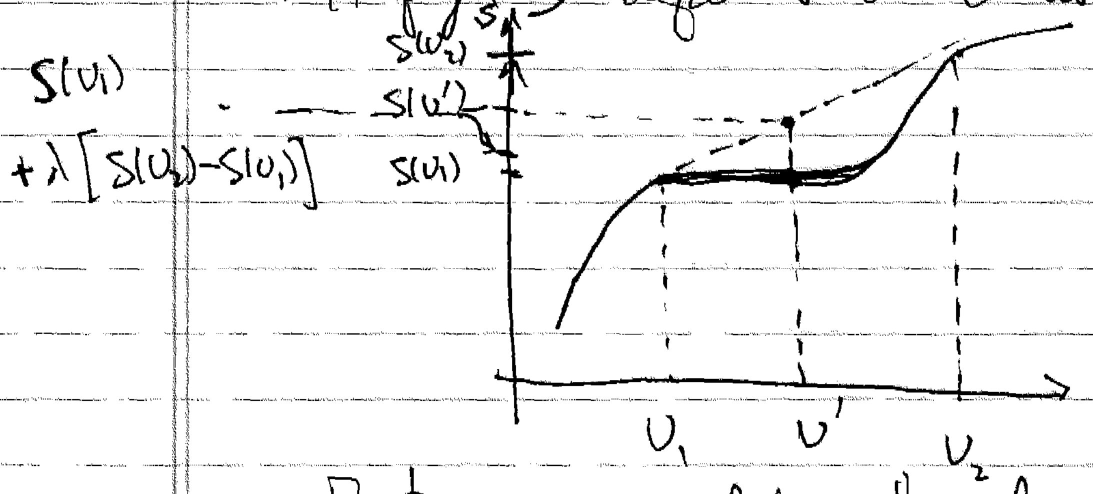
Lecture #4

Thermodynamic Stability.

Consider a system whose ~~energy U de~~ entropy, S depends on U as shown:



(Monotonically increasing)

Between U_1 and U_2, the chord drawn is always greater than the entropy curve.

For any point U', where $U_1 < U' < U_2$

$$U' = U_1 + \lambda(U_2 - U_1)\ ;\ \lambda \in [0,1]$$

$$\therefore \underbrace{S(U_1) + \lambda\left[S(U_2) - S(U_1)\right]}_{\text{straight-line (chord)}} \geq S(U')$$

(Entropy of 1 region)

$$\therefore \lambda S(U_2) + (1-\lambda)S(U_1) \geq S(\lambda U_2 + (1-\lambda)U_1)$$

(Entropy of 2 regions)

$\therefore$ If a system had energy U', then it could increase its entropy by spontaneously subdividing into 2 regions, one w/ energy λU_2 and one with energy $(1-\lambda)U_1$

$\Rightarrow$ Instability

(c) (11)

$\therefore$ For a system to be stable, the entropy must satisfy

$$\lambda S(U_2) + (1-\lambda) S(U_1) \leq S(\lambda U_2 + (1-\lambda) U_1)$$

$\Rightarrow$ S is a concave function of energy U.

$\frac{\partial^2 S}{\partial U^2} < 0$, In a similar fashion, one can show $\frac{\partial^2 S}{\partial V^2} < 0$, or more generally

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \leq 2S(U,V,N)$$

Taylor expand $\Rightarrow$

$$(\Delta U, \Delta V) \begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial U \partial V} \\ \frac{\partial^2 S}{\partial V \partial U} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix} \begin{pmatrix} \Delta U \\ \Delta V \end{pmatrix} \leq 0$$

$\therefore$ both eigenvalues of $\downarrow$ are negative, so

$$\det(\;) = \frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 \geq 0$$

Statistical Mechanics:

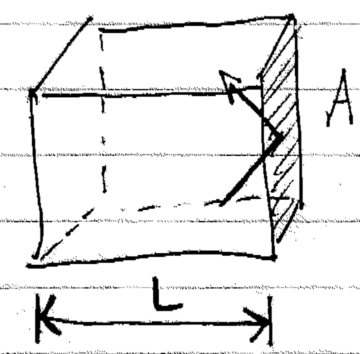
Basic Idea: Thermodynamics is described by the collective variables $(N, V, U, \dots)$ while the underlying dynamics and constituent particles are described by a seperate microscopic theory.

We can treat the microscopic theory with either classical dynamics, quantum dynamics, etc. The power of thermodynamics is the fact that the underlying theory is not so important.

Kinetic Theory: Hyphothesis: Everything is made of microscopic Atoms., $N \gg 1$

$$E = \sum_i \varepsilon_i \ ; \ N = \sum_i n_i$$

Ideal Gas: $\text{Pressure} = \left\langle \frac{F}{A} \right\rangle_{time}$



$$\bar{F} = \frac{\Delta p_\perp}{\Delta t} = (\Delta p_\perp) \cdot \Gamma \quad ; \ \Gamma \sim \text{collision rate.}$$

$$P = \left\langle \frac{\Delta p_\perp \cdot \Gamma}{A} \right\rangle_{time} \qquad \cancel{\frac{\Gamma}{A}} \qquad \frac{\Gamma}{A} = \frac{v_\perp \cdot N}{A \cdot (2L)}$$

$$\left(\Gamma = \frac{v_\perp}{2L}\right)$$

$$\Delta p_\perp = 2mv_\perp$$

$$P = \left\langle \frac{2m v_\perp^2 N}{2 V} \right\rangle_{time} = \frac{mN}{V} \left\langle v_\perp^2 \right\rangle_{time}$$

New idea in physics: Randomness.

If we measure a given atom, it has no preferred direction. It is equally likely to find the atom moving in any direction.

Why? <u>Ergodic</u> <u>Hypothesis</u> - Can be proven for certain classes of dynamical systems. — Much has been recently learned about the boundry between integrable systems (like the harmonic oscillator) and chaotic systems (systems that display exponential sensitivity to initial conditions)

Ergodic → Trajectories uniformly fill phase space subject only to energy conservation.

$$\cancel{\langle p_x^2 \rangle} \Rightarrow \langle O \rangle_{time} = \langle O \rangle_{Energy\text{-}surface}$$

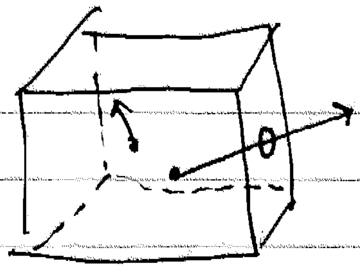
More on this later!

$$\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle$$

$$\therefore \langle p^2 \rangle = \langle p_x^2 + p_y^2 + p_z^2 \rangle = 3 \langle p_x^2 \rangle$$

$$\therefore P = \frac{mN}{3V} \langle v^2 \rangle = \frac{2}{3}\left(\frac{N}{V}\right) \langle K \rangle \; ; \; K = \tfrac{1}{2} m v^2$$

But, from ideal gas, $PV = N k_B T \Rightarrow \langle K \rangle = \frac{3}{2} k_B T = U$



Suppose we now poke a hole in the box and measure the magnitude of the ~~momentum~~ velocity between V and $V+dV$; what is the distribution?

$$\int p(\vec v)\, d^3\vec v = 1$$

Ergodicity $\Rightarrow$ (i) Isotropic (No preferred direction)
(ii) statistic independence

(ii) $\Rightarrow$ $p(\vec v) = P_x(v_x)\, P_y(v_y)\, P_z(P_z)$

(i) $\rightarrow$ $P(\vec v) = P(|\vec v|)$

$$\therefore \quad p(\vec v) = f(v_x^2 + v_y^2 + v_z^2) = f(v^2)$$

Solution $\therefore$ $P_i(v_i) \propto e^{\alpha(v_i^2)}$, so $e^{\alpha(v_x^2+v_y^2+v_z^2)} = e^{\alpha v^2}$

$\Rightarrow$ $P(\vec v)$ is a Gaussian

$$P_i(v_i) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\frac{v_i^2}{2\sigma^2}\right]$$

$\langle v_i \rangle = 0$; $\langle v_i^2 \rangle = \sigma^2$

$$\therefore P(\vec v) = \frac{1}{(2\pi\sigma)^{3/2}} \exp\left[-\left(\frac{1}{2\sigma^2}\right) v^2\right]$$

$$\sigma^2 = \langle v_i^2 \rangle = \frac{1}{3}\langle v^2 \rangle = \frac{2}{3m}\langle K \rangle,$$

but $\langle K \rangle = \frac{3}{2} k_B T$, so $\sigma^2 = k_B T/m$

$$\therefore P(\vec{v}) = \left(\frac{1}{2\pi \frac{k_B T}{m}}\right)^{3/2} \exp\left[-\frac{m v^2}{2 k_B T}\right]$$

$$P(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{K}{k_B T}\right] \; ; K = \frac{1}{2} m v^2$$

[Maxwell Velocity Distribution]

More on the Ergodic Hypothesis

For N particles, in 3 dimensions, the phase space is 6N dimensional, $(q_1, q_2, \ldots, q_{3N}, p_1, p_2, \ldots, p_{3N})$ described by Hamilton's Equations

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

The total Energy $E = H(p_i, q_i)$ is conserved,

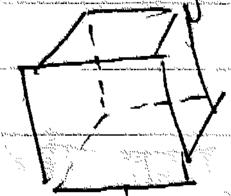
$\Rightarrow$ a $6N-1$ dimensional surface in phase space describes the possible motion.

3N Invariant Tori (phase space)

Action Angle variables

Eg Kepler problem, harmonic oscillator

If the system is integrable, there exist 3N integrals of motion. Example: 1 particle in a box

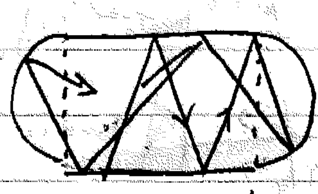


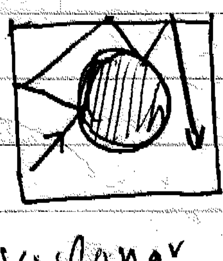
$|p_x|, |p_y|, |p_z|$ are constants of motion seperatly.

Such systems are very rare to find.

The opposite limit is that of chaotic systems:

(stadium billiard)



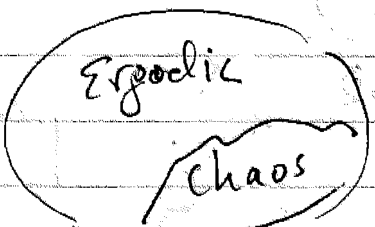


(Siani billiard)

$$|q_1(t) - q_2(t)| \sim q_0 e^{\lambda t}, \quad \lambda = \text{Lyapunov exponent.}$$

$$q_2(0) = q_1(0) + \varepsilon \leftarrow \text{slight perturbation in the initial condition}$$

There are no other constants of motion except from the energy.



Generic situation is rich: phase space is follicted by tori that are partially destroyed by ergodic regions.

$$H = H_0 + \varepsilon H_1 \leftarrow \text{perturbation of Tori, breaks down at certain points}$$

$\uparrow$ integrable