1

Review

1.1   Classical Mechanics

- 1-Dimensional system with 1 particle of mass m

  - Newton's equations of motion for position $x(t)$ and momentum $p(t)$:

$$
\begin{aligned}
\dot{x}(t) &\equiv \frac{dx}{dt} & p &= m\dot{x} \\
F(t) &= ma(t) & a(t) &= \ddot{x}(t) \\
F(t) &= -\frac{dV}{dx} \\
\dot{p}(t) &= m\ddot{x}(t) = F(t) = -\frac{dV}{dx}
\end{aligned}
$$

  - Define an energy function called the *Hamiltonian* $H(x,p) = \frac{p^2}{2m} + V(x)$.
  - Introduce terminology

$$
\frac{p^2}{2m} = \text{kinetic energy} \qquad V(x) = \text{potential energy}
$$

  - Newton's laws can then be expressed as:

$$
\dot{x} = \frac{p}{m} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{dV}{dx} = -\frac{\partial H}{\partial x}.
$$

  - These are coupled ordinary differential equations whose solution is uniquely specified by specifying two conditions, such as $x_0 = x(0)$ and $p_0 = p(0)$ at some reference time $t_0 = 0$.

- 3-dimensional system of 1 particle

  - Notation: $\mathbf{r} = (x, y, z)$ and $\mathbf{p} = (p_x, p_y, p_z)$. Also, $\mathbf{p} \cdot \mathbf{p} = p_x^2 + p_y^2 + p_z^2$.
  - The Hamiltonian is: $\frac{\mathbf{p} \cdot \mathbf{p}}{2m} + V(\mathbf{r})$.
  - The equations of motion are:

  $$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m} \quad \xrightarrow{\text{shorthand for}} \quad \begin{pmatrix} \dot{r}_x \\ \dot{r}_y \\ \dot{r}_z \end{pmatrix} = \frac{1}{m} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix}$$

  $$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V}{\partial \mathbf{r}}$$

- 2 particles in 3-dimensions

  - Hamiltonian: $H = \frac{\mathbf{p}_1 \cdot \mathbf{p}_1}{2m_1} + \frac{\mathbf{p}_2 \cdot \mathbf{p}_2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$
  - Equations of motion are:

  $$\dot{\mathbf{r}}_1 = \frac{\partial H}{\partial \mathbf{p}_1} = \frac{\mathbf{p}_1}{m_1} \qquad \dot{\mathbf{r}}_2 = \frac{\partial H}{\partial \mathbf{p}_2} = \frac{\mathbf{p}_2}{m_2}$$

  $$\dot{\mathbf{p}}_1 = -\frac{\partial H}{\partial \mathbf{r}_1} \qquad \qquad \dot{\mathbf{p}}_2 = -\frac{\partial H}{\partial \mathbf{r}_2}$$

  - Introduce generalized notation: $\mathbf{r}^{(2)} = (\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{p}^{(2)} = (\mathbf{p}_1, \mathbf{p}_2)$.

  $$\mathbf{p}^{(2)} \cdot \mathbf{p}^{(2)} = \mathbf{p}_1 \cdot \mathbf{p}_1 + \mathbf{p}_2 \cdot \mathbf{p}_2$$

  - Equations of motion in this notation:

  $$\dot{\mathbf{r}}^{(2)} = \frac{\partial H}{\partial \mathbf{p}^{(2)}} \qquad \dot{\mathbf{p}}^{(2)} = -\frac{\partial H}{\partial \mathbf{r}^{(2)}}.$$

- *N* particle system in 3-D

  - Equation of motion in generalized notation:

  $$\dot{\mathbf{r}}^{(N)} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \qquad \dot{\mathbf{p}}^{(N)} = -\frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

  - A total of $6N$ equations!
  - At each point in time, the system is specified by $6N$ coordinates $(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t)) \equiv \mathbf{x}^{(N)}(t)$ called the *phase point*.
  - The set of all phase points is called *phase space*.
  - Classical dynamics describes a path through the $6N$-Dimensional phase space.

– Special properties of path through phase space:

1. Certain quantities remain unchanged during the evolution of system.
   * Examples: energy, momentum and angular momentum may be *conserved* (constant) along the path or *trajectory* of the system.
   * Path remains on a hyper-surface of constant energy in phase space.
2. Paths never cross in phase space. Each disjoint path, labelled by initial conditions, passes arbitrarily close to any point on the constant energy hypersurface.
   * Amount of time for the trajectory of the system from a given initial point in phase space to pass arbitrarily close to the initial point is called the *recurrence time*: Absolutely enormous for large, interacting systems.

- Consider an arbitrary function G of the phase space coordinate $\mathbf{x}^{(N)}$,

$$G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = G(\mathbf{x}^{(N)}, t).$$

Taking the time derivative,

$$
\begin{aligned}
\frac{dG(\mathbf{x}^{(N)}, t)}{dt} &= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \dot{\mathbf{r}}^{(N)} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \dot{\mathbf{p}}^{(N)} \\
&= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.
\end{aligned}
$$

– We can define the *Liouville operator* $\mathcal{L}$ to be:

$$\mathcal{L} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{r}^{(N)}} - \frac{\partial H}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{p}^{(N)}}$$

so that in terms of a general function B

$$\mathcal{L}B = \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

– In terms of the Liouville operator,

$$\frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \mathcal{L}G(\mathbf{x}^{(N)}, t).$$

– Functions of the phase space coordinate G that are not explicit functions of time t are conserved by the dynamics if $\mathcal{L}G = 0$.

– Formal solution of evolution is then

$$G(\mathbf{x}^{(N)}, t) = e^{\mathcal{L}t} G(\mathbf{x}^{(N)}, 0).$$

- In particular,

$$\mathbf{x}^{(N)}(t) = e^{\mathcal{L}t}\mathbf{x}^{(N)}(0).$$

- Note that $\mathcal{L}H = 0$.
- Can also define the *Poisson bracket* operator via

$$\{A, B\} \equiv \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{r}^{(N)}}.$$

- The relationship between the Poisson bracket and Liouville operators is

$$\mathcal{L}B = \{B, H\} \qquad \text{so} \qquad \frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \{G(\mathbf{x}^{(N)}, t), H(\mathbf{x}^{(N)})\}.$$

- Important property:

$$e^{\mathcal{L}t}\left(A(\mathbf{x}^{(N)})B(\mathbf{x}^{(N)})\right) = \left(e^{\mathcal{L}t}A(\mathbf{x}^{(N)})\right)\left(e^{\mathcal{L}t}B(\mathbf{x}^{(N)})\right) = A(\mathbf{x}^{(N)}(t))B(\mathbf{x}^{(N)}(t)).$$

1.2 Ensembles and Observables

- Consider some arbitrary dynamical variable $G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = G(\mathbf{x}^{(N)})$ (function of phase space coordinates and hence possibly evolving in time).

- An experimental measurement of quantity corresponds to a *time* average of some (possibly short) sampling interval τ.

$$G_{\text{obs}}(t) = \overline{G(t)} \equiv \frac{1}{\tau} \int_0^\tau d\sigma\, G\left(\mathbf{r}^{(N)}(t + \sigma), \mathbf{p}^{(N)}(t + \sigma)\right).$$

  - $\tau \gg \tau_m$. where τ_m is a *microscopic time scale*. Hence fluctuations on microscopic time scale a smoothed out.
  - For most systems, evolution of $G(t)$ cannot be solved analytically and so must resort to
    1. Numerically solving evolution (computer simulation)
    2. Developing a new theoretical framework relating time averages to something that can be calculated.

- Ensemble Average: Infinite/long time average of dynamical variable corresponds to an average over a properly weighted set of points of phase space (called an *ensemble*). The statistical average is called an *ensemble average*.

  - Each point in phase space corresponds to a different configuration of the system.

– Ensemble average therefore corresponds to a weighted average over different configurations of the system.

• Define a probability density for phase space (often loosely called the "distribution function')':

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \quad = \quad \text{distribution function}$$

and hence

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t)d\mathbf{r}^{(N)}d\mathbf{p}^{(N)} \quad = \quad \begin{array}{l} \text{prob. of finding a system in ensemble with} \\ \text{coordinates between } (\mathbf{r}^{(N)}, \mathbf{r}^{(N)}+d\mathbf{r}^{(N)}) \text{ and} \\ (\mathbf{p}^{(N)}, \mathbf{p}^{(N)} + d\mathbf{p}^{(N)}) \text{ at time } t. \end{array}$$

– Note that the distribution function is normalized:

$$\int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)} \, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1$$

• The *ensemble average* is defined as:

$$\langle G(t) \rangle \equiv \int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)} \, G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t).$$

• *microcanonical ensemble*: All systems in ensemble have the same total energy.

– All dynamical trajectories with same energy compose a set of states in microcanonical ensemble.

– Technically, all conserved quantities should also be the same.

What is the connection between the ensemble average and the experimental observation (time average)?

• **Quasi-ergodic hypothesis:** As $\mathbf{t} \to \infty$, a dynamical trajectory will pass arbitrarily close to each point in the constant-energy (if only conserved quantity) hypersurface of phase space (metrically transitive).

– Another statement: For all initial states except for a set of zero measure, the phase space is connected through the dynamics.

– Hypersurfaces of phase space covered by trajectory.

- So in some sense, as $\tau \to \infty$:, we expect

$$G_{\text{obs}}(t) = \frac{1}{\tau} \int_0^\tau d\sigma\, G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right) = \frac{1}{\Omega} \int{}' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$

where

$$\Omega = \int{}' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} = \int_{E < H(\mathbf{x}^{(N)}) < E + \delta E} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}$$

hence

$$G_{\text{obs}}(t) = \overline{G}(t) = \int G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t)\, d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad \text{if } f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1/\Omega.$$

  – All points on hypersurface have the same weight (equally probable).

  – Ensemble analogy: each point in restricted phase space corresponds to a configuration of the system with the same macroscopic properties.

- Can utilize an axiomatic approach to find equilibrium distributions: Maximize statistical entropy subject to constraints.

- Alternate method: Asymptotic solution of the Boltzmann equation for distribution functions - describes collisions of pairs from Newton's equations and adds an assumption of statistical behavior (molecular chaos).

  – System naturally evolves from an initial state to states with static macroscopic properties corresponding to "equilibrium" properties - Can model this with simple spin systems like the Kac ring model.

  – Measure of disorder, the statistical entropy, increases as the system evolves: maximized in equilibrium (H theorem).

Canonical Ensemble

- Remove restriction of defining probability only on constant energy hypersurface.

- Allow total energy of systems in ensemble to vary (hopefully) narrowly around a fixed average value.

$$f(\mathbf{x}^{(N)}) = \frac{1}{N! h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\}$$

- A is the Helmholtz free energy.

- We define the *partition function* $Q_N(T, V)$ by

$$Q_N(T, V) = \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \exp\{-\beta H(\mathbf{x}^{(N)})\} = \exp\{-\beta A\}$$

so by normalization

$$f(\mathbf{x}^{(N)}) = \frac{1}{N! h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\} = \frac{1}{N! H^{3N}} \frac{\exp\{-\beta H(\mathbf{x}^{(N)})\}}{Q_N(T, V)}.$$

- Relation $A = -kT \ln Q_N(T, V)$ gives thermodynamic connection: For example

1. The pressure is:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT \left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

2. The chemical potential is:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

3. The energy is:

$$
\begin{aligned}
\overline{E} &= \frac{\exp\{\beta A\}}{N! h^{3N}} \int d\mathbf{x}^{(N)} \, H(\mathbf{x}^{(N)}) \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= \frac{\exp\{\beta A\}}{N! h^{3N}} - \frac{\partial}{\partial \beta} \int d\mathbf{x}^{(N)} \, \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= -\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} = -\frac{\partial \ln Q_N}{\partial \beta}.
\end{aligned}
$$

- We can write the canonical partition function as:

$$
\begin{aligned}
Q_N(T, V) &= \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \, \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= \int_0^\infty dE \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \, \exp\{-\beta H(\mathbf{x}^{(N)})\} \delta(E - H(\mathbf{x}^{(N)})) \\
&= \int_0^\infty dE \, \exp\{-\beta E\} \left(\frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \, \delta(E - H(\mathbf{x}^{(N)}))\right) \\
Q_N(T, V) &= \int_0^\infty dE \, \exp\{-\beta E\} N(E)
\end{aligned}
$$

where

$$
\begin{aligned}
N(E) &\equiv \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \, \delta(E - H(\mathbf{x}^{(N)})) \\
&= \text{density of } \textit{unique} \text{ states at energy } E \text{ (microcanonical partition function).}
\end{aligned}
$$

Relationship between ensemble averages

- How likely are we to observe a system in the canonical ensemble with an energy very different from the average energy $\overline{E} = \langle H(\mathbf{x}^{(N)}) \rangle$? From the Tchebycheff inequality, we find that

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{\sigma_E^2}{\lambda^2 \overline{E}^2}$$

- Now the variance in the energy is:

$$\sigma_E^2 = \left\langle H(\mathbf{x}^{(N)})^2 \right\rangle - \langle H(\mathbf{x}^{(N)}) \rangle^2 = \frac{\partial^2 \ln Q_N}{\partial \beta^2} = -\frac{\partial \overline{E}}{\partial \beta} = kT^2 C_v$$

and hence

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{kT^2 C_v}{\lambda^2 \overline{E}^2}$$

- For an ideal gas system, $\overline{E} = 3/2NkT$ and hence $C_v = 3/2Nk$.

- Typically, $\overline{E} \sim N$ and $C_v \sim N$.

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda \overline{E}\right) \leq \frac{kT^2 C_v}{\lambda^2 \overline{E}^2} \sim \frac{1}{N\lambda^2}$$

  – As N increases, it becomes less and less likely to observe a system with energy very different from $\overline{E}$,

$$\langle B(\mathbf{x}^{(N)}) \rangle_{\text{canon}} = \int dE \, P(E) \langle B(\mathbf{x}^{(N)}) \rangle_{\text{micro at } E} \approx \langle B(\mathbf{x}^{(N)}) \rangle_{\text{micro at } \overline{E}} \left(1 + O(1/N)\right).$$

- $P(E)$ is sharply-peaked around $E = \overline{E}$: Can show

$$P(E) \;\approx\; P(\overline{E}) \left(\frac{1}{2\pi\sigma_E^2}\right)^{1/2} \exp\left\{-\frac{(E - \overline{E})^2}{2kT^2 C_v}\right\}$$

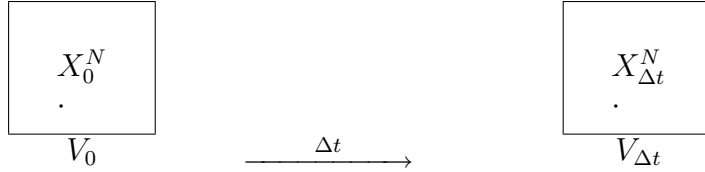- Relative spread of energy $\sigma_E / \overline{E} \sim N^{-1/2}$.

1.3   Liouville Equation for Hamiltonian Systems

Define small volume element V_0 in phase space.

- How does probability of finding the system in this region change in time?

$$P(V_0) = \int_{V_0} dX_0^N \, f(X_0^N, 0)$$

- Allow system to evolve according to dynamics:

$$\boxed{\begin{array}{c} X_0^N \\ \cdot \end{array}} \qquad \xrightarrow{\ \Delta t\ } \qquad \boxed{\begin{array}{c} X_{\Delta t}^N \\ \cdot \end{array}}$$

$$V_0 \qquad\qquad\qquad\qquad V_{\Delta t}$$

  - Volume changes shape in mapping:

$$\begin{aligned} X_0^N \to X_{\Delta t}^N \ &\simeq\ X_0^N + \dot{X}_0^N \Delta t \\ &\equiv\ X_0^N + \delta X^N \end{aligned}$$

  - Maybe changes volume as well.
  - Number of states is V_0 and $V_{\Delta t}$ is same since we follow all points in original volume.
    * Can only change if some points in V_0 aren't in $V_{\Delta t}$ (flow out of volume).

- So $P(V_0, 0) = P(V_{\Delta t}, \Delta t)$: Conservation of probability (like fluid where particles aren't created or destroyed.)

- Changing variables from X_0^N to $X_{\Delta t}^N$,

$$\begin{aligned} P(V_0) \ &=\ \int_{V_0} dX_0^N \, f(X_0^N, 0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \, J(X^N; X_{\Delta t}^N) f(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t) \\ &=\ P_{\Delta t}(V_{\Delta t}) \quad \text{since } P(V_0, 0) = P(V_{\Delta t}, \Delta t). \end{aligned}$$

- Recall that $X_{\Delta t}^N - X_0^N \equiv \delta X_0^N$.

- Evaluation of the Jacobian is a bit complicated, but gives

$$
\begin{aligned}
J(X_0^N; X_{\Delta t}^N) &= \text{Jacobian for transform } X_0^N = X_{\Delta t}^N - \delta X^N \\
&= \left| \frac{\partial X_0^N}{\partial X_{\Delta t}^N} \right| = 1 - \nabla_{X^N} \cdot \delta X^N
\end{aligned}
$$

So

$$
P_{\Delta t}(V_{\Delta t}) = P(V_0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \left(1 - \nabla_{X^N} \cdot \delta X^N\right) f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right)
$$

for small δX^N.

- What is δX^N?

    - For Hamiltonian systems $X_{\Delta t}^N \simeq X_0^N + \dot{X}_0^N \Delta t$, or $\delta X^N = \dot{X}_0^N \Delta t$.
    - Expanding for small displacements δX_0^N and small time intervals Δt:

$$
f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right) \simeq f\left(X_{\Delta t}^N, \Delta t\right)
$$
$$
-\frac{\partial f}{\partial t}\Delta t - (\nabla_{X^N} f) \cdot \delta X^N + \frac{1}{2}\left(\nabla_{X^N}^2 f\right)(\delta X^N)^2 + \dots
$$

    - Inserting this in previous equation for $P_{\Delta t}(V_{\Delta t}) = P(V_0)$, we get

$$
\begin{aligned}
P_{\Delta t}(V_{\Delta t}) &= P_{\Delta t}(V_{\Delta t}) + \int_{V_{\Delta t}} dX_{\Delta t}^N \\
&\quad \left(-\frac{\partial f}{\partial t}\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f(\delta X^N)^2\right)
\end{aligned}
$$

    or

$$
\int_{V_{\Delta t}} dX_{\Delta t}^N \left(-\frac{\partial f}{\partial t}\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f(\delta X^N)^2\right) = 0
$$

    - Since this holds arbitrary volume $V_{\Delta t}$, the integrand must vanish.

$$
\frac{\partial f}{\partial t}\Delta t = -\nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f(\delta X^N)^2 + \cdots
$$

    - Now, let us evaluate this for $\delta X^N = \dot{X}_0^N \Delta t$

        * To linear order in Δt

$$
\nabla_{X^N} \cdot \left(\dot{X}_0^N f\right)\Delta t = \left(\dot{X}^N \cdot \nabla_{X^N} f + \nabla_{X^N} \cdot \dot{X}^N f\right)\Delta t
$$

        but

$$
\nabla_{X^N} \cdot \dot{X}^N = \frac{\partial \dot{R}^N}{\partial R^N} + \frac{\partial \dot{P}^N}{\partial P^N} = \frac{\partial H}{\partial R^N \partial P^N} - \frac{\partial H}{\partial P^N \partial R^N} = 0!
$$

* Note that this implies the volume element does not change with normal Hamiltonian propagation:

$$dX_0^N = dX_{\Delta t}^N \, J(X^N; X_{\Delta t}^N) = dX_{\Delta t}^N \left(1 - \nabla_{X^N} \cdot \dot{X}^N \Delta t\right) = dX_{\Delta t}^N.$$

− Also, $(\delta X^N)^2 \sim O(\Delta t)^2$ since $\delta X^N \sim \Delta t$, so

$$\frac{\partial f}{\partial t} \Delta t = -\dot{X}^N \cdot \nabla_{X^N} f \Delta t + O(\Delta t)^2$$

− In the short-time limit,

$$\boxed{\frac{\partial f}{\partial t} = -\dot{X}^N \cdot \nabla_{X^N} f}$$

Recall

$$
\begin{aligned}
\dot{X}^N \cdot \nabla_{X^N} G &= \left(\dot{R}^N \cdot \nabla_{R^N} + \dot{P}^N \cdot \nabla_{P^N}\right) G \\
&= \left(\frac{\partial H}{\partial P^N} \cdot \nabla_{R^N} - \frac{\partial H}{\partial R^N} \cdot \nabla_{P^N}\right) G \equiv \mathcal{L}G = \{G, H\}
\end{aligned}
$$

So we obtain the **Liouville equation:**

$$\boxed{\frac{\partial f}{\partial t} = -\mathcal{L}f = -\{f, H\}}.$$

- The formal solution is:

$$f(\mathbf{x}^{(N)}, t) = e^{-\mathcal{L}t} f(\mathbf{x}^{(N)}, 0).$$

- Also note:

$$\frac{\partial f}{\partial t} + \dot{X}^N \cdot \nabla_{X^N} f = \frac{df(X^N, t)}{dt} = 0.$$

- Interpretation:

$$
\begin{aligned}
f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), 0) &= f(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t), t) \\
f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), t) &= f(\mathbf{r}^{(N)}(-t), \mathbf{p}^{(N)}(-t), 0).
\end{aligned}
$$

- If follow an initial phase point from time 0 to time t, probability density doesn't change (i.e. you go with the flow).

- Probability density near phase point $\mathbf{x}^{(N)}(0)$ at time t is the same as the *initial* probability density at backward-evolved point $\mathbf{x}^{(N)}(-t)$.

1.3.1   Equilibrium (stationary) solutions of Liouville equation

- Not a function of time, meaning $f(R^N, P^N, t) = f(R^N, P^N)$ or

$$\frac{\partial f}{\partial t} = -\mathcal{L}f = -\{f, H\} = \{H, f\} = 0.$$

- Recall that we showed that energy is conserved by the dynamics so $\frac{dH}{dt} = 0$.

- Suppose $f(R^N, P^N, t)$ is an *arbitrary* function of $H(R^N, P^N)$.

$$\frac{\partial f}{\partial t} = \{H, f(H)\} = \frac{\partial H}{\partial R^N} \cdot \frac{\partial f}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial f}{\partial R^N}$$

but

$$\frac{\partial f}{\partial P^N} = \frac{\partial f}{\partial H} \frac{\partial H}{\partial P^N} \qquad \frac{\partial f}{\partial R^N} = \frac{\partial f}{\partial H} \frac{\partial H}{\partial R^N}$$

$$\frac{\partial f}{\partial t} = \left(\frac{\partial H}{\partial R^N} \cdot \frac{\partial H}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial H}{\partial R^N} \right) \frac{\partial f}{\partial H} = 0$$

Thus any funct. of H is stationary solution of Liouville equation!

- In particular, both the microcanonical and canonical distribution functions are solutions of the Liouville equation.

1.3.2   Time-dependent Correlation Functions

Consider the *time-dependent correlation function* $C_{AB}(t)$ in the canonical ensemble

$$\left\langle A(\mathbf{x}^{(N)}, t)B(\mathbf{x}^{(N)}, 0) \right\rangle = \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, t)B(\mathbf{x}^{(N)}, 0)f(\mathbf{x}^{(N)}).$$

- From the form of the Liouville operator, for arbitrary functions A and B of the phase space coordinates

$$A(\mathbf{x}^{(N)}, t)B(\mathbf{x}^{(N)}, t) = \left(e^{\mathcal{L}t} A(\mathbf{x}^{(N)}, 0) \right) \left(e^{\mathcal{L}t} B(\mathbf{x}^{(N)}, 0) \right) = e^{\mathcal{L}t} \left(A(\mathbf{x}^{(N)}, 0)B(\mathbf{x}^{(N)}, 0) \right).$$

- It can be shown by integrating by parts that:

$$\left\langle \left(\mathcal{L}A(\mathbf{x}^{(N)}) \right) B(\mathbf{x}^{(N)}) \right\rangle = -\left\langle A(\mathbf{x}^{(N)}) \left(\mathcal{L}B(\mathbf{x}^{(N)}) \right) \right\rangle.$$

- Consequence:

$$\left\langle A(\mathbf{x}^{(N)}, t) B(\mathbf{x}^{(N)}, 0) \right\rangle = \left\langle A(\mathbf{x}^{(N)}) B(\mathbf{x}^{(N)}, -t) \right\rangle.$$

  - The *autocorrelation* function $C_{AA}(t)$ is therefore an even function of time.

- Also,

$$\int d\mathbf{x}^{(N)} \left(e^{\mathcal{L}t} A(\mathbf{x}^{(N)}, 0) \right) f(\mathbf{x}^{(N)}, 0) = \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, 0) \left(e^{-\mathcal{L}t} f(\mathbf{x}^{(N)}, 0) \right)$$

$$= \int d\mathbf{x}^{(N)} A(\mathbf{x}^{(N)}, 0) f(\mathbf{x}^{(N)}, t)$$

  - For an equilbrium system where $f(\mathbf{x}^{(N)}, t) = f(\mathbf{x}^{(N)})$,

$$\langle A(t) \rangle = \langle A(0) \rangle$$
$$\langle A(t + \tau) B(\tau) \rangle = \langle A(t) B(0) \rangle.$$