Equilibrium Statistical Mechanics

Earlier we noted that stat mech aims to connect the microscopic equations of motion to the macroscopic equation of state.

- For example, with random walks, we were able to connect simple rules about motion (analogous to an equation of motion) to macroscopic behavior: diffusion.

- An interesting question: How many steps, or how long ($T = N\Delta t$), will it take a random walk to reach equilibrium; that is, before predictions like $\langle S_N^2 \rangle = NL^2$ are accurate?

- This is a hard question! It requires some refinement of our understanding of microscopic processes and macroscopic behavior.

- Here, we're going to address the general equilibrium behavior of N atoms in a box of volume V. The box defines an external potential acting on our system, and we must assume that our system is ISOLATED from external energy transfer.

- First we need to review a few concepts:
  - Generalized coordinates
  - Configuration space
  - Momentum space

How can we solve for the behavior of N atoms?

We could determine the positions

$$\mathbb{Q} = (x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$
$$= (q_1, q_2, \ldots, q_N)$$

and the momenta:

$$\mathbb{P} = (p_1, p_2, p_3, \ldots p_N)$$

of all particles and use the equations of motion + initial conditions to understand their dynamics:

$$\dot{\mathbb{Q}} = m^{-1}\mathbb{P} \qquad \dot{\mathbb{P}} = \mathbb{F}(\mathbb{Q})$$
$$\left(\frac{dx}{dt} = \frac{p}{m}\right) \qquad \left(\frac{dp}{dt} = F\right)$$

For large N, this is computationally impossible; most macroscopic systems have too many particles to compute all of these equations.

<u>Example</u>: The current fastest clock speed for a processor is ~8.5 GHz. The time per operation is 1/clock speed. How long would it take to calculate just 1 time step Δt for $N \sim 10^{26}$ particles?

- Assume we know the initial conditions:

x_i, y_i, z_i
$p_{x_i}, p_{y_i}, p_{z_i}$ for one particle

• We want to compute some time evolution by a given rule (e.g. random walk, Newton's laws, whatever):

$$S_{t+1} = S_t + \text{RULE}$$

• Assume it takes one operation to evolve each degree of freedom using this rule:

$$\begin{aligned} x_1 &\to x_1' & p_{x_1} &\to p_{x_1}' \\ y_1 &\to y_1' & p_{y_1} &\to p_{y_1}' \\ z_1 &\to z_1' & p_{z_1} &\to p_{z_1}' \end{aligned}$$

$\Rightarrow$ For one particle, it takes 6 operations

• For $N \sim 10^{26}$, <u>ONE</u> time step takes $6N$ operations. This will take

$$6N \cdot \frac{1}{8.5\,\text{GHz}} = \frac{6 \times 10^{26}}{8.5 \times 10^{12}} \sim 10^{14}\,\text{s}$$

Now

$$10^{14}\,\text{s} \left(\frac{1\,\text{year}}{3 \times 10^{7}\,\text{s}}\right) \sim 10^{7}\ \text{years}$$

Given this, how can we extract the simple behavior of the system of N particles?

Rather than solving the behavior for a particular set of initial conditions, we hypothesize that some conserved quantity, like energy, is all we need to describe the long-time equilibrium state.

This assumption yields what's called the <u>Microcanonical Ensemble</u>

<u>Microcanonical Ensemble</u>: A statistical ensemble used to represent the possible states of a system which has an <u>exactly specified energy</u>.

<u>Example</u>: The microcanonical ensemble of harmonic oscillators

For harmonic oscillators

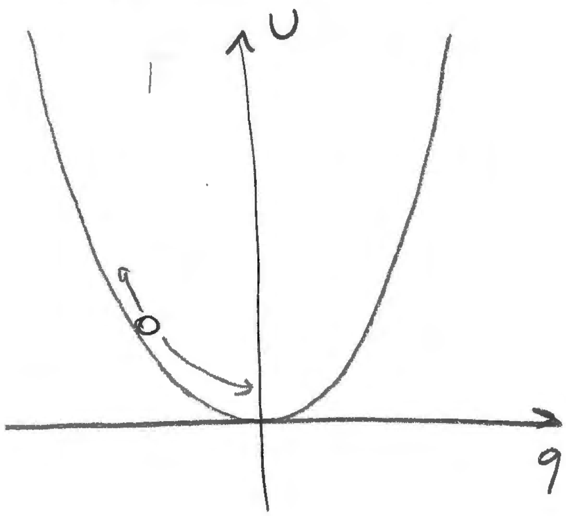
$$E = \frac{p^2}{2m} + \frac{kx^2}{2}$$ 1D SHO with spring constant k

in generalized coordinates,

$$E = \frac{p^2}{2m} + \frac{kq^2}{2}$$

We can think of this as a particle in a potential well $U(q) = \frac{1}{2}kq^2$

$\Rightarrow$ a parabolic potential



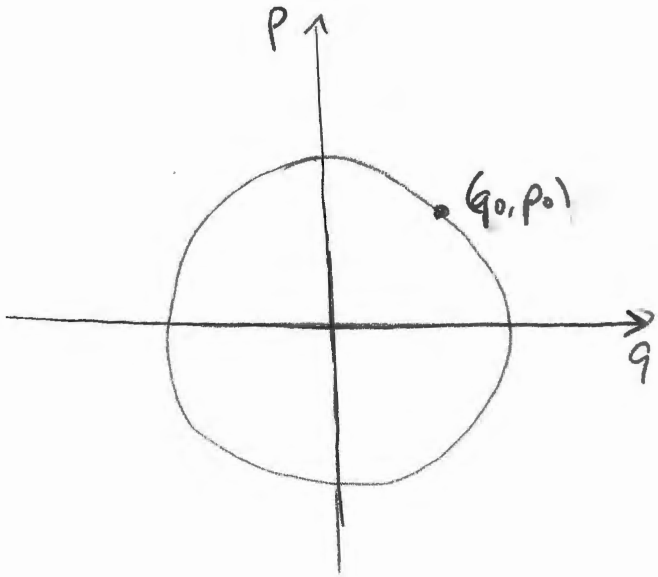
At any given momentum, p, and any given position, q, the particle has energy given by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{kq^2}{2}$$

• At a fixed energy, we can consider all possible combinations of p_0 and q_0 that give the same energy, E_0:

$$E_0 = \frac{p_0'^2}{2m} + \frac{k q_0'^2}{2} \equiv p_0^2 + q_0^2$$

If we consider the momentum and position space, this gives an
$(x^2+y^2=r^2)$

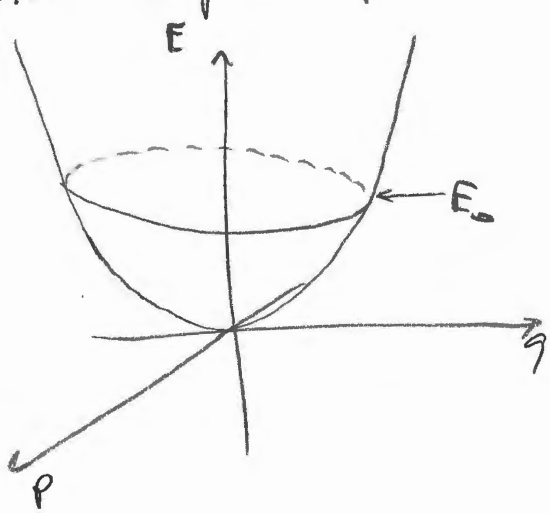


Thus, any combination of p, q that lives on this circle will have the constant energy E_0.

This is called a "phase space" diagram for the Hamiltonian we defined above.

How will this ellipse evolve as energy increases?

Let's plot this phase space circle as a function of the total energy



As E_0 increases, the circle becomes larger