3.2: Microcanonical Ensemble

Assume that we have an isolated system with N particles in a fixed volume V. Because the system is isolated, the total energy E must also be fixed. If we know that the energy must be in an interval $[E, E + \Delta E]$ the probability density in phase space must be zero everywhere outside the region between the two hypersurfaces with constant energies E and $E + \Delta E$. We call this region the energy shell in which the system is confined. If the system is in equilibrium, i.e., the probability density ρ is stationary, ρ must be uniform in this energy shell, i.e., it must not depend on p and q within this shell. We can see this from the Liouville equation ([eq:Liouville_short]), whose left-hand side must be zero for a stationary probability density. The Poisson bracket on the right-hand side will vanish if ρ is uniform.[8]

> ### 🔖 Concept 3.2.1: Microcanonical Ensembles
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> An ensemble with a constant number N of particles in a constant volume V and with constant total energy E has a uniform probability density ρ_{mc} in the part of phase space, where it can reside, which is the energy hypersurface at energy E. Such an ensemble is called a *microcanonical ensemble*.

We are left with computing this constant probability density ρ_{mc}. As the energy is given by the Hamiltonian function $\mathcal{H}(\mathbf{p}, \mathbf{q})$, we can formally write ρ_{mc} for an infinitely thin energy shell $(\Delta E \to 0)$ as

$$\rho_{\mathrm{mc}} = \frac{1}{\Omega(E)} \delta\left(E - \mathcal{H}(\mathbf{p}, \mathbf{q})\right), \tag{3.2.1}$$

where the *statistical weight* Ω depends on energy, volume, and number of particles N, but at constant energy does not depend on momentum $\mathbf{p}$ or spatial coordinates $\mathbf{q}$. Since the probability density is normalized, we have

$$\Omega(E) = \int \int \delta\left(E - \mathcal{H}(\mathbf{p}, \mathbf{q})\right) \mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}. \tag{3.2.2}$$

The probability density in phase space of the microcanonical ensemble is thus relatively easy to compute. However, the restriction to constant energy, i.e. to an isolated system, severely limits application of the microcanonical ensemble. To see this, we consider the simplest system, an electron spin $S = 1/2$ in an external magnetic field B_0. This system is neither classical nor describable in phase space, but it will nicely serve our purpose. The system has a state space consisting of only two states $|\alpha\rangle$ and $|\beta\rangle$ with energies $\epsilon_\alpha = \hbar g_e \mu_\mathrm{B} B_0/2$ and $\epsilon_\beta = -\hbar g_e \mu_\mathrm{B} B_0/2$.[9] In magnetic resonance spectroscopy, one would talk of an ensemble of 'isolated' spins, if the individual spins do not interact with each other. We shall see shortly that this ensemble is not isolated in a thermodynamical sense, and hence not a microcanonical ensemble.

The essence of the microcanonical ensemble is that all systems in the ensemble have the *same* energy E, this restricts probability density to the hypersurface with constant E. If our ensemble of N spins would be a microcanonical ensemble, this energy would be either $E = \hbar g_e \mu_\mathrm{B} B_0/2$ or $E = -\hbar g_e \mu_\mathrm{B} B_0/2$ and all spins in the ensemble would have to be in the same state, i.e., the ensemble would be in a pure state. In almost any experiment on spins $S = 1/2$ the ensemble is in a mixed state and the populations of states $|\alpha\rangle$ and $|\beta\rangle$ are of interest. The system is not isolated, but, via spin relaxation processes, in thermal contact with its environment. To describe this situation, we need another type of ensemble.