

3 Approach to Equilibrium : Summary

- *Distributions*: Equilibrium statistical mechanics describes systems of particles in terms of time-independent statistical distributions. Where do these distributions come from? How does a system with a given set of initial conditions come to have time-independent properties which can be described in this way?

- *Master equation*: Let $P_i(t)$ be the probability that a system is in state $|i\rangle$ at time t . The evolution of the $P_i(t)$ is given by $\frac{dP_i}{dt} = \sum_j (W_{ij}P_j - W_{ji}P_i) = -\sum_j \Gamma_{ij}P_j$, where the rates $W_{ij} \geq 0$ are nonnegative. Conservation of probability means $\sum_i \Gamma_{ij} = 0$ for all j , hence $\psi^t = (1, 1, \dots, 1)$ is a left eigenvector with eigenvalue zero. The corresponding right eigenvector is the equilibrium distribution: $\sum_j \Gamma_{ij}P_j^{\text{eq}} = 0$. In general, the matrix Γ is not normal its eigenvalues λ_a may be complex. (Indeed Γ may have nontrivial Jordan blocks when expressed in canonical form.) Detailed balance, $W_{ij}P_j^{\text{eq}} = W_{ji}P_i^{\text{eq}}$, is a more stringent condition than the requirement of a stationary distribution alone, and when detailed balance holds, all $\lambda_a \in \mathbb{R}$. Boltzmann's H-theorem: $\dot{H} \leq 0$, where $H = \sum_i P_i \ln(P_i/P_i^{\text{eq}})$. Thus, the ME dynamics are *irreversible*. But the underlying microscopic laws are reversible!

- *Hamiltonian evolution*: $\dot{\varphi}_i = J_{ij} \frac{\partial H}{\partial \varphi_j}$, where $\varphi = (q_1, \dots, q_r, p_1, \dots, p_r)$ is a point in $2r$ -dimensional phase space, and $J = \begin{pmatrix} 0 & \mathbb{I} \\ -\mathbb{I} & 0 \end{pmatrix}$. Phase space flow is then incompressible: $\nabla \cdot \dot{\varphi} = 0$, hence phase space densities $\varrho(\varphi, t)$ obey Liouville's equation, $\partial_t \varrho + \dot{\varphi} \cdot \nabla \varrho = 0$ (follows from continuity and incompressibility). Any function $\varrho(\Lambda_1, \dots, \Lambda_k)$, where each Λ_i is conserved by the phase space dynamics, will be a stationary solution to Liouville's equation. In particular, the microcanonical distribution, $\varrho_E(\varphi) = \delta(E - H(\varphi))/D(E)$ is such a solution, where $D(E) = \text{Tr} \delta(E - H(\varphi))$ is the *density of states*.

- *Poincaré Recurrence*: Let $g_\tau \varphi(t) = \varphi(t + \tau)$ be the τ -advance mapping for a dynamical system $\dot{\varphi} = V(\varphi)$. If (i) g_τ is invertible, (ii) g_τ preserves phase space volumes, and (iii) the volume of phase accessible given the dynamics and initial conditions is finite, then in any finite neighborhood $\mathcal{R}_0$ of phase space there exists a point $\varphi_0 \in \mathcal{R}_0$ such that $g_\tau^n \varphi_0 \in \mathcal{R}_0$ with n finite. This means all the perfume molecules eventually go back inside the bottle (if it is opened in a sealed room).

- *Kac ring model*: Normally the recurrence time is orders of magnitude greater than the age of the Universe, but for the Kac ring model, one can simulate the recurrence phenomenon easily. The model consists of a ring of N sites, and a quenched (*i.e.* fixed) random distribution of flippers on F of the links ($F \leq N$). On each site lies a discrete spin variable which is polarized either up or down. The system evolves discretely by all spins advancing clockwise by one site during a given time step. All spins which pass through a flipper reverse their polarization. Viewed probabilistically, if p_n is the probability any given spin is up at time n , then under the assumptions of the *Stosszahlansatz* $p_{n+1} = (1 - x)p_n + x(1 - p_n)$, where $x = F/N$ is the flipper density. This leads to exponential relaxation with a time scale $\tau = -1/\ln|1 - 2x|$, but the recurrence time is clearly N (if F is even) or $2N$ (if F is odd).

- *Ergodicity and mixing*: A dynamical system is *ergodic* if

$$\langle f(\varphi) \rangle_T = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt f(\varphi(t)) = \frac{\text{Tr } f(\varphi) \delta(E - H(\varphi))}{\text{Tr } \delta(E - H(\varphi))} = \langle f(\varphi) \rangle_S \quad .$$

This means long time averages are equal to phase space averages. This does not necessarily mean that the phase space distribution will converge to the microcanonical distribution. A stronger condition, known as *mixing*, means that the distribution spreads out ‘evenly’ over the phase space hypersurface consistent with all conservation laws. Thus, if g is a phase space map, and if $\nu(A) \equiv D_A(E)/D(E)$ is the fraction of the energy hypersurface (assume no conserved quantities other than $H = E$) contained in A , then g is mixing if $\lim_{n \rightarrow \infty} \nu(g^n A \cap B) = \nu(A)\nu(B)$. An example of a mixing map on a two-dimensional torus is the Arnold ‘cat map’,

$$\begin{pmatrix} q' \\ p' \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} q \\ p \end{pmatrix} \mod \mathbb{Z}^2 \quad .$$

- *Thermalization of quantum systems*: This is a current research topic. One proposal, due to Deutsch (1991) and Srednicki (1994) is the *eigenstate thermalization hypothesis* (ETH). This says that thermal information is encoded in each eigenstate, such that if $E_\alpha \in [E, E + \Delta E]$, then

$$\langle \Psi_\alpha | \mathcal{A} | \Psi_\alpha \rangle = \langle \mathcal{A} \rangle_{E_\alpha} \quad ,$$

i.e. the expectation value of some local, translationally-invariant, few-body operator $\mathcal{A}$ in the state $|\Psi_\alpha\rangle$, is given by its average over a small energy window containing E_α . If this is the case, then so long as we prepare an initial state such that the spread of energies is within ΔE of some value E , where $\Delta E \ll E - E_0$ with E_0 the ground state energy, then $\langle \mathcal{A} \rangle_T = \langle \mathcal{A} \rangle_E$, and time averages become energy averages. Equivalently, the *reduced density matrix* ρ_S corresponding to a system S which is a subset of a universe U , with $W \cup S = U$ (W is the ‘world’), is a thermal density matrix: $\rho_S = Z_S^{-1} e^{-\beta \hat{H}_S}$, where $\hat{H}_S$ is the Hamiltonian restricted to S , and with temperature fixed by the requirement $\text{Tr}(\rho_S \hat{H}_S) = E \cdot (V_S/V_U)$, where the last factor is a ratio of volumes. ETH does not hold for so-called *integrable models* with an extensive number of independent conserved quantities. But it has been shown, both perturbatively as well as numerically, to hold for certain model nonintegrable systems. An interesting distinction between classical and quantum thermalization: in the quantum case, time evolution does not create the thermal state. Rather, it *reveals* the thermal distribution which is *encoded in each eigenstate* after sufficient time that dephasing has occurred and all correlations between the different wavefunction expansion coefficients is lost.