Statistical Mechanics of Closed Systems (The Microcanonical Ensemble)

1. On the microscopic level, a complete description of a system requires the specification of a large number (proportional to the system size) of variables, e.g., the position and momentum of every particle. Each possible distinct combination of these variables is termed a *microstate* of the system.

2. Macroscopic measurements on systems in equilibrium are performed over length and time scales that are very long compared to microscopic scales. Therefore, the *macrostate* of an equilibrium system is described by a small number (independent of system size) of space- and time-averaged parameters. Typically, a large number of distinct microstates correspond to the same macrostate. We represent this number by the symbol Ω.

3. Let us consider a *closed* system, completely surrounded by walls which do not allow passage of energy or matter. Such a system has fixed values[1] of certain macroscopic parameters, including the total energy, the total volume, and the total number of each species of conserved particle. Other macroscopic parameters — such as the energy, volume, and particle numbers for individual subsystems of a closed composite system — may be fixed or left free, depending on presence or absence of internal constraints. Let us denote the fixed and free parameters by the sets $\{X_j\}$ and $\{Y_k\}$, respectively.

4. Any microstate which is consistent with all internal and external constraints on the system (i.e., it has the correct value of each X_j) is said to be *accessible*.

5. The *central assumptions* of statistical mechanics are that (i) at any moment, a closed system is equally likely to be in any one of its accessible microstates; and (ii) an experimental measurement of any unconstrained macroscopic quantity will yield the expectation value of that quantity taken over the entire set of accessible microstates.

6. If a macroscopic quantity Z can be expressed as a function of other macroscopic variables, then its expectation value can be expressed as

$$\bar{Z} = \frac{\sum_{Y_1} \sum_{Y_2} \cdots \ \Omega(\{X_j\}, \{Y_k\}) \ Z(\{X_j\}, \{Y_k\})}{\sum_{Y_1} \sum_{Y_2} \cdots \ \Omega(\{X_j\}, \{Y_k\})}.$$

   The sum is taken over all possible values of each unconstrained parameter Y_k.

7. In large systems, $\Omega(\{X_j\}, \{Y_k\})$ is so sharply peaked as a function of the unconstrained parameters $\{Y_k\}$ around a certain set of values $\{\tilde{Y}_k\}$ that the each expectation value $\bar{Z}$ is essentially indistinguishable from the most probable value $\tilde{Z} = Z(\{X_j\}, \{\tilde{Y}_k\})$.

8. By considering the conditions for equilibrium between subsystems of a closed composite system, we find that classical thermodynamics and statistical mechanics are completely consistent provided that

$$S = k_B \ln \Omega.$$

   Detailed comparison of statistical mechanical calculations with experiments indicates that the constant k_B (Boltzmann's constant) satisfies $k_B = R/N_A$, where R is the universal gas constant and N_A is Avogadro's number.

[1]Strictly, in quantum mechanics each parameter is fixed up to a certain level of uncertainty.