Statistical Mechanics: Lecture 6

Entropy in Canonical Ensemble

In microcanonical ensemble, the entropy of the system was defined very simply in terms of the total number of microstates Ω, which are all equally probable

$$S(E) = k \log\left[\Omega(E)\right] \tag{1}$$

Energy of the system is fixed at E. As all microstates are equally probable, the probability of one microstate is $1/\Omega$. The above expression can be written in terms of this probability of one microstate

$$S(E) = -k \log\left[\frac{1}{\Omega(E)}\right] \tag{2}$$

In the canonical ensemble, microstates with different energy occur with different probability. For that reason, one may want to rewrite the above equation as an average over microstates. This will help in extending this relation to the case of canonical ensemble.

$$S(E) = \sum_i \frac{1}{\Omega(E)} \left(-k \log\left[\frac{1}{\Omega(E)}\right]\right) \tag{3}$$

Since all terms in the sum in (3) are equal, and there are exactly Ω terms, it will add to give (2). Defining $1/\Omega$ to be the probability of a microstate ρ_i, the above can be written as

$$S(E) = -k \sum_i \rho_i \log \rho_i \tag{4}$$

This definition of entropy can now be carried over to canonical ensemble, in a straightforward manner. The only difference is that the sum now involves microstates with all possible energies

$$\boxed{S = -k \sum_i \rho_i \log \rho_i} \tag{5}$$

where ρ_i is the probability of the i'th microstate, given by

$$\rho_i = \frac{e^{-\beta E_i}}{Z}, \tag{6}$$

Z is the canonical partition function given by $Z = \sum_i e^{-\beta E_i}$, and E_i is the energy of the system in i'th microstate. In terms of the classical phase space variables, the entropy can be written as

$$\boxed{S = -k\frac{1}{\Delta} \int \rho(p,q) \log\left[\rho(p,q)\right] dp\,dq} \tag{7}$$

where $\rho(p,q)$ is the density function in canonical ensemble, and Δ is the phase volume corresponding to one microstate.
Since for canonical ensemble, ρ_i has a specific form (6), we can put it in (5) and get an expression for entropy in terms of Z.

Helmholtz Free Energy

$$\begin{aligned}
S =& -k \sum_i \rho_i \log \rho_i \\
=& -k \sum_i \frac{e^{-\beta E_i}}{Z} \log\left(\frac{e^{-\beta E_i}}{Z}\right) \\
=& -k \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i - \log Z) \\
=& \beta k \sum_i \frac{e^{-\beta E_i} E_i}{Z} + \frac{k}{Z} \log Z \sum_i e^{-\beta E_i} \\
=& \beta k \langle E \rangle + \frac{k}{Z} \log(Z) Z \\
=& \beta k \langle E \rangle + k \log(Z)
\end{aligned} \tag{8}$$

where $\langle E \rangle$ is the ensemble average of the energy of the system. The above equation can be rewritten as

$$\langle E \rangle - TS = -kT \log Z \tag{9}$$

But from thermodynamics we know that the Hemlholtz free energy is given by $F = U - TS$. Here, $\langle E \rangle$ is the internal energy of the system, what is represented by U in thermodynamics. Thus we find the expression for Helmholtz free energy in canonical ensemble to be

$$\boxed{F = -kT \log Z} \tag{10}$$

Classical Ideal Gas in Canonical Ensemble

Let us study our simplest problem of a classical ideal gas, which we studied using micro-canonical ensemble earlier, now using canonical ensemble. Energy of the gas is given by

$$E = \sum_{i=1}^{N} \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \tag{11}$$

where the sum over i goes over all N particle. The partition function can thus be written as

$$\begin{aligned}
Z =& \frac{1}{\hbar^{3N}} \int e^{-\beta E} \prod_{i=1}^{N} dp_{xi} dp_{yi} dp_{zi} dx_i dy_i dz_i \\
=& \frac{1}{\hbar^{3N}} \int \exp\left[-\beta \sum_{i=1}^{N} \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] \prod_{i=1}^{N} dp_{xi} dp_{yi} dp_{zi} dx_i dy_i dz_i \\
=& \frac{1}{\hbar^{3N}} \int \prod_{i=1}^{N} \exp\left[-\beta \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] dp_{xi} dp_{yi} dp_{zi} dx_i dy_i dz_i \\
=& \frac{1}{\hbar^{3N}} \prod_{i=1}^{N} \int \exp\left[-\beta \left(\frac{p_{xi}^2}{2m} + \frac{p_{yi}^2}{2m} + \frac{p_{zi}^2}{2m} \right) \right] dp_{xi} dp_{yi} dp_{zi} dx_i dy_i dz_i
\end{aligned} \tag{12}$$

Since the particles are non-interacting and identical, these N integrals will also be identicial. Integral over space will just give the volume of the box enclosing the gas, and momenta will vary from $-\infty$ to $+\infty$. Partition function thus looks like

$$Z=\frac{1}{\hbar^{3N}}\prod_{i=1}^{N} V \int_{-\infty}^{\infty} \exp\left[-\beta\frac{p_{xi}^2}{2m}\right] dp_{xi} \int_{-\infty}^{\infty} \exp\left[-\beta\frac{p_{yi}^2}{2m}\right] dp_{yi} \int_{-\infty}^{\infty} \exp\left[-\beta\frac{p_{zi}^2}{2m}\right] dp_{zi} \tag{13}$$

Using the properties of Gaussian integrals, this above equation simplifies to

$$\begin{aligned} Z=&\frac{1}{\hbar^{3N}}\prod_{i=1}^{N} V\left(\frac{2m\pi}{\beta}\right)^{3/2} \\ =&\frac{1}{\hbar^{3N}}V^N\left(\frac{2m\pi}{\beta}\right)^{3N/2} \end{aligned} \tag{14}$$

Average energy is now given by

$$\langle E\rangle=-\frac{\partial}{\partial\beta}N\log\left(\frac{1}{\hbar^3}V\left(\frac{2m\pi}{\beta}\right)^{3/2}\right) \tag{15}$$

The above simplifies to give

$$\boxed{\langle E\rangle = \frac{3}{2}NkT} \tag{16}$$

Entropy of the ideal gas can now be calculated by substituting expression for Z from (14) into (8). Doing that, we get

$$\begin{aligned} S=&\beta k\langle E\rangle + k\log(Z) \\ =&\beta k\frac{3}{2}NkT + k\log\left(\frac{1}{\hbar^{3N}}V^N\left(\frac{2m\pi}{\beta}\right)^{3N/2}\right) \\ =&\frac{3}{2}Nk + Nk\log\left(V\left[\frac{2m\pi kT}{\hbar^2}\right]^{3/2}\right) \\ =&\frac{3}{2}Nk + Nk\log\left(V\left[\frac{4m\pi(3NkT/2)}{3N\hbar^2}\right]^{3/2}\right) \\ =&\frac{3}{2}Nk + Nk\log\left(V\left[\frac{4m\pi\langle E\rangle}{3N\hbar^2}\right]^{3/2}\right) \end{aligned} \tag{17}$$

This result is identical to the one obtained using microcanonical ensemble, if one identifies the average energy $\langle E\rangle$ with the fixed energy E in microcanonical ensemble. For indistinguishable particles, one should have an additional factor of $1/N!$ in the partition function (14). With that addition, the above expression will lead to the Sackur-Tetrode equation. Thus, canonical and microcanonical ensemble yield identical results for the classical ideal gas, as they should.