

CHAPTER OVERVIEW

17: Boltzmann Factor and Partition Functions

Statistical Mechanics provides the connection between microscopic motion of individual atoms of matter and macroscopically observable properties such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. Statistical Mechanics provides the microscopic basis for thermodynamics, which, otherwise, is just a phenomenological theory. Microscopic basis allows calculation of a wide variety of properties not dealt with in thermodynamics, such as structural properties, using distribution functions, and dynamical properties – spectra, rate constants, etc., using time correlation functions. Because a statistical mechanical formulation of a problem begins with a detailed microscopic description, microscopic trajectories can, in principle and in practice, be generated providing a window into the microscopic world. This window often provides a means of connecting certain macroscopic properties with particular modes of motion in the complex dance of the individual atoms that compose a system, and this, in turn, allows for interpretation of experimental data and an elucidation of the mechanisms of energy and mass transfer in a system.

[17.1: The Boltzmann Factor is used to Approximate the Fraction of Particles in a Large System](#)

[17.2: The Boltzmann Distribution represents a Thermally Equilibrated Distribution](#)

[17.3: The Average Ensemble Energy is Equal to the Observed Energy of a System](#)

[17.4: Heat Capacity at Constant Volume is the Change in Internal Energy with Temperature](#)

[17.5: Pressure can be Expressed in Terms of the Canonical Partition Function](#)

[17.6: The Partition Function of Distinguishable, Independent Molecules is the Product of the Molecular Partition Functions](#)

[17.7: Partition Functions of Indistinguishable Molecules Must Avoid Over Counting States](#)

[17.8: Partition Functions can be Decomposed into Partition Functions of Each Degree of Freedom](#)

[17.E: Boltzmann Factor and Partition Functions \(Exercises\)](#)

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