

# Microscopic dynamics

$$\left\{ \begin{array}{l} \text{Particle positions: } \Gamma_1(t), \dots, \Gamma_N(t) \equiv \vec{\Gamma}(t) \\ \text{Velocities: } \dot{\Gamma}_i = \frac{d\Gamma_i}{dt} = v_i \\ \text{Momenta (conjugate vars): } P_i = m_i v_i \end{array} \right.$$

The interaction between the particles is specified through an interaction potential energy  $U(\Gamma_1, \dots, \Gamma_N)$ , e.g.

$$U = \sum_{i,j} u_{ij}(\Gamma_{ij}) = \sum_{i,j} u_{ij}(\Gamma_i - \Gamma_j)$$

The total energy of the particle system is the Hamiltonian

$$H(\vec{p}, \vec{r}) = \sum_i \frac{1}{2} m_i v_i^2 + U(\vec{r})$$

$\swarrow$  kinetic  $\swarrow$  potential energy

and the dynamical law or law of motion is given by Hamilton's equations:

$$\begin{cases} \dot{r}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m_i} = v_i \\ \dot{p}_i = - \frac{\partial H}{\partial r_i} = - \frac{\partial U}{\partial r_i} = F_i(\vec{r}) \end{cases}$$

$\swarrow$  Newton's second law  $\uparrow$  force

Observe that this dynamics conservees energy, i.e., the Hamiltonian is a constant of motion (for an isolated system):

$$\begin{aligned} \frac{dH}{dt} &= \sum_i \left[ \frac{\partial H}{\partial r_i} \dot{r}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right] = \\ &= \sum_i \left[ \frac{\partial H}{\partial r_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial r_i} \right] = 0 \end{aligned}$$

The distinction between positions and momenta is somewhat artificial. Instead, think about all DFs together.

Microstate

$$z = \left\{ \vec{q}, \vec{p} \right\} \in \mathbb{R}^{2Nd}$$

is a point in phase space.

$$\dot{z} = \begin{bmatrix} 0 & \mathbf{I} \\ -\mathbf{I} & 0 \end{bmatrix} \begin{bmatrix} \partial H / \partial q \\ \partial H / \partial p \end{bmatrix} = L_0 \frac{\partial H(z)}{\partial z}$$

 $L_0 = \begin{bmatrix} 0 & \mathbf{I} \\ -\mathbf{I} & 0 \end{bmatrix}$  is a skew-adjoint or skew-symmetric matrix
Reminder: The adjoint of a linear operator:

$$u \cdot (L v) = (L^* u) \cdot v$$

$$\text{Skew-adjoint: } L^* = -L$$

$$\text{Self-adjoint: } L^* = L$$

Take  $u = v$

$$\begin{aligned}
 u \cdot (L u) &= u^* L u = (L^* u) \cdot u = \\
 &= -u \cdot (L u) \quad \text{if } L \text{ is skew-adjoint} \\
 \Rightarrow u \cdot (L u) &= 0 \quad \text{for any } u
 \end{aligned}$$

Take  $\dot{z} = L_0 \frac{\partial H}{\partial z} \Rightarrow$

$$\frac{dH}{dt} = \frac{\partial H}{\partial z} \cdot \dot{z} = \frac{\partial H}{\partial z} \cdot L_0 \frac{\partial H}{\partial z} = 0$$

More generally, Hamiltonian dynamics in non-canonical coordinates can be constructed for some  $L_0$  and  $H$ .

Instead of focusing on a single trajectory, consider the probability density  $g(z; t)$  of an ensemble of trajectories.

$g(z, t)$  is a statistical description of the microstate

The flow map of the points in phase space is the phase-space vector field:

$$u = \dot{z}$$

$$\nabla_z \cdot u = \sum_i \frac{\partial u_i}{\partial z_i} = \sum_i \frac{\partial}{\partial p_i} (\dot{p}_i) + \sum_i \frac{\partial}{\partial q_i} (\dot{q}_i)$$

$$= \sum_i \frac{\partial}{\partial p_i} \left( -\frac{\partial H}{\partial q_i} \right) + \sum_i \frac{\partial}{\partial q_i} \left( \frac{\partial H}{\partial p_i} \right) = 0$$

Therefore the flow in phase space for Hamiltonian dynamics is incompressible

$$\nabla \cdot u = \nabla_z \cdot (\dot{z}) = 0 \quad \left[ \text{Note: } \nabla \cdot \text{ is not the usual spatial divergence} \right]$$

Since microstates do not have sources or sinks, i.e., they do not appear/disappear, the evolution of  $\rho(z)$  follows an advection equation:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho u) = -\rho \nabla \cdot u - u \cdot \nabla \rho$$

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + u \cdot \nabla \rho = 0}$$

Liouville equation

$$\frac{d\rho}{dt} = D_t \rho = 0$$

Recalling

$$u = \dot{z} = \left\{ \frac{\partial H}{\partial \vec{p}}, -\frac{\partial H}{\partial \vec{q}} \right\}$$

$$u \cdot \nabla \mathcal{S} = \frac{\partial H}{\partial \vec{p}} \cdot \frac{\partial \mathcal{S}}{\partial \vec{q}} - \frac{\partial H}{\partial \vec{q}} \cdot \frac{\partial \mathcal{S}}{\partial \vec{p}} \equiv i L \mathcal{S}$$

where  $L$  is the Liouville operator  
(a linear differential operator in phase space)

$$i L = \frac{\partial H}{\partial p} \cdot \frac{\partial}{\partial q} - \frac{\partial H}{\partial q} \cdot \frac{\partial}{\partial p} = -\frac{\partial H}{\partial z} \cdot L_0 \frac{\partial}{\partial z}$$

$$\boxed{\partial_t \mathcal{S} = -i L \mathcal{S}}$$

— microscopic evolution law which we want to coarse-grain



A crucial concept is that of an equilibrium ensemble, or more specifically, thermodynamic equilibrium.

$$\lim_{t \rightarrow \infty} \rho(z, t) = \rho_{\text{eq}}(z)$$

$$\partial_t \rho_{\text{eq}} = 0 \quad - \text{stationarity}$$

Mathematically,  $\rho_{\text{eq}}(z)$  is the invariant distribution (measure) of the microscopic dynamics, and determines the equilibrium properties of the system. The specific form of  $\rho_{\text{eq}}$  determines an equilibrium ensemble.

If we know the equilibrium distribution we can calculate values of physical observables or macroscopic variables as expectation values w.r.t. the equilibrium distribution

$$\bar{A} = \langle A(z) \rangle_{S_{eq}} = \langle A(z) \rangle_{eq} =$$

$$E_{eq}[A] = \int A(z) S_{eq}(z) dz$$

Ergodicity assumption is that the equilibrium space: dynamics samples all of phase space:

$$\langle A \rangle_{eq} = \lim_{T \rightarrow \infty} \frac{1}{T} \int dt \cdot A[z(t)]$$

Assume that the dynamics has a set of dynamical invariants or conserved quantities: energy, angular and translational momentum, etc.

$$\frac{d}{dt} I(z) = 0, \text{ e.g., } I(z) \equiv H(z)$$

Under certain mixing and ergodicity assumptions, which are usually assumed anyway, the equilibrium distribution will be a function only of  $I(z)$ :

$$\rho_{\text{eq}}(z) = \psi(I(z))$$

In particular, for  $I(z) \equiv H(z)$

$$S_{eq}(z) = \Psi [H(z)]$$

Observe that this is a stationary solution of Liouville's equation

$$\partial_t S_{eq} = u \cdot \nabla S_{eq} = \sum_i \left[ \frac{\partial S_{eq}}{\partial q_i} \dot{q}_i + \frac{\partial S_{eq}}{\partial p_i} \dot{p}_i \right]$$

$$= \frac{\partial \Psi}{\partial H} \sum_i \left[ \frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right]$$

$$= \frac{\partial \Psi}{\partial H} \left[ \frac{\partial H}{\partial \vec{q}} \cdot \frac{\partial H}{\partial \vec{p}} - \frac{\partial H}{\partial \vec{p}} \cdot \frac{\partial H}{\partial \vec{q}} \right] = 0$$

The specific form of  $\Psi$  depends on the ensemble

The basic ensemble corresponds to an isolated system with constant number of particles  $N$ , volume  $V$ , and energy  $E$  (NVE or microcanonical ensemble).

POSTULATE of Stat. Mech: All microscopic states are equally probable

$$S_{eq}(z) = \delta [H(z) - E]$$

$$S_{eq}^{micro\ canonical}(z) = \begin{cases} \frac{1}{V_{energy\ shell}} & \text{if } H(z) \in \text{shell} \\ 0 & \text{otherwise} \end{cases}$$

Consider the set of all microstates (may be continuous or discrete) and the probability of observing a particular microstate be given by the PDF  $g(z)$ .

Define the entropy, an additive (extensive) quantity

$$S = - \int g(z) \log [g(z)] dz$$

Postulate of Stat. Mech:

The entropy increases with time and the equilibrium density maximizes the entropy subject to any constraints.

Assume that we have measured  
some macroscopic quantity

$$\bar{\Phi}_i = \int \Phi_i(z) g(z) dz \quad \leftarrow \begin{array}{l} \text{constraint} \\ \text{on} \\ g(z) \end{array}$$

Theorem: The entropy subject to the  
observations  $\bar{\Phi}_i$ ,  $i = 1, \dots, m$ , is maximized  
by the density:

$$S_{eq} = Z^{-1} \exp \left[ - \sum \beta_i \Phi_i(z) \right]$$

where  $Z$  is a normalization constant  
and the  $\beta$ 's are Lagrange multipliers  
(conjugate variables) for the constraints.

For a system that is not isolated, but rather is in contact with a thermal bath at temperature  $T$ , the equilibrium ensemble is the  $NVT$  or canonical ensemble and  $S_{eq}$  is the Gibbs - Boltzmann distribution:

$$\rho_{eq}^{\text{canonical}}(z) = Z^{-1} \exp[-\beta H(z)]$$

where  $\beta = \frac{1}{k_B T}$  Boltzmann constant

and  $Z = \int \exp[-\beta H(z)] dz$  is the partition function



In simulations, and in particular in molecular dynamics, we often use the microcanonical ensemble, even if the canonical or grand-canonical is more appropriate.

This is due because of the principle of equivalence of ensembles for large systems, i.e.; for systems with lots of degrees of freedom (particles).

$$\exp[-\beta H(x)] \longleftrightarrow \delta[H(x) - \bar{H}]$$

↑  
peaked around  $\bar{H}$

In particular, even though  $H$  fluctuates in the canonical ensemble as energy is exchanged with the heat bath, the fluctuations become very small if one looks at a large system.

Recall  $Z = \int e^{-\beta H(z)} dz$

$$\bar{E} = \langle H \rangle = \frac{1}{Z} \int H(z) e^{-\beta H(z)} dz$$

$$\overline{E^2} = \langle H^2 \rangle = \frac{1}{Z} \int H^2 e^{-\beta H} dz$$

But  $\frac{\partial Z}{\partial \beta} = - \int H e^{-\beta H} dz$

so that

$$\langle E \rangle = -z^{-1} \frac{\partial z}{\partial \beta} = - \frac{\partial}{\partial \beta} \ln(z)$$

$$\langle E^2 \rangle = z^{-1} \frac{\partial^2 z}{\partial \beta^2}$$

And the fluctuations in energy are

$$\begin{aligned} \langle (\delta E)^2 \rangle &= \langle E^2 \rangle - \langle E \rangle^2 = \\ &= z^{-1} \frac{\partial^2 z}{\partial \beta^2} - z^{-2} \left( \frac{\partial z}{\partial \beta} \right)^2 = \frac{\partial^2 \ln(z)}{\partial \beta^2} \\ &= - \frac{\partial}{\partial \beta} \langle E \rangle = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} \end{aligned}$$

$$\frac{\partial \langle E \rangle}{\partial T} = N c_v$$

Heat capacity                      per particle

and  $\langle E \rangle = N \epsilon \leftarrow$  energy per particle

$$\Rightarrow \frac{\sqrt{\langle \delta E^2 \rangle}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \leftarrow \text{law of large numbers}$$

which becomes negligible as  $N \rightarrow \infty$

The fluctuations in all macroscopic observables scale like  $N^{-1/2}$  and are essentially constant at equilibrium