Statistical Mechanics Formulas for Physics 398b

(last modified 9/12/96)

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

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

$$P_i = \frac{1}{Z}\mathrm{e}^{-\beta E_i} \tag{1}$$

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

$$\begin{aligned} Z &= \sum_i \mathrm{e}^{-\beta E_i} && (2)\\ &= \mathrm{Tr}[\mathrm{e}^{-\beta H}] && \text{(QM definition, H is the Hamiltonian)} \quad (3)\\ &= \mathrm{e}^{-\beta F} && \text{(Defines the free energy F).} \quad (4) \end{aligned}$$

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

$$\begin{aligned} \langle A \rangle &= \frac{1}{Z}\sum_i A_i \mathrm{e}^{-\beta E_i}, && (5)\\ &= \frac{1}{Z}\mathrm{Tr}[A\mathrm{e}^{-\beta H}]; \qquad \text{(QM)}, && (6) \end{aligned}$$

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: $(\mathbf{r_1}, \mathbf{r_2}, ...\mathbf{r_N}, \mathbf{p_1}, \mathbf{p_2}, ..., \mathbf{p_N},) = (\mathbf{R}, \mathbf{P})$. (*Note:* $\mathbf{p}_i = m\mathbf{v}_i$ is the momentum of particle i.) A classical state is defined as having as volume h^{3N} in phase space.

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

$$P(R,P)dRdP = \frac{1}{Z}\frac{\mathrm{e}^{-\beta E}dRdP}{N!h^{3N}}, \tag{7}$$

where the energy is

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

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),

$$\begin{aligned} \left\langle \frac{p^2}{2m} \right\rangle &= \frac{3}{2}Nk_BT && \text{(Equipartion of KE)}, \quad (9)\\ P(v)dv &= \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_BT}\right)^{\frac{3}{2}} v^2 \mathrm{e}^{-\frac{mv^2}{2k_Bt}}dv && \text{(Maxwell Velocity Distribution)}, \quad (10)\\ Z &= \frac{f^{3N}}{N!}\int dR\mathbf{e}^{-\beta V(R)}; \qquad f = \left(\frac{2\pi m\beta}{h^2}\right)^{\frac{1}{2}}. && (11) \end{aligned}$$

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

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