II.1B Liouville Dynamics

Newtonian dynamics

$$\boxed{\begin{aligned}\dot{\vec{R}}_i(t) &= \frac{1}{m}\vec{P}_i(t)\\ \dot{\vec{P}}_i(t) &= -\vec{\nabla}_i\, U(\{\vec{R}_i\}_{i=1\dots N})\end{aligned}}$$

time evolution in classical mechanics

also Hamilton function

$$\mathcal{H} = \sum_{i=1}^{N}\frac{1}{2m}\vec{P}_i^{\,2}(t) + U(\{\vec{R}_i(t)\})$$

canonical equations of motion

$$\boxed{\begin{aligned}\dot{\vec{R}}_i(t) &= \partial_{\vec{P}_i}\mathcal{H} = \{\vec{R}_i(t), \mathcal{H}\}\\ \dot{\vec{P}}_i(t) &= -\partial_{\vec{R}_i}\mathcal{H} = \{\vec{P}_i(t), \mathcal{H}\}\end{aligned}}$$

with Poisson brackets

$$\{A, B\} = \sum_{i=1}^{N}\left(\partial_{\vec{R}_i}A\,\partial_{\vec{P}_i}B - \partial_{\vec{P}_i}A\,\partial_{\vec{R}_i}B\right)$$

dynamics of observable A

$$A(\Gamma, t) = A(\{\vec{R}_i(t), \vec{P}_i(t)\}) = A(\Gamma_t)$$

no explicit time dependence of A, dynamics driven only by time evolution of phase space

$$\frac{d}{dt}A(\Gamma, t) = \sum_{i=1}^{N}\Big(\partial_{\vec{R}_i}A\cdot\underbrace{\dot{\vec{R}}_i}_{\partial_{\vec{P}_i}\mathcal{H}} + \partial_{\vec{P}_i}A\cdot\underbrace{\dot{\vec{P}}_i}_{-\partial_{\vec{R}_i}\mathcal{H}}\Big)$$

$$\boxed{\frac{d}{dt} A(\Gamma,t) = \{A, \mathcal{H}\} =: i\mathcal{L}A}$$

Liouville operator $\mathcal{L}$

$\mathcal{L}$ a linear operator in $L^2(\Gamma, P)$

formal solution $\boxed{A(t) = e^{i\mathcal{L}t} A}$

$A = A_0 = A(t=0)$

definition of time-dependent correlation functions

$$C_{AA}(t) = \langle A(t)^* A \rangle = \langle A(t) | A \rangle$$

$\mathcal{L}$ is hermitian operator: $\boxed{\langle A | \mathcal{L} B \rangle = \langle \mathcal{L} A | B \rangle}$

proof: $\langle A | \mathcal{L} B \rangle = \frac{1}{Z} \int d\Gamma\, e^{-\beta\mathcal{H}} A^* \mathcal{L} B$

using $\mathcal{L}B = -\{B, \mathcal{H}\}$

$$= \frac{1}{Z} \int d\Gamma\, e^{-\beta\mathcal{H}} A^* (-i) \sum_{i=1}^{N} (\partial_{R_i} B\, \partial_{p_i} \mathcal{H} -$$

$$- \partial B_{p_i}\, \partial_{R_i} \mathcal{H}) =$$

integration by parts

$$= \frac{1}{Z} \int d\Gamma\, B\, i \sum_{i=1}^{N} [\partial_{R_i} (A^* \partial_{p_i} \mathcal{H} e^{-\beta\mathcal{H}}$$

$$- \partial_{p_i} (A^* \partial_{R_i} \mathcal{H} e^{-\beta\mathcal{H}})] =$$

$$= \frac{1}{Z} \int d\Gamma\, B e^{-\beta\mathcal{H}} \underbrace{i\{A^*, \mathcal{H}\}}_{= i\{A,\mathcal{H}\}^* = (\mathcal{L}A)^*} = \langle \mathcal{L} A | B \rangle$$

$\square$

time evolution operator unitary in Hilbert space

$$\left(e^{i\mathcal{L}t}\right)^{\dagger}\left(e^{i\mathcal{L}t}\right) = e^{-i\mathcal{L}t}e^{+i\mathcal{L}t} = \mathbb{1}$$

time evolution of correlation functions

$$C_{AA}(t) = \langle e^{i\mathcal{L}t}A|A\rangle = \langle A|e^{-i\mathcal{L}t}A\rangle$$

$$\boxed{C_{AA}(t) = \langle A|e^{-i\mathcal{L}t}|A\rangle}$$

matrix element of backwards time evolution operator $\mathcal{R}(t) = e^{-i\mathcal{L}t}$

properties of Liouville operator

spectral decomposition, Eigenstates

$$\mathcal{L}|\lambda\rangle = \lambda|\lambda\rangle, \quad \lambda \in \mathbb{R}$$

real spectrum for hermitian operator
projection onto Eigenspace

$$\mathcal{L} = \sum_{\lambda} \lambda|\lambda\rangle\langle\lambda| = \int \lambda \, dE(\lambda)$$

↳ spectral measure

$$e^{-i\mathcal{L}t} = \sum_{\lambda} e^{-i\lambda t}|\lambda\rangle\langle\lambda| = \int e^{-i\lambda t} dE(\lambda)$$

$$\rightarrow C_{AA}(t) = \sum_{\lambda} |\langle A|\lambda\rangle|^2 e^{-i\lambda t}$$

↳ auto correlation functions are positive linear superpositions of exponentials

II. 1 C Fluctuation Dissipation Theorem

time-dependent perturbation, starting in equilibrium

$$\mathcal{H}_0(\Gamma) \to \mathcal{H}(\Gamma,t) = \mathcal{H}_0(\Gamma) - \alpha^i(t)\, Y_i(\Gamma)^*$$

$\alpha^i(t) = 0 \;,\; t<0 \;,$ generalized forces

fluctuations $\quad \delta Y_i(\Gamma) = Y_i(\Gamma) - \langle Y_i(\Gamma)\rangle_0$

$$\mathcal{H}(\Gamma,t) = \mathcal{H}_0(\Gamma) - \alpha^i(t)\,\delta Y_i(\Gamma)^*$$

goal $\boxed{\langle \delta X\rangle(t) = \mathrm{Tr}[\,\rho(t)\, X\,] - \langle X_0\rangle}$

and equation of motion (eom) for $\rho(t)$

$$\boxed{\frac{d}{dt}\rho(\Gamma,t) = \partial_t \rho(t) + \{\rho(\Gamma,t), \mathcal{H}(\Gamma,t)\}}$$

Liouville equation, conservation of probability

$$\to \partial_t \rho(t) = -i\mathcal{L}(t)\,\rho(t)$$

decomposition $\rho(\Gamma,t) = \rho_0(\Gamma) + \delta\rho(\Gamma,t)$

with $\delta\rho(\Gamma,t) = 0 \,,\; t\leq 0$

↳ linearized eom

$$\partial_t\, \delta\rho(\Gamma,t) = -\{\delta\rho(\Gamma,t), \mathcal{H}_0(\Gamma)\} + \{\rho_0(\Gamma), \alpha^i \delta Y_i(\Gamma)^*\} + \mathcal{O}(\alpha^2)$$

$$\partial_t \delta\rho(\Gamma,t) = -i\underbrace{\mathcal{L}_0}_{\text{unperturbed Liouvillian}}\delta\rho(\Gamma,t) + \alpha^i(t)\{\rho_0(\Gamma), \delta Y_i(\Gamma)^*\}$$

note $\{\rho_0(\Gamma), \delta Y_i(\Gamma)^*\} = -\beta\rho_0(\Gamma)\{\mathcal{H}_0(\Gamma), \delta Y_i(\Gamma)^*\}$

$$= -\beta\rho_0(\Gamma)\, i\mathcal{L}_0\, \delta Y_i(\Gamma)^*$$

$$\Rightarrow \boxed{\partial_t \delta\rho(t) = -i\mathcal{L}_0\delta\rho(t) + \beta\rho_0(\Gamma)\alpha^i(t)\, i\mathcal{L}_0\delta Y_i(\Gamma)^*}$$

closed equation $\rightarrow$ solution

auxiliary quantity $\delta\tilde\rho(t) = e^{i\mathcal{L}_0 t}\delta\rho(t)$

$\rightarrow \partial_t\, \delta\tilde\rho(\Gamma,t) = \beta\rho_0(\Gamma)\alpha^i(t)\, i\mathcal{L}_0\, e^{i\mathcal{L}_0 t}\delta Y_i(\Gamma)^*$

NB: $\mathcal{L}_0$ commutes with $\mathcal{H}_0$ and hence with ρ_0

$$\delta\rho(\Gamma,t) = \beta\rho_0(\Gamma)\int_0^t ds\, \alpha^i(s) e^{-i\mathcal{L}_0(t-s)} \cdot i\mathcal{L}_0\delta Y_i(\Gamma)^*$$

$$= -\beta\rho_0(\Gamma)\int_0^t ds\, \alpha^i(s)\left[e^{i\mathcal{L}_0(t-s)} i\mathcal{L}_0\delta Y_i(\Gamma)\right]^*$$

$$\boxed{\delta\rho(\Gamma,t) = -\beta\rho_0\Gamma\int_0^t ds\, \alpha^i\, \delta\dot Y_i(\Gamma, t-s)^*}$$

$$\langle\delta X\rangle(t) = -\beta\int_0^t ds\, \alpha^i(s)\langle\delta\dot Y_i(t-s)|\delta X\rangle$$

response function

$$\chi_{xy}(t) := -\beta\langle\delta\dot Y(t)|\delta X\rangle = -\beta\frac{d}{dt}C_{YX}(t)$$

$$\boxed{\langle\delta X\rangle(t) = \int_0^t ds\, \alpha(s)\chi_{xy}(t-s)}$$

- microscopic expression for linear response
→ causality: response collects history
- shift of initial point to t_0

$$\langle \delta X \rangle (t) = \int_{t_0}^{t} ds\, \alpha(s) \chi_{xy}, \text{ in particular } t_0 \to -\infty$$

- convolution integral

$$\chi_{xy}(t) = -\beta \langle \delta \dot{Y}(t) | \delta X \rangle \underset{\text{Heaviside function}}{\theta(t)}$$

$$\langle \delta X \rangle (t) = \int_{-\infty}^{\infty} ds\, \alpha(s) \chi_{xy}(t-s)$$

Fourier trafo $\langle \widehat{\delta X} \rangle (\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \delta X \rangle (t)$

$\langle \widehat{\delta X} \rangle (\omega) = \hat{\alpha}(\omega) \hat{\chi}_{xy}(\omega)$ convolution theorem

response is local in frequency
(cf. Electrodynamics $\varepsilon(\omega)$)

$\hat{\chi}_{xy}(\omega) = \int_0^{\infty} dt\, e^{i\omega t} \chi_{xy}(t)$ one-sided Fourier trafo

invoke Fluctuation-Dissipation Theorem

$$\hat{\chi}_{xy}(\omega) = -\beta \int_0^{\infty} dt\, e^{i\omega t} \frac{d}{dt} C_{yx}(t) =$$
$$= \beta \left[C_{yx}(t=0) + \omega \hat{C}_{yx}(z = i0 + \omega) \right]$$

with Laplace transform

$$\hat{C}_{yx}(z) := i \int_0^{\infty} dt\, e^{izt} C_{yx}$$

complex frequency $z \in \mathbb{C}_+ =$

$= \{ z \in \mathbb{C} : \operatorname{Im}(z) > 0 \}$

upper half plane

$\rightarrow$ dynamic response determined by time-dependent correlation function