

General Remarks

The field of Statistical Thermodynamics is probably the branch of physical chemistry whose coverage in textbooks is most diverse. A canonical way of teaching this subject still appears to be missing, which is partially due to the fact that practitioners have not completely agreed on interpretation of the probabilistic character, on the postulates, and on the way how the mathematical apparatus is derived from a set of postulates. While this may appear troublesome, actually there exists rarely any problem in *applying* statistical thermodynamics¹. Accordingly, textbooks usually ignore the more problematic aspects and try to give reasons why the interpretation and formulation used by the respective author should be the preferred one. This being an advanced lecture course, we shall not do so, but we shall still present an apparatus that is ready-made for application.

The basic idea of statistical thermodynamics is simple: On the one hand we have Newtonian and quantum mechanics and we know that molecules should adhere to it, and on the other hand we know that systems consisting of many molecules can be adequately described by phenomenological (or classical) thermodynamics. Now let's try to derive the latter theory from the former one. Some care will have to be taken for systems that are subject to quantum statistics, but we might expect that straightforward application of probability theory will provide the required connection. Chapter will discuss this basic idea in some more detail and will present a set of postulates due to Oliver Penrose. The discussion of these postulates clarifies what the remaining mathematical problem is and how we avoid it in applications.

In this course we do not assume that students are already familiar with probability theory, rather we will introduce its most important concepts in Chapter . We do assume that the concepts of phenomenological thermodynamics are known, although we shall shortly explain them on first use in these lecture notes. The most important new concept in this course is the one of an ensemble description, which will be introduced in Chapter first only for classical particles. This will set the stage for discussing the concepts of irreversibility and entropy in Chapter . We will complete the foundations part with a discussion of quantum ensembles in Chapter . This Chapter will also make the transition to applications, by treating first the harmonic oscillator and second the Einstein model of a crystal with the apparatus that we command at that point.

We shall then illustrate the relation to phenomenological thermodynamics by discussing the partition functions of gases and by computing thermodynamical state functions from these partition functions in Chapter . The final Chapter will shortly discuss the consequences of statistical thermodynamics for macromolecular systems and introduce the concepts of lattice models, random walks, and entropic elasticity.

The time available for this course does not permit to treat all aspects of statistical thermodynamics and statistical mechanics that are important in physical chemistry, chemical physics, polymer physics, and biophysics, let alone in solid-state physics. The most important omissions are probably kinetic aspects of chemical reactions, which are treated in detail in a lecture course on Advanced Kinetics, and the topic of phase transitions, including the famous Ising chain model. We believe that the foundations laid in the present course will allow students to understand these topics from reading in the textbooks listed in the following Section.