Foundations of statistical mechanics and thermodynamics

This field can be approached from a purely macroscopic point of view, which does not make use of the knowledge that matter is made of *itsy bitsy particles* (atoms and molecules). Then it is called **thermodynamics**. From that point of view, the following statements are postulates. Or, the subject can begin from the atomic level and work up to macroscopic results. In that approach, the following statements are the result of a lot of hard work. Then it is called **statistical mechanics**. Statements 0–3 are the laws of thermodynamics. Statement 4 broadens the possibilities to statistical thermodynamics. With Statement 5, we are moving into the full possibilities of statistical mechanics.

Statement 0: **Zeroth law of thermodynamics**

If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

This leads to thermometers and the state variable T the *temperature* as part of the characterization of an equilibrium macroscopic state of a system.

Statement 1: **First law of thermodynamics**

There is a quantity U, the *internal energy*, associated with an equilibrium macrostate. For an isolated system, U is a constant. In interaction, when the macrostate changes.

$$\Delta U = Q + W. \tag{1}$$

W is the macroscopic work done on the system due to a volume change. Q is the heat flow into the system.

This is the conservation of energy. Heat is the energy transfer unaccompanied by any change in the volume.

Statement 2: **Second law of thermodynamics**

There is a quantity S, the *entropy*, associated with an equilibrium macrostate. In an infinitesimal, quasistatic process with heat flow dQ,

$$dS = dQ/T. \tag{2}$$

T is the absolute temperature. For any change in the macrostate of an isolated system.

$$\Delta S \geq 0. \tag{3}$$

Statement 3: **Third law of thermodynamics**

As $T \to 0$, $S \to 0$.

Statement 4: **Statistical relation**

In an equilibrium, isolated system, the probability of a macrostate with entropy S is

$$P \propto e^{S/k}. \tag{4}$$

k is Boltzmann's constant. With this, one can calculate the probability of fluctuations of quantities away from their equilibrium values.

Statement 5: **Microscopic description of entropy**

If Ω is the number of microstates accessible to a system, then

$$S = k \ln \Omega. \tag{5}$$

This is the path to statistical mechanics.