Dynamics and Non-equilibrium Phenomena

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1 Stochastic systems

- Consider a 1-D lattice on the x-axis.
- Suppose we have a particle originally at the origin, and particle moves in either direction with Prob = 1/2 (drunkards walk). What is the statistical behavior of this walker?
- Define: $P(x,t)$ =Prob of finding walker at pos. x at time t.
- $P(x,t)$ determines all behavior of system.
- What could this model?
  - Motion of defects on a lattice: defect hopping (not specifying mechanism)
  - Heavy particle being rapidly bombarded by solvent: $X(t+\tau) = X(t) + \xi(t)$, where $\xi(t)$ is a random displacement.
  - Statistical properties of $\xi(t)$ important: called *stochastic* since random element to dynamics.
  - On average, over realizations denoted by $\overline{X(n\tau)}$
    - ∗ All initial trajectories start from origin and proceed in steps
    - ∗ Could also have a nontrivial *distribution* of original positions:

$$\begin{aligned} \rho_0(i) &\neq \delta_{i,0} \\ \langle X(n\tau)\rangle &= \sum_{n=\infty}^{\infty} P_0(i)\overline{X(n\tau)}^i, \end{aligned}$$

where $\overline{X(n\tau)}^i$ is the stochastic average of position of walker over all trajectories starting at site i.

- How is the stochastic step distributed?
  - One possibility: constant probability.

$$f(\xi) = \left(\begin{array}{ll} 1 & Prob = p \\ -1 & Prob = q = 1-p \end{array} \right. \text{at all times}$$

– Another possibility: Gaussian-distributed (called Gaussian "noise").

$$f(\xi) \quad = \quad (1/2\pi\sigma^2)^{1/2} \mathrm{e}^{-\xi^2/2\sigma^2}$$

- Dynamics of probability determined by the *Master Equation*:

$$P_{t+\tau}(\ell) = \frac{1}{2}P_t(\ell-1) + \frac{1}{2}P_t(\ell+1)$$

  – This equation is in form of a *difference equation* on a lattice.
  – Can convert this into a continuous time, continuous space equation to solve (continuum limit):
    * **Continuous time** $P(l,t)$:

$$\begin{aligned}
\frac{\partial P(\ell,t)}{\partial t} &= \lim_{\tau\to 0}\left[\frac{P_{t+\tau}(\ell)-P_t(\ell)}{\tau}\right] \\
&= \lim_{\tau\to 0}\left[\frac{P_t(\ell)-P_{t-\tau}(\ell)}{\tau}\right] \qquad \text{but since} \\
P_{t+\tau}(\ell)-P_t(\ell) &= \frac{1}{2}P_t(\ell-1)+\frac{1}{2}P_t(\ell+1)-P_t(\ell) \\
\frac{\partial P(\ell,t)}{\partial t} &= \lim_{\tau\to 0}\frac{1}{\tau}\left[\frac{1}{2}P_t(\ell-1)+\frac{1}{2}P_t(\ell+1)-P_t(\ell)\right]
\end{aligned}$$

    * **Continuous Space** $\ell \to x, \quad \ell+1 \to \ell+\Delta$ where Δ is the lattice spacing

$$\begin{aligned}
\frac{\partial P(X,t)}{\partial t} &= \lim_{\substack{\tau\to 0\\ \Delta\to 0}}\frac{1}{2\tau}\Big(P_t(\ell-\Delta)-2P_t(\ell)+P_t(\ell+\Delta)\Big) \\
P_t(\ell-\Delta) &= P_t(\ell)-P_t'(\ell)\Delta+\frac{1}{2}\Delta^2 P_t''(\ell) \qquad \text{implies} \\
\frac{\partial P(X,t)}{\partial t} &= lim_{\substack{\tau\to 0\\ \Delta\to 0}}\frac{\Delta^2}{2\tau}P_t''(\ell) = D\frac{\partial^2}{\partial X^2}P(X,t)
\end{aligned}$$

    where

$$D \equiv \lim_{\Delta\to 0}\frac{1}{2\tau}$$

  – Called "diffusion equation".

1.1 Solution of the diffusion equation

- Solve by Fourier transform:

$$\begin{aligned}
\frac{\partial P}{\partial t} &= D\frac{\partial^2}{\partial x^2}P(x,t) \\
\tilde{P}(k,t) &= \frac{1}{\sqrt{2\pi}}\int dx\ \mathrm{e}^{ikx}P(x,t) \\
P(x,t) &= \frac{1}{\sqrt{2\pi}}\int dk\ \mathrm{e}^{-ikx}\tilde{P}(k,t)
\end{aligned}$$

$$
\begin{aligned}
\frac{\partial \tilde{P}(k,t)}{\partial t} &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \; \mathrm{e}^{ikx} \frac{\partial P(x,t)}{\partial t} = \frac{D}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \; \mathrm{e}^{ikx} \frac{\partial^2}{\partial x^2} P(x,t) \\
&= \frac{D}{\sqrt{2\pi}} \left[\mathrm{e}^{ikx} \frac{\partial P(x,t)}{\partial x} \Big|_{-\infty}^{\infty} - ik \int_{-\infty}^{\infty} dx \; \mathrm{e}^{ikx} \frac{\partial P(x,t)}{\partial x} \right] \\
&= \frac{D}{\sqrt{2\pi}} \left[-ik \; \mathrm{e}^{ikx} \; P(x,t) \Big|_{-\infty}^{\infty} + (ik)^2 \int_{-\infty}^{\infty} dx \; \mathrm{e}^{ikx} P(x,t) \right] \\
&= -Dk^2 \tilde{P}(k,t) \Rightarrow \tilde{P}(k,t) = \mathrm{e}^{-Dk^2 t} \tilde{P}(k,0)
\end{aligned}
$$

If $P(x,0) = \delta(x), \quad \tilde{P}(k) = \frac{1}{\sqrt{2\pi}} \Rightarrow \tilde{P}(k,t) = \frac{1}{\sqrt{2\pi}} \; \mathrm{e}^{-Dk^2 t}$

This implies $\boxed{P(x,t) = \left(\frac{1}{4\pi Dt}\right)^{1/2} \; \exp\left\{-\frac{x^2}{4Dt}\right\}}$

- Gaussian-distributed position, $\sigma^2 = 2Dt$

- $P(x,t)$ spreads from a delta-function at $t = 0$ to a Gaussian distribution:

  Width = 2Dt

  - Becomes more and more likely to find particle a long way from origin as width grows linearly in time
  - What is asymptoptic limit? $\lim_{t\to\infty} P(x,t) = C$

- All positions are equally likely since dynamics doesn't favor one position over another.
  - Expect $P_{eq}(x) = C$ since no biasing potential.
  - Master equation describes the evolution of $P(x,t)$ toward stationary solution. In this case, it is the unique equil distribution.

1.2 More on Gaussian distributions

1. Distribution specified by first + second moments:

$$
P(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \; \mathrm{e}^{-\frac{x^2}{2\sigma^2}} \qquad
\begin{aligned}
\langle x \rangle &= 0 \\
\langle x^2 \rangle &= \sigma^2 \\
P(x) &= \left(\frac{1}{2\pi \langle x^2 \rangle}\right)^{1/2} \; \mathrm{e}^{-\frac{x^2}{2\langle x^2 \rangle}}
\end{aligned}
$$

2. Important properties: $\langle x^{2n+1} \rangle = 0$ and $\langle x^{2n} \rangle = f(\sigma^2)$.

3. If $P(x_1,\ldots,x_n)=\left(\frac{1}{2\pi\langle x_1^2\rangle}\right)^{1/2}\ldots\left(\frac{1}{2\pi\langle x_n^2\rangle}\right)^{1/2}\exp\left\{-\left(\frac{x_1^2}{2\langle x_1^2\rangle},\ldots+\frac{x_n^2}{2\langle x_n^2\rangle}\right)\right\}$

   Then

$$\begin{aligned}\langle x_i\rangle &= 0\\ \langle x_i x_j\rangle &= \sigma_i^2\delta_{i,j}\end{aligned}$$

4. Continuum limit:

$$\begin{aligned}P(\xi(t)) &\sim e^{-\int d\tau\frac{\xi(\tau)^2}{2\sigma}}\\ \overline{\xi(t)} &= 0 \qquad \overline{\xi(t)\xi(t')}=\sigma\ \delta(t-t')\end{aligned}$$

   — Values of ξ are Gaussian distributed at all times

5. Any variable which is a linear combination of GRV is Gaussian distributed.

   (a)

$$X=\sum_{i=1}^{n}a_i x_n \overset{x_n GRV}{\Longrightarrow} P(X)=\left(\frac{1}{2\pi\langle X^2\rangle}\right)^{1/2}\ e^{-\frac{X^2}{2\langle X^2\rangle}}$$

   - Can show $\langle X^2\rangle=\sum_{i,j}a_i a_j\langle x_n x_m\rangle$

   (b) $A(t)=\int_0^t\ dq\ a(\tau)\xi(\tau)$ is Gaussian for all times t.

6. $\langle e^{ikx}\rangle=e^{-\frac{k^2\sigma^2}{2}}$.

1.3 The Langevin equation

What is artificial in this model for Brownian motion?

- Dynamics inherently inconsistent with Newtonian mechanics
- No conservation of momentum and no momentum
- Collisions exert a force on particle so momentum should change stochastically

Langevin 1872-1946:

- Solvent exerts a stochastic force on particle
- Friction as particle moves

Model Stochastic process as a GR process: One Brownian particle

$$\begin{aligned}\dot{R}(t) &= \frac{P(t)}{m} \qquad \dot{P}(t)=-\gamma P(t)+\xi(t)\\ P(\xi(t)) &\propto e^{-\int_0^t dt\frac{\xi(\tau)^2}{2\sigma^2}}\\ \overline{\xi(t)} &= 0\\ \overline{\xi(t)\xi(t')} &= \sigma^2\delta(t-t')\equiv 2\alpha\delta(t-t')\end{aligned}$$

- Solutions of equations of motion:

$$\begin{aligned} P(t) &= \mathrm{e}^{-\gamma t} P_0 + \int_0^t d\tau \ \mathrm{e}^{-\gamma(t-\tau)} \xi(\tau) \\ R(t) - R_0 &= \frac{1}{m} \int_0^t d\sigma \ P(\sigma) \end{aligned}$$

- How do we prove this: Take time derivatives of both sides

$$\dot{P}(t) = -\gamma \ \mathrm{e}^{-\gamma t} P_0 + \xi(t) - \gamma \int_0^t d\tau \ \mathrm{e}^{-\gamma(t-\tau)} \xi(\tau) = -\gamma P(t) + \xi(t).$$

- Also, $P(t=0) = P_0$.
  - We have used the property

$$\frac{\partial}{\partial x} \int_{a(x)}^{b(x)} dy \ g(x,y) = \int_{a(x)}^{b(x)} dy \ \frac{\partial g(x,y)}{\partial x} + g\left(x, b(t)\right) \frac{db}{dx} - g\left(x, a(x)\right) \frac{dg}{dx}$$

- Note that solution tells us

$$\begin{aligned} P(t) - \mathrm{e}^{-\gamma t} P_0 &= \int_0^t d\tau \ \mathrm{e}^{-\gamma(t-\tau)} \xi(\tau) \qquad \text{is a linear comb. of GRV, hence} \\ \overline{P(t)} &= \mathrm{e}^{-\gamma t} P_0 = \int_0^t d\tau \ \mathrm{e}^{-\gamma(t-\tau)} \ \overline{\xi(\tau)} \Longrightarrow \overline{P(t)} = \mathrm{e}^{-\gamma t} P_0 \end{aligned}$$

- Average means average over all realizations of process staring from (R_0, P_0)

$$\begin{aligned} \left(P(t) - \overline{P(t)}\right)^2 &= \int_0^t d\tau_1 \ \mathrm{e}^{-\gamma(t-\tau_1)} \xi(\tau_1) \int_0^t d\tau_2 \ \mathrm{e}^{-\gamma(t-\tau)} \xi(\tau_2) \\ \sigma_P^2(t) &\equiv \overline{\left(P(t) - \overline{P(t)}\right)^2} = \int_0^t d\tau_1 d\tau_1 \ \mathrm{e}^{-\gamma(t-\tau_1)} \ \mathrm{e}^{-\gamma(t-\tau_2)} \ \overline{\xi(\tau_1)\xi(\tau_2)} \\ &= 2\alpha \int_0^t d\tau_1 \ \mathrm{e}^{-2\gamma(t-\tau_1)} = \frac{\alpha}{\gamma} \left(1 - \mathrm{e}^{2\gamma t}\right) \end{aligned}$$

- What about the spatial coord?

$$\begin{aligned} \dot{R}(t) - R_0 &= \frac{1}{m} \int_0^t d\sigma \ P(\sigma) = \frac{1}{m} \int_0^t d\sigma \ \left[\mathrm{e}^{-\gamma\sigma} \ P_0 + \int_0^\sigma d\tau \ \mathrm{e}^{-\gamma(\sigma-\tau)} \ \xi(\tau) \right] \\ &= \frac{P_0}{m_\gamma} \left(1 - \mathrm{e}^{-\gamma t}\right) + \frac{1}{m} \int_0^t d\sigma \int_0^\sigma d\tau \ \mathrm{e}^{-\gamma(\sigma-\tau)} \ \xi(\sigma) \\ R(t) - R_0 &= \frac{P_0}{m\gamma} \left(1 - \mathrm{e}^{-\gamma t}\right) + \frac{1}{m\gamma} \int_0^t d\tau \ \left(1 - \mathrm{e}^{-\gamma(t-\tau)}\right) \xi(\tau) \\ \underline{\text{Note:}} \quad \overline{R(t) - R_0} &= \frac{P_0}{m\gamma} \left(1 - \mathrm{e}^{-\gamma t}\right) \Longrightarrow \frac{P_0}{m\gamma} \quad \text{at long times} \end{aligned}$$

- System moves in direction of initial velocity: extent determined also by friction.

$$\begin{aligned} Q(t) &\equiv R(t) - R_0 - \frac{P_0}{m\gamma}\left(1-\mathrm{e}^{-\gamma t}\right) = \frac{1}{m\gamma}\int_0^t d\tau \ \left(1-\mathrm{e}^{\gamma(t-\tau)}\right)\xi(\tau) \qquad \text{is a GRV} \\ \overline{Q(t)} &= 0 \\ \sigma_R^2(t) &= \overline{Q(t)^2} = \frac{2\alpha}{(m\gamma)^2}\left[t - \frac{1-\mathrm{e}^{-2\gamma t}}{2\gamma}\right] \qquad \frac{\alpha}{\gamma} = mkT \end{aligned}$$

- Long time limit: $\overline{\left[R(t) - \left(R_0 + \frac{P_0}{m\gamma}\right)\right]^2} \sim \frac{2kT}{m\gamma}\ t \equiv 2Dt$
- $D \equiv \frac{kT}{m\gamma}$: This is known as the *Stokes-Einstein law*.
- What does the distribution of positions look like as a function of time?

$$\begin{aligned} W\left(R(t)|R_0,P_0\right) &= \left(\frac{1}{2\pi\sigma_R^2(t)}\right)^{1/2} \exp\left\{-\frac{\left(R(t)-R_0-\beta D P_0(1-\mathrm{e}^{-2\gamma t})\right)^2}{2\sigma_R^2(t)}\right\} \\ \sigma_R^2(t) &\rightarrow 2Dt \qquad \text{as} \qquad t\rightarrow\infty \end{aligned}$$

  - At long times $\gamma t >> 1$,

$$W\left(R_0,P_0|R(t)\right) \rightarrow \left(\frac{1}{4\pi Dt}\right)^{1/2} \exp\left\{-\frac{\left(R(t)-(R_0+\frac{P_0}{m\gamma})\right)^2}{4Dt}\right\}$$

  - Obeys Diffusion equation at long times.
  - Same behavior as random walk model.

- Distribution of momentum:

$$W\left(P(t),t|P_0\right) = \left(2\pi\sigma_P^2(t)\right)^{-1/2} \exp\left\{\frac{-\left(P(t)-\mathrm{e}^{-\gamma t}P_0\right)^2}{2\sigma_P^2(t)}\right\}$$

  - Note: As $t\rightarrow\infty$, $\sigma_p^2(t)\rightarrow\frac{\alpha}{\gamma}$ and

$$W\left(P(t),t|P_0\right) \rightarrow \left(\frac{2\pi\alpha}{\gamma}\right)^{-1/2} \exp\left\{-\frac{P(t)^2}{2\frac{\alpha}{\gamma}}\right\}$$

  - This corresponds to a *Maxwell* distribution of velocities provided we set:

$$\frac{\alpha}{\gamma} = mkT = \frac{m}{\beta}$$

  - Fluctuation (α) and dissipation (γ) are connected if we are to get equilibration. This is known as the **Fluctuation-dissipation theorem**

– Note:

$$\begin{aligned}
\delta P(t) &\equiv \overline{(P(t+\Delta t)-P(t))} = \mathrm{e}^{-\gamma(t+\Delta t)} P_0 + \int_0^{t+\Delta t} d\tau\ \mathrm{e}^{-\gamma(t+\Delta t-\tau)} \overline{\xi(\tau)} \\
& \quad -\mathrm{e}^{-\gamma(t)} P_0 - \int_0^t d\tau\ \mathrm{e}^{-\gamma(t-\tau)}\ \overline{\xi(\tau)} \\
&= \left(\mathrm{e}^{-\gamma(t+\Delta t)} - \mathrm{e}^{-\gamma t}\right) P_0
\end{aligned}$$

so for small Δt,

$$\delta P(t) \simeq -\gamma \Delta t\ \mathrm{e}^{-\gamma t}\ P_0 = -\gamma \Delta t \overline{P(t)}.$$

– $P(t)$ fluctuates little on small time scales due to friction.

2 Liouville Equationn, Fokker-Planck Eqn and approach to equilibrium

- Suppose we have more than one Brownian particle, and these particles interact. Newton's equations are:

$$\begin{aligned}
\frac{dP^N(t)}{\partial t} \equiv \dot{P}^N(t) &= -\frac{\partial H}{\partial R^N} \overbrace{-\gamma P^N(t) + \xi^N(t)}^{Interaction\ with\ bath} \\
\dot{R}^N(t) &= \frac{\partial H}{\partial P^N} = \frac{P^N(t)}{M} \qquad \text{where} \qquad H = \frac{P^N \cdot P^N}{2M} + U(R^N)
\end{aligned}$$

- How does the prob distribution $f(R^N, P^N t)$ evolve for this system?
  - $X^N(t) \equiv \left(R^N(t), P^N(t)\right)$ is phase point
  - Dynamical evolution of system is a trajectory in 6N dimensional space
  - For deterministic systems (no bath interactions), trajectories *never* cross. Each point on a unique trajectory.
  - For stochastic process, many trajectories connect.

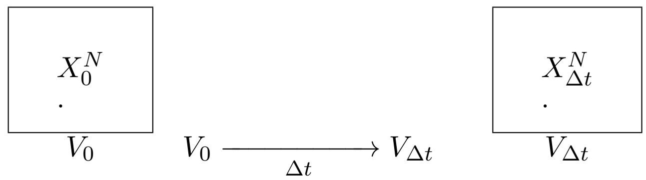
2.1 The Liouville equation for Hamiltonian and Non-Hamiltonian Systems

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:



  - Volume changes shape in mapping:

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

  - Maybe changes volume as well.
  - Number of states is V_0 and $V_{\Delta t}$ is same since we change variables to $X^N(\Delta t)$ from X_0^N 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

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

  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_0^N?
  - For Hamiltonian systems $\quad X_{\Delta t}^N \simeq X_0^N + \dot{X}_0^N \Delta t$, or $\delta X^N = \dot{X}_0^N \Delta t$.
  - More complicated for stochastic systems.

- Expanding for small displacements δX_0^N and small time intervals Δt:

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

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

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

  or

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

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

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

- 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

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

- 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

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

  So we obtain the **Liouville equation:**

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

- Also note:

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

2.2 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!

- Why should we expect the stationary solution to look like $f(R^N, P^N, t) = Z^{-1}\,\mathrm{e}^{-\beta H}$? What about the entropy? How does it evolve?
  - Brownian system gave Maxwellian distribution, not just any function of H !

2.3 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,

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

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

$$\begin{aligned}\langle A(t)\rangle &= \langle A(0)\rangle \\ \langle A(t+\tau)B(\tau)\rangle &= \langle A(t)B(0)\rangle .\end{aligned}$$

2.4 Non-Hamiltonian systems

- In real systems, always interaction with environment.
  - Use stochastic terms to describe system-bath interactions.
  - Build in stochastic nature into $f(R^N, P^N, t)$ from a given intial condition $f(R^N, P^N, 0)$.
- Now each phase point mapping is stochastic.

- We will average over these processes to get equation for $f(R^N, P^N, t)$
  - Assumption: For each infinitesimal interval Δt, both interaction is time-averaged.
  - Adiabatic assumption: both equilibrates instantly as system evolves.
- Dynamics has a stochastic element:

$$\begin{aligned}\dot{R}^N &= \frac{\partial H}{\partial P^N} = \frac{P^N}{M} \\ \dot{P}^N &= \frac{-\partial H}{\partial R^N} - \gamma P^N + \xi^N \\ \overline{\xi(t)} &= 0 \qquad \overline{\xi(t)\xi(t')} = 2\alpha\delta(t-t')\end{aligned}$$

- $\xi(t)$ independent of phase point X^N.

- Recall that we derived

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

and here we have

$$\begin{aligned}
\delta R^N \simeq \frac{P^N}{M}\Delta t &= \frac{\partial H}{\partial P^N}\Delta t \\
\delta P^N &= \int_0^{\Delta t} d\tau\ \dot{P}^N(\tau) \simeq -\left(\frac{\partial H}{\partial R^N} + \gamma P^N\right)\Delta t + \int_0^{\Delta t} d\tau\ \xi^N(\tau) \\
&= -\left(\frac{\partial H}{\partial R^N} + \gamma P^N\right)\Delta t + \delta P^N_s
\end{aligned}$$

  - The term δP^N_s is the stochastic part of the force.

- Now

$$\nabla_{X^N} \cdot \delta X^N = \nabla_{R^N}\delta R^N + \nabla_{P^N}\delta P^N = -\gamma\Delta t \nabla_{P^N} \cdot P^N + \nabla_{P^N}\delta P^N_s$$

unlike before where $\nabla_{X^N} \cdot \delta X^N = 0$

- By assumption, $\xi(\tau)$ is ind. of $X^N(t)$ at all times, so $\nabla_{X^N}\delta P^N_s = 0$ and

$$\begin{aligned}
\frac{\partial f}{\partial t}\Delta t &= -(\nabla_{X^N} \cdot \delta X^N) f - \delta X^N \cdot \nabla_{X^N} f + \frac{1}{2}\nabla^2_{P^N} f \cdot (\delta P^N_s)^2 + O(\Delta t)^2 \\
&= \left(\gamma \nabla_{P^N} \cdot P^N - \frac{\partial H}{\partial P^N} \cdot \nabla_{R^N} f + \frac{\partial H}{\partial R^N} \cdot \nabla_{P^N} f + \gamma P^N f\right)\Delta t \\
&\quad -\delta P^N_s \cdot \nabla_{P^N} f + \frac{1}{2}\nabla^2_{P^N} f (\delta P^N_s)^2 + O(\Delta t)^2
\end{aligned}$$

Now, we average over the stochastic bath interactions

$$\begin{aligned}
\overline{\delta P^N_s} &= \int_0^{\Delta t} d\tau\ \overline{\xi^N(\tau)} = 0 \\
\overline{(\delta P^N_s)^2} &= \int_0^{\Delta t} d\tau_1 d\tau_2\ \overline{\xi^N(\tau_1)\xi^N(\tau_2)} = 2\alpha \int_0^{\Delta t} d\tau_1 = 2\alpha\Delta t.
\end{aligned}$$

- Inserting this relation, dividing by Δt and taking limit $\Delta t \to 0$ gives

$$\begin{aligned}
\frac{\partial f}{\partial t} &= -\mathcal{L}f + \gamma(\nabla_{P^N} \cdot P^N) f + \gamma P^N \cdot \nabla_{P^N} f + \alpha \nabla^2_{P^N} f \\
&= -\mathcal{L}f + \gamma \nabla_{P^N} \cdot (P^N f) + \alpha\nabla^2_{P^N} f \\
\frac{\partial f}{\partial t} &= -\mathcal{L}f + \gamma\nabla_{P^N} \cdot \left[P^N + \frac{\alpha}{\gamma}\ \nabla_{P^N}\right] f
\end{aligned}$$

- Recall from our previous analysis that $\frac{\alpha}{\gamma} = \frac{m}{\beta}$ so we obtain the *Fokker-Planck equation.*

$$\boxed{\frac{\partial f}{\partial t} = -\mathcal{L}f + \frac{\gamma m}{\beta}\nabla_{P^N} \cdot \left[\nabla_{P^N} + \frac{\beta}{m}P^N\right] f}$$

2.5 Comments on the Fokker-Planck equation

1. Stationary solution when $\frac{\partial f}{\partial t} = 0$

   - If $f(H)$ then $-\mathcal{L}f = 0$ as we knew

   $$\frac{\beta}{m} P^N = \beta \nabla_{P^N} H$$

   so we get a stationary solution when

   $$(\nabla_{P^N} + \beta \nabla_{P^N} H) f = 0 \Longrightarrow f(H) \propto \mathrm{e}^{-\beta H} \; !$$

   - Interactions with environment give unique stationary distribution
   - Justifies hypothesis of relaxation to equil. distribution in long-time limit

2. A number of assumptions were made

   - Fast bath equil.
   - Gaussian stochastic process

   How can this be justified?

   Answer: Treat a system-bath as closed system (Hamiltonian)

   - Use Liouville equation and eliminate the bath degrees of freedom — Can do exactly
   - Obtain as generalized Langevin equation: ex

   $$\begin{aligned} \dot{P}^N(t) &= \frac{-\partial H}{\partial R^N} - \int_0^t d\tau \; M(\tau) P^N(t-\tau) + \xi(t) \\ M(\tau) &\propto \langle \xi(\tau) \xi \rangle \end{aligned}$$

   $M(\tau)$ is a memory function: if system-bath coupling is weak and $\tau_s \gg \tau_b$, then can justify Fokker-Planck equation

   - Not always valid

2.6 General case: probability theory

- Can devise a general procedure to go from *moments* constructed from stochastic average to a stochastic differential equation.
- It can be shown that for a *Markov* process where $\gamma = \int_0^\infty d\tau \, M(\tau)$ is valid that

$$\begin{aligned} \frac{\partial f}{\partial t} &= \sum_{j=1}^{\infty} \frac{(-1)^j}{j!} \nabla^j_{X^N} \left(A_j(X^N) f \right) \qquad \text{where} \\ A_j(X^N) &= \lim_{\Delta \to 0} \frac{\overline{(X^N(t+\Delta) - X^N(t))^j}}{\Delta} = \text{transition moments} \\ &= \lim_{\Delta \to 0} \frac{\overline{(\Delta X^N)^j}}{\Delta} \qquad \text{with } \Delta X^N \equiv X^N(t+\Delta) - X^N(t). \end{aligned}$$

- Example: for the Fokker-Planck equation, $X^N = (R^N, P^N)$ and

$$\frac{\partial f}{\partial t} = \lim_{\Delta \to 0} \left[-\frac{\partial}{\partial X^N} \cdot \left(\frac{\overline{\Delta X^N}}{\Delta} f \right) + \frac{1}{2} \frac{\partial^2}{\partial (X^N)^2} \left(\frac{\overline{(\Delta X^N)^2}}{\Delta} f \right) + \cdots \right]$$

- It is simple to show that as $\Delta \to 0$:

$$\begin{aligned} \frac{\overline{\Delta P^N}}{\Delta} &\to -\gamma P^N(t) - \frac{\partial H}{\partial R^N(t)} \qquad \frac{\overline{(\Delta P^N)^2}}{\Delta} \to 2\alpha + O(\Delta) \\ \frac{\overline{\Delta R^N}}{\Delta} &\to -\frac{P^N(t)}{m} \qquad \frac{\overline{(\Delta R^N)^2}}{\Delta} \to O(\Delta) \\ \frac{\overline{\Delta R^N \Delta P^N}}{\Delta} \to O(\Delta). \end{aligned}$$

and

- $A_n(X^N) \to 0$ for $n \geq 3$ as $\Delta \to 0$.
- For "Gaussian" noise, the Fokker-Planck equation (truncation at order $n = 2$ is exact.