Classical Statistical Mechanics and The Distribution Function

What is Statistical Mechanics

- **Conceptually:** Statistical mechanics is a formalism developed to connect the fundamental description of a large system (microstates) with its thermodynamical description (macrostates); Notice that this does not specify how one goes from one to the other, but we will need a specific prescription in order to prove results.

- **Historically:** Mid 1800s, phenomenological formulation of thermodynamics by Lord Kelvin and R Clausius; Late 1800s, Kinetic theory and statistical mechanics, developed by L Boltzmann, J Gibbs and then others; 1900s, Understanding of the quantum basis and the correct description of microstates.

- **What we will cover:** Mostly equilibrium states, of which there are various types. We will start with the microcanonical state, then switch to the canonical or grand canonical states. For these equilibrium states we will show how thermodynamics is recovered in the thermodynamical limit $N, V \to \infty$ with $N/V = \text{constant}$.

Setup for Statistical Mechanics: Classical Phase Space

- **Hamiltonian system:** The type of system we will consider in this course, both classically and quantum mechanically. Defined by a phase space, a manifold $\Gamma$ usually of the form

$$\Gamma = \{(\vec{r}_i, \vec{p}_i)\} \subseteq \mathbb{R}^{6N},$$

in terms of configuration and momentum variables, in which we know how to calculate Poisson brackets $\{f, g\}$ between any two observables $f(q,p)$ and $g(q,p)$, and there is a special function governing time evolution, the Hamiltonian $H(q,p)$, usually written as a sum over degrees of freedom ("dof") $i$ of the form

$$H(q,p) = \sum_{\text{dof}} \frac{p_i^2}{2m_i} + V(q,p).$$

- **Example:** For $N$ free particles in a box of volume $V = L_1 L_2 L_3$, the canonical variables $\vec{r}_i$ have values bounded by the size of the box, the momenta $\vec{p}_i$ have any values in $\mathbb{R}^3$, and $H = \sum_{i=1}^N \frac{p_i^2}{2m}$.

- **Microstates and macrostates:** A (pure) microstate is a full specification of the values for the phase-space variables of the system at some time $t$, e.g., $\{(\vec{r}_i, \vec{p}_i), i = 1, \ldots, N\}$ for the particles in a gas. A macrostate is a specification of the values for some complete set of thermodynamic variables, e.g., $(N, V, E)$. In statistical mechanics, each macrostate can correspond to different ensembles or collections of microstates, copies of the system which give rise to the given macrostate, together with a probability for each microstate in it. This probability distribution is used to determine the corresponding values of the macroscopic quantities for the system: Some are just values of parameters characterizing the distribution, others can be found from mean values or variances of observables calculated using the probability distribution.

- **Phase space volumes and state counting:** The volume of a region $R \subset \Gamma$ is given by $\omega(R) = \int_R d\omega$, with $d\omega = d^{3N}q \, d^{3N}p$ the phase-space volume element. Using a constant $h$ with the dimensions of an action, whose value is to be determined later, we can think of $\Omega(R) = \int_R d\Omega = h^{-3N} \int_R d^{3N}q \, d^{3N}p$ as the "number of states" in $R$ (we will soon see, however, that for a system of identical particles we need to modify this definition of $d\Omega$). Then, if $\Omega(E)$ is the number of states with energy $H(q,p) \leq E$, the density of states

$$g(E) = \frac{d\Omega(E)}{dE}.$$

- **Density/distribution function:** A non-negative function $\rho : \Gamma \to \mathbb{R}$ giving the probability density for the system to be in each microstate of an ensemble. In other words, the probability that the system is in a region of volume $d\omega$ around $(q,p) \in \Gamma$ at time $t$ is $dP = \rho(q,p,t) d\omega$. Thus, $\rho$ is dimensionless and we will always take it to be normalized to $1$, $\int_{\Gamma} \rho(q,p,t) d\Omega = 1$.

- **Use of the distribution function:** Like any probability density, $\rho$ gives mean values of observables by

$$\langle A \rangle = \int_{\Gamma} d\Omega \, \rho(r,p) \, A(r,p).$$

One could say that determining $\rho$ for some interesting systems in equilibrium is our goal for this course.

- **Example:** The $\delta$-function distribution or "pure state" (all other classical states are considered "mixed")

$$\rho(r,p) = h^{3N} \prod_{i=1}^N \delta^3(\vec{r}_i - \vec{r}_i^0) \delta^3(\vec{p}_i - \vec{p}_i^0).$$
Setup for Statistical Mechanics: Hamiltonian Dynamics

- **Hamilton equations of motion:** For a particle starting at a point \((q'(t_0), p_i(t_0))\) in phase space (a pure state), the Hamiltonian gives the time evolution through the equations of motion obtained from \(H(q, p)\),

\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}.
\]

These are special cases of the general fact that, for any observable \(A : \Gamma \to \mathbb{R}\), we have \(\dot{A} = \{A, H\}\), or

\[
\dot{A} = \sum_{\text{dof}} \left( \frac{\partial A}{\partial q^i} \dot{q}^i + \frac{\partial A}{\partial p_i} \dot{p}_i \right) = \sum_{\text{dof}} \left( \frac{\partial A}{\partial q^i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial q^i} \frac{\partial H}{\partial q^i} \right).
\]

- **Energy surface/shell:** Because the value of the Hamiltonian, the energy, is conserved, a system that starts with a certain value \(E\) of the energy will remain on the \(H(q, p) = E\) hypersurface in phase space. If the energy is only known to be in a certain range of width \(\Delta\), then the system will remain in an energy shell \(H(q, p) \in [E - \frac{1}{2} \Delta, E + \frac{1}{2} \Delta]\).

- **Liouville theorem:** The value of the distribution function \(\rho\) is a constant along a trajectory \((q'(t), p_i(t))\) in phase space satisfying the equations of motion. In other words \(\rho\) evolves like an incompressible fluid, or

\[
\frac{d\rho}{dt} = \sum_{\text{dof}} \left( \frac{\partial \rho}{\partial q^i} \dot{q}^i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0.
\]

**Proof:** The time rate of change of the probability \(\int_R \rho(q, p) \, d\omega\) of a region \(R\) in \(\Gamma\) must equal the flux of probability \(-\oint_{\partial R} \mathbf{v} \cdot d\mathbf{A}\) through its surface, which means that \(\rho\) must satisfy an equation of continuity,

\[
0 = \frac{d\rho}{dt} + \nabla \cdot (\mathbf{v} \rho) = \frac{d\rho}{dt} + \sum_{\text{dof}} \left( \frac{\partial \dot{q}^i}{\partial q^i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) \rho + \sum_{\text{dof}} \left( \frac{\partial \rho}{\partial q^i} \dot{q}^i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right),
\]

where \(\mathbf{v} = (\dot{q}^1, \dot{q}^2, \ldots, \dot{q}^N; \dot{p}_1, \dot{p}_2, \ldots, \dot{p}_N)\) and the terms in the first set of parentheses cancel by virtue of the Hamilton equations of motion. The result would not hold, for example, for a dissipative system.

- **Evolution of the distribution function:** From the Liouville theorem, we get that

\[
\dot{\rho} = \frac{d\rho}{dt} = -\sum_{\text{dof}} \left( \frac{\partial \rho}{\partial q^i} \dot{q}^i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = -\{\rho, H\}.
\]

**Remark:** Notice the difference between observables and distribution functions (all of which are functions on phase space), related to the sign difference between the Liouville equation and the evolution of an observable \(\dot{A}(q, p)\) along the orbit of a point in phase space.

**Comments**

- **Equilibrium distribution functions:** Our systems of interest will be the ones in thermodynamic equilibrium, so they should be described by time-independent distribution functions. The condition that \(\partial \rho / \partial t = 0\) or, equivalently, using Liouville’s theorem, \(\{\rho, H\} = 0\), can be satisfied in different ways. One possibility is that \(\rho(q, p)\) be constant over the region of phase space compatible with the system’s macrostate(s), which expresses the assumption of *equal a priori probabilities*; if the system’s energy has a fixed value, this leads to the *microcanonical distribution*. Other possibilities lead to the canonical and grand canonical distributions.

- **Thermodynamic limit:** The limit in which the number of particles and the volume of the system are taken to infinity, holding the number density \(\rho := N/V\) fixed. In this limit, from results related to the central limit theorem, the fractional fluctuations of statistical quantities go to zero and can be ignored.

**Reading**

- **Pathria & Beale:** Beginning of Chapter 1; Chapter 2, Sections 2.1 and 2.2.

- **Other textbooks:** Chandler, Sec 3.1; Halley, First half of Ch 1; First half of Ch 2; Schwabl, Sec 1.3.