Theo. 4. Statistical Physics
Lecture 10.
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Last time: 6D phase space + Hamiltonian.
Liouville theorem.

Today: Consequences of Liouville theorem, Ergodicity
Streaming + collision.

We now want to address the question of whether phase density time-evolves towards an equilibrium ρ_{eq}. In particular, this would suppose that non-stationary densities converge to ρ_{eq}, but we also know that time-reversal dictates that every $\rho(t)$ converging to ρ_{eq} has a corresponding time-reversed solution that diverges from ρ_{eq}

This is where we can include a time-averaging, s.t. a time-average is dominated by behavior near ρ_{eq} and thus stationary solutions are "attractive" as we avg. over time. This formally asks the question of ergodicity, which asks whether it is justified to replace time averages with ensemble averages.

Intuitively, an ensemble average is similar to a time average, if, for some finite time interval, the macrostate representative point moves around and uniformly samples the accessible points in phase space. This is the ergodic hypothesis, and is only known in systems with time intervals growing exponentially with the number of particles involved.

We have seen the ergodic hypothesis before, when constructing the Boltzmann distribution, in order to claim the system, after a sufficiently long time, spends an equal amount of time in each microstate. This again emphasizes the conceptual distinction between time averaging and ensemble averaging ~~and~~ for extracting equilibrium and near-equilibrium behavior. So in order to study the appropriate timescale for averaging, we should understand inter-particle interactions and the timescales involved.

We will study the Hamiltonian

$$\mathcal{H}(\vec{p},\vec{q}) = \sum_{i=1}^{N}\left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i)\right] + \frac{1}{2}\sum_{i,j=1}^{N} V(\vec{q}_i - \vec{q}_j)$$

where we see the classical K.E. of particle i, the $U(\vec{q}_i)$ external potential energy for particle i, and a two-body interaction $V(\vec{q}_i - \vec{q}_j)$. The two-body term should dominate over three-body and four-body terms in a dilute approximation.

We need to partition the $\mathcal{H}$ into interactions within (an arbitrary) subset of $s \ll N$ particles, and interactions between s and $N-s$.

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}'$$

$$\mathcal{H}_s = \sum_{n=1}^{s}(KE+U) + \frac{1}{2}\sum_{n,m=1}^{s} V(\vec{q}_n - \vec{q}_m)$$

$$\mathcal{H}_{N-s} = \sum_{i=s+1}^{N}(KE+U) + \frac{1}{2}\sum_{i,j=s+1}^{N} V(\vec{q}_i - \vec{q}_j)$$

and the interaction between s + $N-s$ is

$$\mathcal{H}' = \sum_{n=1}^{s} \sum_{i=s+1}^{N} V(\vec{q}_n - \vec{q}_i)$$

Here, it is useful to construct an s-particle density built from 1-particle densities with combinatorial factors.

Use $\quad f_1(\vec{p},\vec{q},t) = \left\langle \sum_{i=1}^{N} \delta^3(\vec{p}-\vec{p}_i)\,\delta^3(\vec{q}-\vec{q}_i) \right\rangle$

as the exp. value to find any of the N particles at $(\vec{q},\vec{p},t)$.

$$f_1(\vec{p},\vec{q},t) = N \int \prod_{i=2}^{N} d^3\vec{p}_i\, d^3\vec{q}_i \;\rho(\vec{p}_1=\vec{p},\, \vec{q}_1=\vec{q},\, \vec{p}_2, \vec{q}_2, \ldots, \vec{p}_N, \vec{q}_N, t)$$

(symmetric phase space density for permuting particles).

The two-particle density is

$$f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,t) = N(N-1)\int \prod_{i=3}^{N} dV_i\; \rho(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,\ldots \vec{p}_N,\vec{q}_N,t)$$

with $dV_i = d^3\vec{p}_i\, d^3\vec{q}_i$ for each particle i.

So $\quad f_s(\vec{p}_1,\ldots,\vec{q}_s,t) = \dfrac{N!}{(N-s)!}\displaystyle\int \prod_{i=s+1}^{N} dV_i\; \rho(\vec{p},\vec{q},t)$

$$= \frac{N!}{(N-s)!}\; \rho_s(\vec{p}_1,\ldots,\vec{q}_s,t)$$

with ρ_s the unconditional PDF for coordinates of s particles, $\rho_N \equiv \rho$.

So we can study time-evolution of ρ_s:

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^{N} dV_i\; \frac{\partial \rho}{\partial t} = -\int \prod_{i=s+1}^{N} dV_i\; \{\rho, \mathcal{H}_s + \mathcal{H}_{N-s} + \mathcal{H}'\}$$

Evaluate each Poisson bracket.

Note that first s coordinates are <u>not</u> integrated, so can swap integration & diff. in first term:

$$\int \prod_{i=s+1}^{N} dV_i \{\rho, H_s\} = \left\{ \left(\int \prod_{i=s+1}^{N} dV_i \rho \right), H_s \right\}$$
$$= \{\rho_s, H_s\}$$

The second term:

$$-\int \prod_{i=s+1}^{N} dV_i \{\rho, H_{N-s}\} = \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \frac{\partial H_{N-s}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \frac{\partial H_{N-s}}{\partial \vec{p}_j} \right]$$

$$= \int \prod_{i=s+1} dV_i \sum_{j=s+1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \left(\frac{\partial U}{\partial \vec{q}_j} + \frac{1}{2} \sum_{k=s+1}^{N} \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} \right) - \frac{\partial \rho}{\partial \vec{q}_j} \frac{\vec{p}_j}{m} \right]$$

no dep. on p_j

no dep. on q_j

$= 0$ after IBP.

Last term:

$$\int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \frac{\partial H'}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \frac{\partial H'}{\partial \vec{p}_j} \right]$$

$$= \int \prod_{i=s+1}^{N} dV_i \left[\sum_{n=1}^{s} \frac{\partial \rho}{\partial \vec{p}_n} \sum_{j=s+1}^{N} \frac{\partial V(\vec{q}_n - \vec{q}_j)}{\partial \vec{q}_n} + \sum_{j=s+1}^{N} \frac{\partial \rho}{\partial \vec{p}_j} \sum_{n=1}^{s} \frac{\partial V(\vec{q}_j - \vec{q}_n)}{\partial \vec{q}_j} \right]$$

no dep. on p_j, IBP $= 0$.

First term is sum of $(N-s)$ expressions all equal by symmetry.

$$(N-s)\int \prod_{i=s+1}^{N} dV_i \sum_{n=1}^{s} \frac{\partial V(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n} \frac{\partial \rho}{\partial \vec{p}_n}$$

$$= (N-s)\sum_{n=1}^{s}\int dV_{s+1} \frac{\partial V}{\partial \vec{q}_n}(\vec{q}_n-\vec{q}_{s+1}) \cdot \frac{\partial}{\partial \vec{p}_n}\Big[\underbrace{\int \prod_{i=s+2} dV_i\, \rho}_{\rho_{s+2}}\Big]$$

We get

$$\frac{\partial \rho_s}{\partial t} - \{\mathcal{H}_s, \rho_s\} = (N-s)\sum_{n=1}^{s}\int dV_{s+1}\frac{\partial V(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\cdot\frac{\partial \rho_{s+1}}{\partial \vec{p}_n}$$

or
$$\frac{\partial f_s}{\partial t} - \{\mathcal{H}_s, f_s\} = \sum_{n=1}^{s}\int dV_{s+1}\frac{\partial V(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\frac{\partial f_{s+1}}{\partial \vec{p}_n}.$$

Interpretation: LHS are streaming terms.
RHS is collision terms.

Can think of RHS as sum of terms where any particle in s "sees" one of the $N-s$ particles, and this has to carry the joint PDF of $s+1$ particles described by ρ_{s+1}. Consequently, $\frac{\partial \rho_1}{\partial t}$ depends on ρ_2, $\frac{\partial \rho_2}{\partial t}$ depends on ρ_3, etc.

We will terminate this hierarchy by imposing an appropriate ~~timescale~~ time-scale next time.