Phys. 528 Lecture 4

Intro. to Ensemble Theory

1) Phase space of a classical system

Hamilton's equations

$$\left.\begin{aligned} \dot{q}_i &= \frac{\partial H(q_i, p_i)}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H(q_i, p_i)}{\partial q_i} \end{aligned}\right\} \quad i = 1, 2, \ldots, 3N$$

The state of the system is specified by the 6N coordinates in <u>phase space</u> (q_i, p_i).

If we know

$$E = H(q_i, p_i),$$

then the state of the system

lies on the $(6N-1)$-dimensional hypersurface of fixed energy in phase space. If

$$E - \frac{\Delta}{2} \leq H(q_i, p_i) \leq E + \frac{\Delta}{2},$$

then the state of the system lies in the hypershell corresponding to this energy range.

The principle of *equal a priori probabilities* implies that the system is equally likely to be anywhere in the allowed region of phase space, and we shall see that the total number of (quantum) states in a given region is proportional to its volume.

e.g. $$\omega = \int\limits_{E-\frac{\Delta}{2} \le H(q,p) \le E+\frac{\Delta}{2}} d^{3N}q \, d^{3N}p \, .$$

The <u>micro-canonical ensemble</u> is the ensemble of systems whose probability distribution in phase space is constant over all allowed states:

$$\rho(q,p) = \begin{cases} \text{const.}, & E-\frac{\Delta}{2} \le H(q,p) \le E+\frac{\Delta}{2} \\ 0, & \text{otherwise} \end{cases}$$

As the system evolves in time, its state follows a trajectory in phase space. The <u>ergodic hypothesis</u> states that the trajectory of any particular system explores all allowed regions of phase space over sufficiently long times. The ergodic principle is satisfied for generic systems (whose dynamics are chaotic), at least for all states except for some regions of measure zero in phase space.

Thus the time average $\bar{f}$ of a physical quantity f should be equal to the ensemble average $\langle f \rangle$:

$$\bar{f} \simeq \langle f \rangle \equiv \frac{\int d^{3N}q \, d^{3N}p \; \rho(q,p,t) f(q,p)}{\int d^{3N}q \, d^{3N}p \; \rho(q,p,t)}$$

An ensemble is said to be <u>stationary</u> if $\frac{\partial \rho}{\partial t} = 0$.

Clearly $\frac{d}{dt}\langle f \rangle = 0$ if ρ is stationary. Ensembles representing systems in equilibrium are stationary.

2) <u>Liouville's theorem</u>

The total # of systems in the ensemble is fixed, so the flow in phase space is conserved:

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

where ∇ is the 6D-dim. gradient and $\vec{v} = (\dot{q}_i, \dot{p}_i)$ is a 6D-dim. velocity vector.

$$\frac{\partial \rho}{\partial t} + \sum_i \left[\frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i)\right] = 0$$

$$0 = \frac{\partial \rho}{\partial t} + \sum_i \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] + \rho \sum_i \underbrace{\left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right]}_{\to 0}$$

But $\dot{q}_i = \dfrac{\partial H}{\partial p_i}$, $\dot{p}_i = -\dfrac{\partial H}{\partial q_i}$,

so $\dfrac{\partial \dot{q}_i}{\partial q_i} = \dfrac{\partial^2 H}{\partial q_i \partial p_i}$, $\dfrac{\partial \dot{p}_i}{\partial p_i} = -\dfrac{\partial^2 H}{\partial p_i \partial q_i}$

$$\boxed{\frac{\partial \rho}{\partial t} + [\rho, H] = 0,}$$

where $[f, g] \equiv \sum_i \left[\dfrac{\partial f}{\partial q_i}\dfrac{\partial g}{\partial p_i} - \dfrac{\partial f}{\partial p_i}\dfrac{\partial g}{\partial q_i}\right]$

is the <u>Poisson bracket</u>.

One may also write,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0.$$

The <u>total time derivative</u>

$$\frac{d}{dt}\rho \equiv \frac{\partial \rho}{\partial t} + \sum_i \left[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right] = 0.$$

This means the density of systems in phase space is constant if one moves with the flow.

<u>stationary distributions</u>

$$\frac{\partial \rho}{\partial t} = 0 \quad \text{if} \quad [\rho, H] = 0.$$

One way to satisfy this is

$$\rho(q, p) = \text{const.}$$

over the relevant region of phase space (closed under the flow) and zero elsewhere.

This is just the uniform distribution of the <u>micro-canonical ensemble</u>.

More generally, if

$$\rho(q,p) = \rho\left[H(q,p)\right],$$

then $[\rho, H] = 0$.

$$[\rho, H] = \sum_i \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$$

$$= \rho'(H) \sum_i \left[\frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right] \to 0$$

Another important stationary ensemble is the <u>canonical ensemble</u>:

$$\rho(q, p) \propto e^{-\beta H(q, p)}$$