4.3: Irreversibility

Historical Discussion

Daily experience tells us that some processes are irreversible. Phenomenological thermodynamics had provided recipes for recognizing such processes by an increase in entropy for an isolated system or decrease of free energy for a closed system. When Boltzmann suggested a link between classical mechanics of molecules on a microscopic level and irreversibility of processes on the macroscopic level, many physicists were irritated nevertheless. In retrospect it is probably fair to say that a controversial discussion of Boltzmann's result could only ensue because atomistic or molecular theory of matter was not yet universally accepted at the time. It is harder to understand why this discussion is still going on in textbooks. Probably this is related to the fact that physicists in the second half of the 19^{th} and first half of the 20^{th} believed that pure physics has implications in philosophy, beyond the obvious ones in epistemology applied to experiments in the sciences. If statistical mechanics is used to predict the future of the universe into infinite times, problems ensue. If statistical mechanics is properly applied to well-defined experiments there are no such problems.

Classical mechanics of particles does not involve irreversibility. The equations of motion have time reversal symmetry and the same applies to quantum-mechanical equations of motion. If the sign of the Hamiltonian can be inverted, the system will evolve backwards along the same trajectory in phase space (or state space) that it followed to the point of inversion. This argument is called *Umkehreinwand* or Loschmidt paradox and was brought up (in its classical form) by Loschmidt. The argument can be refined and is then known as the *central paradox*: Each microstate can be assigned a time-reversed state that evolves, under the same Hamiltonian, backwards along the same trajectory. The two states should have the same probability. The central paradox confuses equilibrium and non-equilibrium dynamics. At equilibrium a state and the corresponding time-reversed state indeed have the same probability, which explains that the macrostate of the system does not change and why processes that can be approximated by a series of equilibrium states are reversible. If, on the other hand, we are not at equilibrium, there is no reason for assuming that the probabilities of any two microstates are related. The system is at some initial condition with a given set of probabilities and we are not allowed to pose symmetry requirements to this initial condition.

The original *Umkehreinwand*, which is based on sign inversion of the Hamiltonian rather then the momenta of microstates, is more serious than the central paradox. Time-reversal experiments of this type can be performed, for instance, echo experiments in magnetic resonance spectroscopy and optical spectroscopy. In some of these echo experiments, indeed the Hamiltonian is sign-inverted, in most of these experiments application of a perturbation Hamiltonian for a short time (pulse experiment) causes sign inversion of the density matrix. Indeed, the first paper on observation of such a spin echo by Erwin Hahn was initially rejected with the argument that he could not have observed what he claimed, as this would have violated the Second Law of Thermodynamics. A macroscopic 'time-reversal' experiment that creates a 'colorant echo' in corn syrup can be based on laminar flow . We note here that all these time-reversal experiments are based on preparing a system in a non-equilibrium state. To analyze them, changes in entropy or Helmholtz free energy must be considered during the evolution that can be reversed. These experiments do not touch the question whether or not the same system will irreversibly approach an equilibrium state if left to itself for a sufficiently long time. We can see this easily for the experiment with colorants and corn syrup. If, after setup of the initial state and evolution to the point of time reversal, a long time would pass, the colorant echo would no longer be observed, because diffusion of the colorants in corn syrup would destroy spatial correlation. The echo relies on the fact that diffusion of the colorants in corn syrup can be neglected on the time scale of the experiment, i.e., that equilibrium cannot be reached. The same is true for the spin echo experiment, which fails if the evolution time is much longer than the transverse relaxation time of the spins.

Another argument against irreversibility was raised by Zermelo, based on a theorem by Poincaré. The theorem states that any isolated classical system will return repeatedly to a point in phase space that is arbitrarily close to the starting point. This argument is known as *Wiederkehreinwand* or Zermelo paradox. We note that such quasi-periodicity is compatible with the probability density formalism of statistical mechanics. The probability density distribution is very sharply peaked at the equilibrium state, but it is not zero at the starting point in phase space. The system fluctuates around the equilibrium state and, because the distribution is sharply peaked, these fluctuations are very small *most of the time*. Once in a while the fluctuation is sufficiently large to revisit even a very improbable starting point in phase space, but for a macroscopic system this while is much longer than the lifetime of our galaxy. For *practical purposes* such large fluctuations can be safely neglected, because they occur so rarely. That a system will never evolve far from the equilibrium state once it had attained equilibrium is an approximation, but the approximation is better than many other approximations that we use in physics. The statistical error that we make is certainly much smaller than our measurement errors.

Irreversibility as an Approximation

If the whole of phase space is accessible the system will always *tend* to evolve from a less probable macrostate to a more probable macrostate, until it has reached the most probable macrostate, which is the equilibrium state. Equilibrium is dynamic. The microstate of each individual system evolves in time. However, for most microstates the values of all state variables are the same as for equilibrium within experimental uncertainty. In fact, the fraction of such microstates does not significantly differ from unity. Hence, a system that has attained equilibrium once will be found at equilibrium henceforth, as long as none of the external parameters is changed on which the probability density distribution in phase space depends. In that sense, processes that run from a non-equilibrium state to an equilibrium state are irreversible.

We should note at this point that all our considerations in this lecture course assume systems under thermodynamic control. If microstate dynamics in phase space is slow compared to the time scale of the experiment or simulation, the equilibrium state may not be reached. This may also happen if dynamics is fast in the part of phase space where the initial state resides but exchange dynamics is too slow between this part of phase space and the part of phase space where maximum probability density is located.
