1.3: Statistical Mechanics Based on Postulates

The Penrose Postulates

Penrose has made the attempt to strictly specify what results can be expected from statistical mechanics if the theory is based on a small number of plausible postulates.

1. Macroscopic physical systems are composed of molecules that obey classical or quantum mechanical equations of motion (*dynamical description of matter*).
2. An observation on such a macroscopic system can be idealized as an instantaneous, simultaneous measurement of a set of dynamical variables, each of which takes the values 1 or 0 only (*observational description of matter*).
3. A measurement on the system has no influence whatsoever on the outcome of a later measurement on the same system (*compatibility*).
4. The Markovian postulate. (Concept [concept:Markovian])
5. Apart from the Bose and Fermi symmetry conditions for quantum systems, the whole phase space can, in principle, be accessed by the system (*accessibility*).

After the discussion above, only the second of these postulates may not immediately appear plausible. In the digital world of today it appears natural enough: Measurements have resolution limits and their results are finally represented in a computer by binary numbers, which can be taken to be the dynamical variables in this postulate.

Implications of the Penrose Postulates

Entropy is one of the central quantities of thermodynamics, as it tells in which direction a spontaneous process in an isolated system will proceed. For closed systems that can exchange heat and work with their environment, such predictions on spontaneous processes are based on free energy, of which the entropy contribution is usually an important part. To keep such considerations consistent, entropy must have two fundamental properties

1. If the system does not exchange energy with its environment, its entropy cannot decrease. (*non-decrease*).
2. The entropy of two systems considered together is the sum of their separate entropies. (*additivity*).

Based on the Penrose postulates it can be shown that the definition of Boltzmann entropy (Chapter) ensures both properties, but that statistical expressions for entropy ensure only the non-decrease property, not in general the additivity property. This appears to leave us in an inconvenient situation. However, it can also be shown that for large systems, in the sense that the number of macrostates is much smaller than the number of microstates, the term that quantifies non-additivity is negligibly small compared to the total entropy . The problem is thus rather a mathematical beauty spot than a serious difficulty in application of the theory.