

The deterministic classical Newtonian description of an assembly of a large number of moving particles or wavepackets poses a difficult mathematical problem. A statistical thermodynamic alternative is provided by a Maxwell-Boltzmann or Gibbs statistical description, which yields equilibrium properties (pressure, average energy, entropy) at a temperature T of such systems. Maxwell-Boltzmann statistics is usually applied to N body classical gases while Gibbs statistics applies as well to quantum systems.

In the Gibbs statistical view, a class of N observable macro-canonical systems forms a virtual assembly. Each class has a total energy E distinguished by n_i sub-populations, each in discrete energy states ε_i , subject to Lagrange conditions $\sum_i n_i = N$ and $\sum_i n_i \varepsilon_i = E$, where $i=1,2,\dots,l < N$. Since there are $N!$ possible ordered arrangements of the N systems and $n_1!, n_2!, n_3!, \dots, n_l!$, of the n_i sub-populations, the number of different n_i ordered arrangements in the class members of the assembly is:

$$P = \frac{N!}{n_1! n_2! n_3! \dots n_l!} \quad (1)$$

The maximum of P , subject to the above stated Lagrange conditions, then yields the most probable distribution of the n_i characterizing the equilibrium state of the assembly. This result also follows from the probability and sampling theory of a large number of objects N distributed in n_i sub-populations each characterized by a property ε_i .

For example, at temperature T , the equilibrium properties of a classical non-relativistic monatomic gas comprising an N particle assembly, with n_i particles of momentum p_i and mass m in an energy state $\varepsilon_i = p_i^2/2m$, follow from the most probable distribution of the n_i derived from the maximum of P . This distribution n_i/N , from which equilibrium properties of the gas may be calculated, follows from a partition function $Z = \sum_i \exp(-\varepsilon_i/k_b T)$ summed over all energy states ε_i (k_b being the Boltzmann constant 0.86×10^{-4} ev per degree K) as:

$$\frac{n_i}{N} = -\frac{1}{T} \frac{d}{d\varepsilon_i} (k_b \ln Z) = \frac{\exp(-\varepsilon_i/k_b T)}{\sum_i \exp(-\varepsilon_i/k_b T)}$$

The average energy per particle U also follows from Z as:

$$U = \frac{\bar{E}}{N} = T^2 \frac{\partial}{\partial T} (k_b \ln Z) = \frac{\sum_i \varepsilon_i \exp(-\varepsilon_i/k_b T)}{\sum_i \exp(-\varepsilon_i/k_b T)}$$

To within an additive constant, one finds from Z that the quantity $\Psi = k_b \ln Z$, the thermodynamic free energy per particle is known to be:

$$\Psi = k_b \ln V + (3/2)k_b \ln T,$$

V being the assembly volume. It follows from Ψ that the average energy \bar{E} of the gas of N atoms is $(3/2)N k_b T$. The gas pressure p also follows from Ψ as $p = T(d/dV) \Psi = (N/V) k_b T = (2/3)U/V$.

An alternative and more revealing statistical thermodynamic procedure, suggested by Schroedinger, considers a virtual macroscopic ensemble with each system of the ensemble in an eigen state of total energy E at temperature T and composed of degenerate energy states E_r having a degeneracy m_r with $r=1,2,3,..N$. To find the most probable m_r he again introduces a “sum over states” now in the form:

$$Z = \sum_r m_r \exp\left(-\frac{E_r}{k_b T}\right) \quad (2)$$

where the n_i used previously is identical to m_r . One then infers the average energy \bar{E}_r of the equilibrium distribution as

$$\bar{E}_r = k_b T^2 \frac{d}{dT} (\ln Z) = \frac{\sum_r E_r m_r \exp\left(-\frac{E_r}{k_b T}\right)}{\sum_r m_r \exp\left(-\frac{E_r}{k_b T}\right)},$$

and by rearranging finds

$$d(k_b \ln Z + \frac{\bar{E}_r}{T}) = \frac{d\bar{E}_r}{T}$$

which identifies the equilibrium entropy as

$$S = k_b \ln Z + \frac{\bar{E}_r}{T}$$

To determine the equilibrium m_r one returns to the definition of Z in (2) and sets its differential form to zero, namely

$$d \ln Z = 0 = d\left(\ln m_r - \frac{E_r}{k_b T}\right)$$

whence at equilibrium

$$d(k_b \ln m_r) = d\bar{E}_r / T$$

and thus one identifies the equilibrium entropy as

$$S = k_b \ln m_r,$$

in accord with the identification of the entropy with the maximum possible m_r and of the average \bar{E}_r with E .

For quantum “particles” (photons, bosons, or fermions), the thermodynamic properties of a virtual particle assembly at temperature T are

calculated via quantum statistical methods. Consider an assembly of N such “particles”, the i th of which is in a quantum state of energy

$\alpha_i = mc^2 = \sqrt{m_0^2 c^4 + p_i^2 c^2}$, $m = m_0 / \sqrt{1 - v_i^2 / c^2}$ being its mass, m_0 its rest mass, $p_i = mv$ its momentum, and v_i/c its velocity relative to light velocity c . If n_i is the number of quanta excited in the i th energy state of an i th type “particle”, then the thermodynamic properties of the assembly follow from the statistics of the partition function $Z = \sum_{n_i} \exp(-n_i \alpha_i / k_b T)$ summed over all possible sets of

n_i subject to $\sum n_i = N$ (except for photons). At the quantum level, boson statistics yields for the partition function:

$$Z = \sum_{i=0}^{\infty} \exp\left[\frac{hv}{k_b T}(i + 1/2)\right] = \frac{\exp(-\frac{hv}{k_b T})}{1 - \exp(-\frac{hv}{k_b T})}$$

where, as in the classical case, the thermodynamic free energy $\Psi = k_b \ln Z$ permits the average energy of a single boson to be calculated as:

$$U = T^2 \frac{\partial \Psi}{\partial T} = \frac{hv}{2} + \frac{hv}{\exp(hv/k_b T) + 1}.$$

For fermions with only 2 energy levels 0 and ε

$$Z = 1 + \exp(-\varepsilon / k_b T)$$

$$U = T^2 \frac{\partial \Psi}{\partial T} = \frac{\varepsilon}{2} + \frac{\varepsilon}{\exp(\varepsilon / k_b T) + 1}.$$

The expression for Ψ is different in the two cases. In bose and fermion statistics,

$$\Psi = k_b \ln Z = -Nk_b T \ln \zeta + pV / T^2$$

where

$$\zeta = \frac{N}{V} \left(\frac{\hbar^2}{2\pi m k_b T} \right)^{\frac{3}{2}}$$