Theo. 4. Statistical Physics. (1/8)

Lecture #9.

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Last time: Discussion of equipartition theorem + virial theorem.
Moments + cumulants. Central limit theorem.

Today: 6D phase space + Hamiltonian.
Liouville theorem.
Streaming + collision.

From last time, we discussed the importance of the equipartition theorem + virial theorem as rules governing the behavior of systems in equilibrium. We also focused on the details of statiscal methods and the use of moments + cumulants to analyze expectation values given some prob. distribution & motivated the Gaussian distrib. as a end result of collections of randomly selected objects via the central limit theorem.

Now, we want to analyze more about the <u>dynamics</u> of how systems time-evolve to equilibrium states. This will partially recap classical mechanics + collision/scattering theory, but we will also develop the H-theorem, a precursor to the 2nd law of thermodynamics and then encounter the notion of Shannon entropy, which has wide application in information theory. This will also help illustrate the utility of ensemble averaging. ↳time evolution study

Our goal will be to understand how to understand the dynamical impact of the second law of thermodynamics, which will also clarify important concepts of time-reversal and irreversibility. We can then finish the unit on the second law of thermodynamics & begin "simple" applications of constrained systems / ensembles to develop enthalpy, Helmholtz free energy, & Gibbs free energy. We can then introduce the third law of thermodynamics & the concept of absolute zero. This will complete the toolbox for studying classical statistical mechanics.

We are now trying to understand the relationship between "stable" equilibrium (velocity) distributions like the Maxwell-Boltzmann distribution and "unstable" distributions like a room where all gas particles are in one-half of the room or where all speeds are exactly the same. We have three qualitative questions to ask & answer:

1. How can we define "equilibrium" for a system of moving particles?
2. Do all systems naturally evolve towards an equilibrium state?
3. What is the time evolution of a system that is not (quite) in equilibrium?

The starting point for this discussion is the 6D phase space for N dof. governed by the Hamiltonian, $\mathcal{H}(\vec{p},\vec{q})$ with coordinates $\vec{q} = (\vec{q}_1, \vec{q}_2, \ldots \vec{q}_N)$ and $\vec{p} = (\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$.

A microstate of the system of N particles is clearly a specification of $\vec{q}_i$ & and $\vec{p}_i$ for a given time t. This will be denoted by a point $\mu(t)$ in the 6N-dim. phase space $\Gamma = \prod_{i=1} \{\vec{q}_i, \vec{p}_i\}$.

Time-evolution given by canonical eqns.,

$$\begin{cases} \frac{d\vec{q}_i}{dt} = \frac{\partial H}{\partial \vec{p}_i} \\ \frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{q}_i} \end{cases}$$

Note that Hamiltonian time evolution obeys time-reversal symmetry, so $\vec{p} \to -\vec{p}$ leads to $\vec{q}(t) \Rightarrow \vec{q}(-t)$, if the reversal of $\vec{p}$ occurs at $t=0$.

We know that macrostates, characterized by thermodynamic coordinates such as T, P and N, enjoy a large degeneracy (in equilibrium) of microstates μ. To analyze trajectories in the 6N-dim. phase space for a macrostate, it is therefore useful to consider an ensemble of microstates: We copy the macrostate N times and construct the phase space density $\rho(\vec{p}, \vec{q}, t)$. Each copy of the macrostate is a different representative point $\mu(t)$. The phase space density is defined as the

$$\rho(\vec{p}, \vec{q}, t)\, d\Gamma = \lim_{N \to \infty} \frac{dN(\vec{p}, \vec{q}, t)}{N}$$

for $dN(\vec{p}, \vec{q}, t)$ as the number of representative points in an infinitesimal volume $d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i\, d^3\vec{q}_i$.

Note that this number is not continuously connected in phase space.

Note also that $\int d\Gamma\, \rho = 1$ + ρ is a properly normalized probability density function in phase space. This lets us calculate ensemble averages

$$\langle \mathcal{O} \rangle = \int d\Gamma\; \rho(\vec{p}, \vec{q}, t)\; \mathcal{O}(\vec{p}, \vec{q})$$

for "operators" or functions of phase space coordinates $\mathcal{O}(\vec{p}, \vec{q})$.

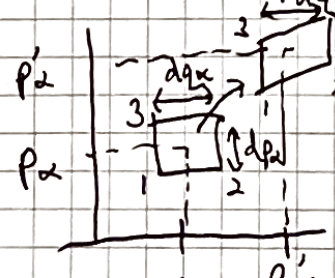
Nomenclature: An exact microstate μ specifies the system as a "pure state." The time evolution is, in principle, deterministic (classically) and so it is not so meaningful to talk about equilibrium and $\mu(t)$ changes in time.

For knowledge of the microstate of a system via probabilistic weights, the system is in a mixed state, and the study of equilibrium dynamics is governed by the time evolution of the phase space density $\rho(t)$.

Liouville's theorem:

How does phase space density time evolve?

Liouville's theorem states that $\rho(\Gamma, t)$ behaves like an incompressible fluid.



We follow the evolution of dN pure states in an infinitesimal volume element $d\Gamma = \prod_{i=1}^{3N} d^3\vec{p}_i\, d^3\vec{q}_i$ around the point $(\vec{p}, \vec{q})$

After a time interval δt, the states are now in the vicinity of (p', q') according to Hamiltonian evolution with

$$q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t + \mathcal{O}(\delta t^2)$$

$$p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t + \mathcal{O}(\delta t^2)$$

where q_α, p_α are any of the $6N$ coordinates and $\dot{q}_\alpha$ and $\dot{p}_\alpha$ are the corresponding velocities.

We can show that the new volume element is $d\Gamma' = \prod_{i=1}^{N} d^3\vec{p}_i' \, d^3\vec{q}_i'$

where $$dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + \mathcal{O}(\delta t^2)$$

$$dp'_\alpha = dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + \mathcal{O}(\delta t^2)$$

so for each pair of conjugate coordinates,

$$dq'_\alpha \, dp'_\alpha = dq_\alpha \, dp_\alpha \left[1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right)\delta t + \mathcal{O}(\delta t^2)\right]$$

We use the Hamiltonian evolution:

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha} = \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}$$

$$\frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = \frac{\partial}{\partial p_\alpha}\left(-\frac{\partial H}{\partial q_\alpha}\right) = -\frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}$$

So $d\Gamma' = d\Gamma$, and all pure states around $(\vec{p}, \vec{q})$ become a new neighborhood around $(\vec{p}', \vec{q}')$ but occupy the same volume. The ratio $dN/d\Gamma$ is unchanged $\Rightarrow \rho$ is like the density of an incompressible fluid.

This incompressibility requires $\rho(\vec{p}', \vec{q}', t+\delta t) = \rho(\vec{p}, \vec{q}, t)$

so we have a differential relation

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \cdot \frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha} \cdot \frac{dq_\alpha}{dt} \right) = 0$$

We get, from Hamiltonian evolution,

$$\frac{\partial \rho}{\partial t} = \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right) = -\{\rho, H\}$$

The curly brace denotes the Poisson bracket:

$$\{A, B\} \equiv \sum_{\alpha=1}^{3N} \left(\frac{\partial A}{\partial q_\alpha} \frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \frac{\partial B}{\partial q_\alpha} \right) = -\{B, A\}$$

Consequences of Liouville's theorem.

① Time reversal sends $(\vec{p}, \vec{q}, t)$ to $(-\vec{p}, \vec{q}, -t)$, so $\{\rho, H\} \to -\{\rho, H\}$, and density reverses its evolution, so $\rho(\vec{p}, \vec{q}, t) = \rho(-\vec{p}, \vec{q}, -t)$.

② Time-evolution of ensemble average is

$$\frac{d\langle \theta \rangle}{dt} = \int d\Gamma \, \frac{\partial \rho(\vec{p}, \vec{q}, t)}{\partial t} \, \theta(\vec{p}, \vec{q})$$

$$= -\int d\Gamma \, \rho \{H, \theta\} = \langle \{\theta, H\} \rangle .$$

(See Kardar for derivation, p. 60)

③ Given ensemble members represent an equilibrium macroscopic state, the ensemble averages must be time-independent.

It is sufficient to require a stationary density, $\frac{\partial \rho_{eq}}{\partial t} = 0$, s.t. $\{\rho_{eq}, H\} = 0$.

One way to ensure this condition is to require $\rho_{eq}(\vec{p},\vec{q}) = \rho(H(\vec{p},\vec{q}))$, so ρ_{eq} is a fcn. of H.

Then $\{\rho(H), H\} = \rho'(H)\{H, H\} = 0$, and value of ρ is const. on surfaces of constant energy H in phase space. [This is the basic assumption of statistical mechanics.]

We can also have additional conserved quantities, $\{L_n, H\} = 0$. A stationary density exists for any fcn. of the form $\rho_{eq}(\vec{p},\vec{q}) = \rho(H(\vec{p},\vec{q}), L_1(\vec{p},\vec{q}), L_2(\vec{p},\vec{q}), \ldots)$

Can show $\frac{d}{dt} L_n(\vec{p},\vec{q}) \equiv \frac{L_n(\vec{p}(t+dt),\vec{q}(t+dt)) - L_n(\vec{p}(t),\vec{q}(t))}{dt}$

$$= \sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial p_\alpha}\frac{\partial p_\alpha}{\partial t} + \frac{\partial L_n}{\partial q_\alpha}\frac{\partial q_\alpha}{\partial t} \right)$$

$$= -\sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial p_\alpha}\frac{\partial H}{\partial q_\alpha} - \frac{\partial L_n}{\partial q_\alpha}\frac{\partial H}{\partial p_\alpha} \right)$$

$$= \{L_n, H\} = 0 \quad \text{(by assumption)}.$$

We have now answered the first question!
All members of a microcanonical ensemble are located on a surface $H(\vec{p},\vec{q}) = E$ in phase space. A uniform density of points on this surface is stationary in time, and stat. mech. assumes that the macrostate is indeed represented by such a uniform density of microstates.

The next question to tackle is whether phase density generally time-evolves to ρ_{eq} solutions or away from them. This will require revisiting ergodicity & will be the focus of the next lecture.