Introduction and The Distribution Function

What is Statistical Mechanics

• *Conceptually:* Statistical mechanics is a formalism 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 a specific prescription will be needed in order to prove results.
• *Historically:* Mid 1800s, phenomenological formulation of thermodynamics; Late 1800s, Kinetic theory and statistical mechanics, with 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, mostly the canonical ensemble.

Systems and States

• *Hamiltonian system:* The type of system we will consider in this course, both classically and quantum mechanically. Defined by a phase space, i.e., a manifold Γ in which we know hot to calculate Poisson brackets $\{f, g\}$ between any two functions f and g (this often means that we have identified configuration and momentum variables r_i, p_i), and there is a special function $H(r,p)$ which governs time evolution.
• *Example:* For N free particles in a box of volume $V = L_1 L_2 L_3$, the canonical variables are the $\mathbf{r}_i$ with values bounded by the size of the box and $\mathbf{p}_i$ with any values in $\mathbb{R}$, and $H = \sum_i p_i^2/2m$.
• *Equilibrium state:* A state in which no macroscopically observable quantity for the system depends on time, and there is no flow; Important historically for the field, and also the only case that is quite well understood in general.

The Distribution Function

• *The system:* Usually a Hamiltonian system $H(r,p)$, often of the general form $H = \frac{1}{2}\, g^{ij}\, p_i p_j + V(r)$, which leads to dynamical equations. In this context, an observable will be any function $f(r,p)$ on the phase space.
• *What we want to achieve:* Relate the values of an observable ϕ in a microstate of a system to what we measure macroscopically. This may mean one of various things; start by assuming that it means an average over long times compared to characteristic microscopic time scales. Then, for an equilibrium system,

$$\bar\phi_t = \lim_{\tau\to\infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} \mathrm{d}t'\, \phi(q(t'), p(t'))\ .$$

• *How it works:* Ergodic hypothesis, which can be proved for a few systems. Then

$$\bar\phi_t = \int \mathrm{d}^3r_1 ... \,\mathrm{d}^3r_N \mathrm{d}^3p_1 ... \,\mathrm{d}^3p_N\, \rho(r,p)\, \phi(r,p)\ .$$

• *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.

Interpretations

• *In terms of fractional amount of time:* (Boltzmann);
• *In terms of probability or information theory:* (Jaynes, Katz) The point of view on the meaning of probability may vary, but this interpretation makes the general tools of probability theory available;
• *In terms of ensembles:* This is now mostly of historical significance, but has greatly influenced the field, and still affects its terminology.

Relevant Sections: PHY 731; Chandler; Halley, first half of Ch 1.

Related Topics

• *Approach to equilibrium:* A 1D Bose-Einstein gas that never approaches equilibrium [@ news pw(06)apr].
• *Temperature and entropy:* For how general a ρ can T and S be meaningfully defined?