Classical Statistical Mechanics and The Distribution Function

What is Statistical Mechanics

• Conceptually: Statistical mechanics is a formalism developed to derive thermodynamic properties of a large system and its macroscopic states (macrostates, here assumed to be time independent) from a fundamental description in terms of microscopic states of its constituents (microstates, here assumed to be classical).

• *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 thermodynamic limit $N, V \to \infty$ with N/V = 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. The space of microstates is a phase space, a manifold Γ often of the form $\Gamma = \{(\vec{r_I}, \vec{p_I})\} \subseteq \mathbb{R}^{6N}$ in terms of configuration and momentum variables for N particles, in which we know how to calculate Poisson brackets $\{f, g\}$ between 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 of kinertic and potential energies,

$$H(q,p) = \sum_{I} \frac{\vec{p}_{I}^{\ 2}}{2 \, m_{I}} + V(q,p) \; .$$

• Examples: For N free particles in a box of volume $V = L_1 L_2 L_3$, the positions $\vec{r_I}$ have values bounded by the L_1 , the momenta $\vec{p_I} \in \mathbb{R}^3$, and V(q, p) = 0. For N magnetic dipoles, $V(q, p) = -\sum_I \vec{\mu_I} \cdot \vec{B}$.

• 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., $\{(\vec{r_I}, \vec{p_I}), I = 1, ..., N\}$ 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.

• State counting, density of states: The volume of a region R of phase space 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 is

$$q(E) = \mathrm{d}\Omega(E)/\mathrm{d}E$$
.

• 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, ρ 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, ρ gives mean values of observables by

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

as well as fluctuations $\sigma_A^2 = \langle (\Delta A)^2 \rangle$. One of the main goals for this course is to determine ρ for some interesting equilibrium systems, make sure that ρ is sharply peaked, and make physical predictions using ρ .

• Example: The δ -function distribution or "pure state" (all other classical states are considered "mixed")

$$\rho(\vec{r},\vec{p}) = h^{3N} \prod_{I=1}^{N} \delta^3(\vec{r}_I - \vec{r}_I^{\,0}) \,\delta^3(\vec{p}_I - \vec{p}_I^{\,0}) \,.$$

Setup for Statistical Mechanics: Hamiltonian Dynamics

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

$$\label{eq:phi} \dot{q}^i = \frac{\partial H}{\partial p_i} \;, \qquad \dot{p}_i = -\frac{\partial H}{\partial q^i}$$

These are special cases of the general fact that, for any observable $A: \Gamma \to \mathbb{R}$, we have

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

• 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 Δ , then the system will remain in an energy shell $H(q, p) \in [E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta]$. \star Examples: 1D free particle, oscillator.

• Liouville theorem: The value of the distribution function ρ is a constant along a trajectory $(q^i(t), p_i(t))$ in phase space satisfying the equations of motion. In other words ρ evolves like an incompressible fluid, or

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum_{\mathrm{dof}} \left(\frac{\partial\rho}{\partial q^i}\,\dot{q}^i + \frac{\partial\rho}{\partial p_i}\,\dot{p}_i\right) = 0\;.$$

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

$$0 = \frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\vec{v} \, \rho) = \frac{\partial \rho}{\partial t} + \sum_{\text{dof}} \left(\frac{\partial \dot{q}^i}{\partial q^i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) \rho + \sum_{\text{dof}} \left(\frac{\partial \rho}{\partial q^i} \, \dot{q}^i + \frac{\partial \rho}{\partial p_i} \, \dot{p}_i \right) = \frac{\mathrm{d}\rho}{\mathrm{d}t},$$

where $\vec{v} = (\dot{q}^1, \dot{q}^2, ..., \dot{q}^{3N}; \dot{p}_1, \dot{p}_2, ..., \dot{p}_{3N})$, because the terms in the first summation 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: A consequence of the Liouville theorem is the Liouville equation,

$$\dot{\rho} \equiv \frac{\partial \rho}{\partial t} = -\sum_{\rm dof} \left(\frac{\partial \rho}{\partial q^i} \, \dot{q}^i + \frac{\partial \rho}{\partial p_i} \, \dot{p}_i \right) = -\{\rho, \, H\} \; .$$

• 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 A(q, p) along the orbit of a point in phase space.

Comments

• Equilibrium distribution functions: Our systems of interest will be 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 the energy E is fixed and known within some small uncertainty ΔE , and $\rho(q, p)$ is constant over the corresponding region of phase space, which expresses the assumption of equal a priori probabilities; this leads to the microcanonical distribution. Other possibilities lead to the canonical and grand canonical distributions. An important physical question is whether realistic systems actually approach these equilibrium states.

• 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

• Kennett: Chapter 3.

• Other books: Chandler, Sec 3.1; Halley, First half of Ch 1; First half of Ch 2; Pathria & Beale, Beginning of Chapter 1 and Chapter 2, Sections 2.1 and 2.2; Schwabl, Sec 1.3.