Statistical Mechanics Formulas for Physics 398b  
(last modified 9/12/96)

The Boltzmann constant $k_B$ is used to express temperature in units of energy, $k_B T$. The inverse of $k_B T$ is often needed and is notated $\beta = 1/(k_B T)$, which has units of inverse energy. Note that $\beta \to \infty$ is the (absolute) zero temperature limit, and $\beta \to 0$ the high-temperature limit.

For a Boltzman distribution at temperature $T$, the probability of a state $i$ being occupied is

$$P_i = \frac{1}{Z} e^{-\beta E_i}$$  \hspace{1cm} (1)

where the normalizing factor, $Z$, is the partition function, defined as the sum over all states:

$$Z = \sum_i e^{-\beta E_i}$$  \hspace{1cm} (2)

$$= \text{Tr}[e^{-\beta H}] \quad \text{(QM definition, H is the Hamiltonian)} \quad \text{(3)}$$

$$= e^{-\beta F} \quad \text{(Defines the free energy F)}.$$  \hspace{1cm} (4)

Using Eq. (1), the average value of an observable can be written as

$$\langle A \rangle = \frac{1}{Z} \sum_i A_i e^{-\beta E_i},$$  \hspace{1cm} (5)

$$= \frac{1}{Z} \text{Tr}[A e^{-\beta H}]; \quad \text{(QM)},$$  \hspace{1cm} (6)

where $A_i$ is the value of $A$ for the state $i$ in the ensemble. In the QM case, $A$ is an operator.

A state of a classical system of $N$ particles is a point in phase space, described by $2 \times 3N$ coordinates: $(r_1, r_2, \ldots, r_N, p_1, p_2, \ldots, p_N) = (R, P)$. \textit{(Note: $p_i = mv_i$ is the momentum of particle $i$.)} A classical state is defined as having as volume $\hbar^{3N}$ in phase space.

The probability of a state $(R, P)$ with energy $E$ being occupied in the canonical ensemble is

$$P(R, P)dRdP = \frac{1}{Z} \frac{e^{-\beta E} dRdP}{N! \hbar^{3N}},$$  \hspace{1cm} (7)

where the energy is

$$E = V(R) + \sum_i \frac{p_i^2}{2m_i}.$$  \hspace{1cm} (8)

Since the details of the system only enter in the interactions $V(R)$, the momentum part can be solved to give some general results for any classical system (gas, solid or liquid),

$$\langle \frac{p^2}{2m} \rangle = \frac{3}{2} N k_B T \quad \text{(Equipartion of KE)},$$  \hspace{1cm} (9)

$$P(v)dv = \frac{1}{\sqrt{2\pi}} \left(\frac{m}{k_B T}\right)^\frac{3}{2} v^2 e^{-\frac{mv^2}{2k_B T}} dv \quad \text{(Maxwell Velocity Distribution)},$$  \hspace{1cm} (10)

$$Z = \frac{f^{3N}}{N!} \int dR e^{-\beta V(R)}; \quad f = \left(\frac{2\pi m k_B}{\hbar^2}\right)^\frac{1}{2}.$$  \hspace{1cm} (11)

The last line, Eq. (11), shows that only the configurational part of the partition function is needed classically.

Please email any questions or corrections to shumway@uiuc.edu