Liouville Equation

[R. Zwanzig, "Nonequilibrium Statistical Mechanics", P.31]

— Phase space

Let $\mathbb{q} = (q_1, \ldots, q_{3N})$ and $\mathbb{P} = (P_1, \ldots, P_{3N})$ be the coordinate and momentum vectors, where N is the number of atoms.

The pair of the vectors, $\mathbb{X} = (\mathbb{q}, \mathbb{P})$, specifies a phase-space point.

— Phase-space trajectory : Liouville operator

The motion of the system in the phase space is described by the trajectory, $\mathbb{X}(t)$ $(t \in \mathbb{R})$, which is governed by Hamilton's equations,

$$\begin{cases} \dot{\mathbb{q}} = \dfrac{d\mathbb{q}}{dt} = \dfrac{\partial H}{\partial \mathbb{P}}, & (1a) \\[2ex] \dot{\mathbb{P}} = \dfrac{d\mathbb{P}}{dt} = -\dfrac{\partial H}{\partial \mathbb{q}}. & (1b) \end{cases}$$

For the Hamiltonian, $\mathbb{H}(\mathbb{q}, \mathbb{P})$, we assume a form

$$\mathbb{H}(\mathbb{q}, \mathbb{P}) = \sum_{i=1}^{3N} \frac{P_i^2}{2m_i} + V(\mathbb{q}) \qquad (2a)$$

$$= \frac{1}{2} \mathbb{P}^T \mathbb{M}^{-1} \mathbb{P} + V(\mathbb{q}), \qquad (2b)$$

where m_i is the mass associated with the i-th coordinate, $M_{ij} = m_i \delta_{ij}$ is the diagonal mass matrix, and $V(\mathbb{q})$ is the potential energy.

Substituting Eq. (2) in (1), the equations of motion become

$$\begin{cases} \dot{\mathbb{q}} = \mathbb{M}^{-1} \mathbb{P} & (3a) \\[2ex] \dot{\mathbb{P}} = -\dfrac{\partial V}{\partial \mathbb{q}} & (3b) \end{cases}$$

②

Consider an arbitrary function, $A(\mathbb{q},\mathbb{P})$, of a phase-space point. The time evolution of the function value along the trajectory, $\mathbb{X}_t$, is given by

$$\frac{dA}{dt} = \underbrace{\dot{\mathbb{q}}}_{\frac{\partial H}{\partial \mathbb{P}}}\cdot\frac{\partial A}{\partial \mathbb{q}} + \underbrace{\dot{\mathbb{P}}}_{-\frac{\partial H}{\partial \mathbb{q}}}\cdot\frac{\partial A}{\partial \mathbb{P}}$$

$$= \left(\frac{\partial H}{\partial \mathbb{P}}\cdot\frac{\partial}{\partial \mathbb{q}} - \frac{\partial H}{\partial \mathbb{q}}\cdot\frac{\partial}{\partial \mathbb{P}}\right)A$$

$$\therefore \frac{dA}{dt} = LA \qquad (4)$$

where the Liouville operator is defined as

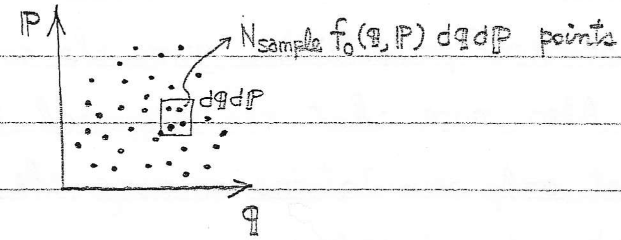
$$L = \frac{\partial H}{\partial \mathbb{P}}\cdot\frac{\partial}{\partial \mathbb{q}} - \frac{\partial H}{\partial \mathbb{q}}\cdot\frac{\partial}{\partial \mathbb{P}} \qquad (5)$$

The formal solution of Eq.(4) is

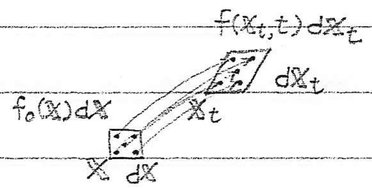
$$A(t) = e^{tL}A(\mathbb{P},\mathbb{q}) \qquad (6)$$

Phase space distribution: Liouville's theorem

Consider an ensemble of phase-space points, and let $f_0(\mathbb{q},\mathbb{P})\,d\mathbb{q}\,d\mathbb{P} = f_0(\mathbb{X})\,d\mathbb{X}$ be the probability to find the system in a volume element $d\mathbb{X}$ around $\mathbb{X}$.



Let all the phase-space points in the ensemble evolve in time, $\mathbb{X}_t = e^{tL}\mathbb{X}$, and consider the distribution, $f(\mathbb{X},t)$, at time t.



We consider a volume element, $d\mathbb{X}$, around $\mathbb{X}$, and follow the trajectories of $N_{sample} f_0(\mathbb{X})\,d\mathbb{X}$ for time t, at which the points occupie a volume element, $d\mathbb{X}_t$, around $\mathbb{X}_t$:

$$\cancel{N_{sample}}\, f(\mathbb{X}_t, t)\, d\mathbb{X}_t = \cancel{N_{sample}}\, f_0(\mathbb{X})\, d\mathbb{X} \tag{7}$$

$$f(\mathbb{X}_t, t) \left|\frac{\partial \mathbb{X}_t}{\partial \mathbb{X}}\right| \cancel{d\mathbb{X}} = f_0(\mathbb{X})\, \cancel{d\mathbb{X}} \tag{8}$$

Now consider the Jacobian, $|\partial\mathbb{X}_t/\partial\mathbb{X}|$, in Eq. (8). For small time, dt, from Eq. (3),

$$\begin{cases} \mathbb{q}_{dt} = \mathbb{q} + \dot{\mathbb{q}}\,dt = \mathbb{q} + \mathbb{M}^{-1}\mathbb{P}\,dt & (9a) \\ \mathbb{P}_{dt} = \mathbb{P} + \dot{\mathbb{P}}\,dt = \mathbb{P} - \dfrac{\partial V}{\partial \mathbb{q}}\,dt & (9b) \end{cases}$$

$$\therefore \begin{vmatrix} \partial \mathbb{q}_t/\partial \mathbb{q} & \partial \mathbb{q}_t/\partial \mathbb{P} \\ \partial \mathbb{P}_t/\partial \mathbb{q} & \partial \mathbb{P}_t/\partial \mathbb{P} \end{vmatrix}$$

$$= \left|\begin{array}{c:c} \mathbb{I} & \mathbb{M}^{-1}dt \\ \hdashline -\frac{\partial^2 V}{\partial \mathbb{q}^2}dt & \mathbb{I} \end{array}\right|$$

Note that the identical permutation gives the contribution 1 to the determinant. Also note that the diagonal blocks are identity matrices, so that only permutations mixing the $\mathbb{q}$ and $\mathbb{P}$ blocks need to be considered. Consider

$$\underset{1}{J_{11}}\ \underset{1}{J_{22}} \cdots \underbrace{J_{q_i p_j}}_{m_j^{-1}\delta_{ij}} \cdots\cdots \underbrace{J_{p_j q_i}}_{-\frac{\partial^2 V}{\partial q_j \partial q_i}} \cdots J_{NN} = -\frac{1}{m_j}\frac{\partial^2 V}{\partial q_j \partial q_i}\delta_{ij}\,dt^2$$

Any such permutation thus introduces a factor dt^2. Therefore,

$$\left|\frac{\partial \mathbb{X}_{dt}}{\partial \mathbb{X}}\right| = 1 + O(dt^2) \tag{10}$$

and

$$\left|\frac{\partial \mathbb{X}_t}{\partial \mathbb{X}}\right| = \lim_{N\to\infty}\left(1 + a\left(\frac{t}{N}\right)^2\right)^N$$

$$= \exp\left(\lim_{N\to\infty} N \log_e\left[1 + a\left(\frac{t}{N}\right)^2\right]\right)$$

$$= \exp\left(\lim_{N\to\infty} \cancel{N}\cdot a\frac{t^2}{N^{\cancel{2}}}\right) = e^0 = 1$$

$$\therefore \left|\frac{\partial \mathbb{X}_t}{\partial \mathbb{X}}\right| = 1 \tag{11}$$

Combining Eqs. (8) and (11),

$$f(\mathbb{X}_t, t) = f_0(\mathbb{X}) \tag{12}$$

For small dt, Eq. (12) results in

$$\underbrace{f(\mathbb{X}+\dot{\mathbb{X}}\,dt,\ dt)}\ =\ f(\mathbb{X},0)$$

$$f(\mathbb{X},dt)\ +\ \dot{\mathbb{X}}\,dt\cdot\frac{\partial f}{\partial \mathbb{X}}\bigg|_{\mathbb{X},\underbrace{dt}_{0 \text{ in the leading term}}}\ =\ f(\mathbb{X},0)$$

$$\frac{f(\mathbb{X},dt)-f(\mathbb{X},0)}{dt}\ =\ -\dot{\mathbb{X}}\cdot\frac{\partial}{\partial \mathbb{X}}f$$

$$=\ -\left(\dot{\mathbb{q}}\cdot\frac{\partial}{\partial \mathbb{q}}+\dot{\mathbb{P}}\cdot\frac{\partial}{\partial \mathbb{P}}\right)f(\mathbb{X},0)$$

$$=\ -\left(\frac{\partial H}{\partial \mathbb{P}}\cdot\frac{\partial}{\partial \mathbb{q}}\ \ \frac{\partial H}{\partial \mathbb{q}}\cdot\frac{\partial}{\partial \mathbb{P}}\right)f(\mathbb{X},0)$$

$$=\ -L\,f(\mathbb{X},0) \tag{13}$$

note the negative sign.

$$\therefore\ \frac{\partial f}{\partial t}\ =\ -L\,f \tag{14}$$

and its formal solution is

$$f(\mathbb{X},t)\ =\ e^{-tL}\,f(\mathbb{X},0) \tag{15}$$

Continuity equation

From Eq. (14)

$$\frac{\partial f}{\partial t} = -\frac{\partial H}{\partial \mathbb{P}}\cdot\frac{\partial f}{\partial \mathbb{q}} + \frac{\partial H}{\partial \mathbb{q}}\cdot\frac{\partial f}{\partial \mathbb{P}}$$

$$= -\frac{\partial}{\partial \mathbb{q}}\cdot\Big(\underbrace{\frac{\partial H}{\partial \mathbb{P}}}_{\dot{\mathbb{q}}} f\Big) + \cancel{\frac{\partial^2 H}{\partial \mathbb{q}\cdot\partial \mathbb{P}} f} + \frac{\partial}{\partial \mathbb{P}}\cdot\Big(\underbrace{\frac{\partial H}{\partial \mathbb{q}}}_{-\dot{\mathbb{P}}} f\Big) - \cancel{\frac{\partial^2 H}{\partial \mathbb{P}\cdot\partial \mathbb{q}} f}$$

$$= -\frac{\partial}{\partial \mathbb{q}}\cdot(\dot{\mathbb{q}} f) - \frac{\partial}{\partial \mathbb{P}}\cdot(\dot{\mathbb{P}} f)$$

$$= -\frac{\partial}{\partial \mathbb{X}}\cdot(\dot{\mathbb{X}} f) \qquad (16)$$

$$\therefore \frac{\partial f}{\partial t} + \frac{\partial}{\partial \mathbb{X}}\cdot(\dot{\mathbb{X}} f) = 0 \qquad (17)$$

(Useful identity)

For arbitrary function, $A(\mathbb{X})$,

$$LA(\mathbb{X}) = \dot{\mathbb{X}}\cdot\frac{\partial}{\partial \mathbb{X}} A = \frac{\partial}{\partial \mathbb{X}}\cdot(\dot{\mathbb{X}} A) \qquad (18)$$

$$\because LA(\mathbb{X}) = \Big(\underbrace{\frac{\partial H}{\partial \mathbb{P}}}_{\dot{\mathbb{q}}}\cdot\frac{\partial}{\partial \mathbb{q}} - \underbrace{\frac{\partial H}{\partial \mathbb{q}}}_{+\dot{\mathbb{P}}}\cdot\frac{\partial}{\partial \mathbb{P}}\Big) A = \dot{\mathbb{X}}\cdot\frac{\partial}{\partial \mathbb{X}} A$$

$$= \frac{\partial}{\partial \mathbb{q}}\cdot\Big(\underbrace{\frac{\partial H}{\partial \mathbb{P}}}_{\dot{\mathbb{q}}} A\Big) - \cancel{\frac{\partial^2 H}{\partial \mathbb{q}\partial \mathbb{P}} A} - \frac{\partial}{\partial \mathbb{P}}\cdot\Big(\underbrace{\frac{\partial H}{\partial \mathbb{q}}}_{-\dot{\mathbb{P}}} A\Big) + \cancel{\frac{\partial^2 H}{\partial \mathbb{P}\cdot\partial \mathbb{q}} A}$$

$$= \frac{\partial}{\partial \mathbb{X}}\cdot(\dot{\mathbb{X}} A) \quad //$$