

Statistical Mechanics Formulas for Atom Scale Simulation

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 $\beta \rightarrow \infty$ is the (absolute) zero temperature limit, and $\beta \rightarrow 0$ is the high-temperature limit.

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

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

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

$$Z = \sum_i e^{-\beta E_i} \quad (2)$$

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

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

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

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

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

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: $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) = (\mathbf{R}, \mathbf{P})$. (*Note:* $\mathbf{p}_i = m\mathbf{v}_i$ is the momentum of particle i .) A classical state is defined as having a volume h^{3N} in phase space, h is Planck's constant.

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

$$P(R, P) dR dP = \frac{1}{Z} \frac{e^{-\beta E} dR dP}{N! h^{3N}}, \quad (7)$$

where the energy is

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

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

$$\left\langle \frac{p^2}{2m} \right\rangle = \frac{3}{2} N k_B T \quad (\text{Equipartition of KE}), \quad (9)$$

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

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

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 ceperley@uiuc.edu