# Equilibrium Distribution Functions. I: Microcanonical Distribution

#### General Considerations on Equilibrium Systems

• Equilibrium state: A state in which no macroscopically observable quantity for the system depends on time, in practice  $\partial \rho / \partial t = 0$ , and there is no flow. It is historically important for the subject, and also the only case that is well understood in general. We want to find a general form for  $\rho(q, p)$  for such a state.

• Distribution functions: At equilibrium  $\rho$  depends on parameters such as T, V, N, but its phase-space dependence can only be through the energy E. If its possible values  $E_i$  are discrete and there are  $g(E_i)$  states with the same energy for each i, then the distribution function has the same value  $\rho(E_i) = \rho(\alpha)$  for all states  $\alpha$  with energy  $E(\alpha) = E_i$ , and the probability that the system has that energy is  $P(E_i) = \rho(E_i) g(E_i)$ . On the other hand, if the values of the energy are continuous, then the probability that E has a value in some interval dE can be written in terms of a probability density p(E) that depends on  $\rho(E)$  and on the density of states  $g(E) = d\Omega/dE$ ,

$$p(E) dE = \rho(E) g(E) dE$$

• Possible cases: In terms of physical situations, the main types of equilibrium systems are isolated ones (in which case we will assume that the value of the energy is known, either precisely or within some range  $\Delta$ ), and ones that can exchange either heat, or heat and particles with a bath at fixed temperature. Systems of the latter type are much easier to handle mathematically, if there are no long-range interactions so correlations with the bath can be neglected, but in the large-N limit they all lead essentially to the same predictions.

# The Microcanonical Distribution

• Idea: The distribution function for an isolated system, whose energy and number of particles are fixed. The energy either has a definite value, H(q, p) = E, or is within a small interval,  $H(q, p) \in [E - \frac{\Delta}{2}, E + \frac{\Delta}{2}]$ .

• Approach to equilibrium: For what systems, and under what circumstances, does  $\rho$  approach an equilibrium form? This is a very difficult question to answer in general, but results are known for some types of classical systems, and for this discussion it is useful to distinguish the following:

 $\rightarrow$  Integrable system: A system with as many commuting constants of the motion (their Poisson brackets vanish) as degrees of freedom; Then in principle solving the dynamics can be reduced to quadratures.

 $\rightarrow$  Ergodic system: One for which a trajectory starting at any initial point in phase space fills the entire constant-energy hypersurface  $\Gamma(E)$  under time evolution. More specifically, for almost every  $(q_0, p_0)$  the long-time average value of any observable A(q, p) along a dynamical trajectory (q(t), p(t)), which is sometimes taken to model the result of measuring the value of A over a microscopically long time,

$$\bar{A}_t(q_0, p_0) := \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} \mathrm{d}t' \, A(q(t'), p(t')) \qquad \text{equals} \qquad \langle A \rangle := \int_{\Gamma(E)} \mathrm{d}\Omega \, A(q, p) \, \rho(q, p) \, A(q, p) \, A(q, p) \, \rho(q, p) \, A(q, p) \, A(q, p) \, \rho(q, p) \, A(q, p) \, A(q$$

the phase-space average of A over  $\Gamma(E)$ . Despite this, an ergodic system need not be chaotic; for that we need the sensitive dependence on initial conditions that characterizes chaos (it may even be integrable).  $\rightarrow$  Chaotic system: One which "forgets" its initial state under time evolution. For example a mixing system, for which the correlation between the state at a time t and the initial state goes to zero as  $t \rightarrow \infty$ ; i.e., for any observables A and B,  $\langle A(q(t), p(t)) B(q_0, p_0) \rangle - \langle A(q_0, p_0) \rangle \langle B(q_0, p_0) \rangle \rightarrow 0$ . [Or in terms of volumes.]

• Equal probabilities assumption: We will assume that the isolated systems we treat have reached equilibrium and that they are equally likely to be in any allowed state. Because all states on the allowed energy shell  $\Gamma(E)$  or  $\Gamma(E, \Delta)$  in phase space are included, we get a microscopic justification for the fact that the entropy S is maximized. This happens for mixing systems (which are also ergodic). Most realistic large systems are expected to be mixing, although the statement is difficult to prove for specific cases. [See ergodic hierarchy.]

• Observables: We would like to be able to predict the experimental values  $A_{\text{meas}}$  of macroscopic quantities, which rely on observations over microscopically long times and are often identified with  $\bar{A}_t$ . This long-time average is difficult to calculate directly, but if the system is ergodic its value is the same for all copies of the system and independent of  $(q_0, p_0)$ , and we can calculate it as a phase-space average,  $A_{\text{meas}} = \bar{A}_t = \langle A \rangle$ .

• Justification: This step is justified for ergodic systems. Ergodicity is weaker than mixing and not sufficient to prove that the system will approach equilibrium, but it is simpler to work with, and it tells us that if the system approaches equilibrium, that state is unique.

• Distribution function: If the system is known to have a certain energy E, and to be in any of the states on the hypersurface  $\Gamma(E) := \{(p,q) \mid H(q,p) = E\}$  in phase space with equal probability,

$$\rho(q,p) = \text{constant} \times \delta(H(q,p) - E) = \frac{h^{3N}}{\omega(E)} \,\delta(H(q,p) - E) = \frac{1}{\Omega(E)} \,\delta(H(q,p) - E) \,,$$

the microcanonical distribution, where  $\omega(E) = \int d\omega \,\delta(H(q,p) - E)$  is the "area" of the constant-energy hypersurface  $\Gamma(E)$ . If the energy of the system is only known to be in a certain range of width  $\Delta$  around E, then the phase-space point is in a shell  $\Gamma(E, \Delta)$  of width  $\Delta$  around H(q, p) = E, for which the scaled volume

$$\Omega(E,\Delta) = \int_{\Gamma(E,\Delta)} \mathrm{d}\Omega = \frac{1}{h^{3N}} \int_{H=E-\Delta/2}^{H=E+\Delta/2} \mathrm{d}\omega$$

where h is a constant, is interpreted as the number of states in  $\Gamma(E, \Delta)$ . The microcanonical distribution is a constant on that shell and vanishes elsewhere. In normalized form it can then be written as

$$\rho(q,p) = \begin{cases} \Omega(E,\Delta)^{-1} & \text{if } H \in [E-\Delta/2, E+\Delta/2] \\ 0 & \text{otherwise} \end{cases} = \frac{1}{\Delta \Omega(E)} \chi_{E,\Delta}(q,p) \ .$$

#### Obtaining Thermodynamics from the Microcanonical Distribution

• Entropy: Assume that S is a function of the number of classical states  $\Omega_{\vec{X}}(E, \Delta)$  available to a system. Then, since for independent subystems A and B we have  $\Omega_S = \Omega_A \Omega_B$  and S is extensive,  $S = S_A + S_B$ , the entropy we use as a starting point for thermodynamics is the Boltzmann entropy,

$$S(E, \vec{X}) = k_{\rm B} \, \ln \Omega(E, \Delta)$$

For sufficiently large systems this S is independent of  $\Delta$ .

• Other quantities: Temperature is defined as  $T^{-1} := \partial S/\partial E|_{\vec{X}}$  (recall that in a microcanonical state the system is not in thermal equilibrium with an environment), and find additional quantities using regular thermodynamic relations such as F = E - TS; for a fluid, for example,  $p = -\partial F/\partial V|_T$ , or  $p/T = \partial S/\partial V|_{N,E}$ .

# Example: The Monatomic Ideal Gas

• Multiplicity: For N pointlike particles of mass m the number of phase-space states in  $\Gamma(E, \Delta)$  is

$$\Omega_{V,N}(E,\Delta) = \int_{\Gamma(E,\Delta)} \frac{\mathrm{d}^{3N} q \,\mathrm{d}^{3N} p}{h^{3N}} = \frac{V^N}{h^{3N}} \int_{E-\Delta/2}^{E+\Delta/2} \mathrm{d}E \,\frac{\mathrm{d}p}{\mathrm{d}E} \, p^{3N-1} \oint \mathrm{d}\Omega^{3N-1} \approx \frac{V^N}{h^{3N}} \cdot \frac{\Delta}{E} \cdot \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2)} \;,$$

in the  $\Delta \ll E$  approximation (and using the fact that the surface of an (n-1)-sphere of radius R in n-dimensional Euclidean space is  $A(S^{n-1}, R) = 2\pi^{n/2}R^{n-1}/\Gamma(n/2)$ , with  $\Gamma(n+1) = n!$  and  $\Gamma(1/2) = \sqrt{\pi}$ ), where the Hamiltonian for a monatomic ideal gas is  $H(q, p) = \sum_{i=1}^{3N} p_i^2/2m$ , and  $\Gamma(3N/2) \approx (3N/2)!$ .

• Entropy: Using  $S = k_{\rm B} \ln \Omega$  and the Stirling approximation  $\ln n! \sim n \ln n - n$ , we get the expression

$$S(E, V, N) = Nk_{\rm B} \left\{ \ln \left[ V \left( \frac{4\pi mE}{3Nh^2} \right)^{3/2} \right] + \frac{1}{N} \ln \frac{\Delta}{E} + \frac{3}{2} \right\}$$

Recall the expression for S obtained earlier from purely thermodynamical considerations. The one we derived here, without the last two terms which become negligible in the large-N limit, looks similar to that one, but it cannot be correct because it is not extensive. We will see that to fix this problem we need to use Boltzmann statistics, but for now one can still proceed and find the relationship between E and T, the pressure, chemical potential  $\mu$ , and other thermodynamical quantities.

• Boltzmann statistics: To correctly count microstates labelled by (q, p) for N indistinguishable 3D particles, the correct measure for the space of states must include an N!, and we must use  $d\Omega = d^{3N}q d^{3N}p/N! h^{3N}$ .

### Reading

• Our textbook: Kennett, Ch 2 and parts of Ch 3. Other textbooks: in Plischke & Bergersen, §§ 2.1–2.3; Halley, part of Ch 1; Mattis, §§ 4.1–4.4; Reif, Ch 3; Schwabl, Ch 2; Pathria & Beale, parts of Ch 1 and § 2.3.