Lecture 14

Ideal gas

Boltzmann distribution for ideal gas

\[ n_{\mu} = e^{\frac{(\mu - E\mu)}{T}} \]

\[ n(p,q) = e^{\frac{(\mu - E(p,q))}{T}} \]

Free energy

\[ F = -T \log Z = -T \log \sum_{\mu} e^{-E\mu/T} , \text{ where} \]

\[ E\mu = \sum_{\mu} \frac{n_{\mu} E\mu}{E_{\mu}} \]

Remember that \( E\mu \) is the energy of a given state, which is defined by the set of \( N \) values of \( E\mu \) and distribution of particles between these states.

For a given state \( n \), \( e^{-E\mu/T} = e^{-E_1/T} \cdot e^{-E_2/T} \cdot \ldots \cdot e^{-E_N/T} \), because in the rarefied gas each energy level is at most occupied by one particle.

The set of possible values of \( E\mu \) is the same for each state (of for example, a molecule)

\[ \sum_{\mu} e^{-E\mu/T} \Rightarrow \left( \sum_{k} e^{-E_k/T} \right)^N \cdot \frac{N!}{N!} \]

\( N! \) counts all permutations of particles between different states.
Next let us find the free energy of the ideal gas:

\[ F = -T \ln \left( \frac{\sum e^{-\frac{E}{kT}}}{N!} \right) \frac{1}{N!} = \]

\[ = -T N \ln \sum e^{-\frac{E}{kT}} + T \ln N! \]

Using Stirling's formula, we get

\[ \ln N! \propto N \ln \frac{N}{e} = N (\ln N - 1) \]

\[ \Rightarrow F = -T N \ln \frac{\sum e^{-\frac{E}{kT}}}{N!} \]

Free energy of ideal quantum gas.

For classical case, we easily obtain

\[ F = -T N \ln \frac{\sum e^{-\frac{E(R, P)}{kT}}}{N!} \int \frac{d^3p \, d^3q}{(2\pi\hbar)^3} \]

This is actually quasiclassical.

Note that translational motion of molecules in the gas is always quasiclassical.

\[ E_n(P_x, P_y, P_z) = \frac{P_x^2}{2m} + \frac{P_y^2}{2m} + \frac{P_z^2}{2m} + E_u \]

\[ E_u \] denotes the energy levels corresponding to the rotation and internal state of the molecule.
\[ \sum_{\nu} e^{-\epsilon_\nu / T} = \sum_{\nu} \frac{1}{\nu (2\pi h^2)^{3/2}} \int e^{-\epsilon}\nu(p)/T \, d^3p \, d\nu = \]

\[ = \frac{\pi}{\nu} e^{-\epsilon_\nu / T} \sqrt{\frac{mT}{2\pi h^2}}^{3/2} \sum_{\nu} e^{-\epsilon_\nu / T} \]

Separating \( F \) into terms containing volume, we get

\[ F = -NT \epsilon_\nu \frac{eV}{N} \left( \frac{mT}{2\pi h^2} \right)^{3/2} \sum_{\nu} e^{-\epsilon_\nu / T} \]

some function of \( T \) which can be calculated only knowing details of the molecules.

\[ P = -\frac{\partial F}{\partial V} = \frac{NT}{V} \Rightarrow PV = NT \]

equation of state for ideal gas

(Clausius's formula)

Example

Consider the simplest case of inert gas with molecules which have \( L=S=0 \). Find \( \mu \) and \( c_1 \).

\[ \Delta \epsilon_0 = \text{ground state (GS)} \]

GS is non-degenerate.

\[ \Delta - \text{ionization energy} \]

\[ \epsilon_\nu - \text{excited states} \]

If \( T \ll \Delta \), then all atoms are in the GS.

\[ n = e^{-\epsilon_0 / T} \]
We can set \( \epsilon_0 = 0 \Rightarrow Z = 1 \).

Then \[ G = N U = F + P V = - N T \, \epsilon_u \left[ \frac{e^u}{N} \left( \frac{m T}{2 \pi h^2} \right)^{3/2} \right] + N T \]

\[ \mu N = - N T \, \epsilon_u \, \frac{V}{N} \left( \frac{m T}{2 \pi h^2} \right)^{3/2} \]

\[ \Rightarrow \mu = N T \, \epsilon_u \, \frac{V}{N} \left( \frac{2 \pi h^2}{m T} \right)^{3/2} \]

Remember that \[ \frac{\mu}{N} = e^{\mu / T} \ll 1 \Rightarrow e^{\mu / T} \ll 1 \]

\[ \Rightarrow \frac{N}{V} \left[ \frac{2 \pi h^2}{m T} \right]^{3/2} \ll 1 \]

For a given gas at temperature \( T \), this condition guarantees that the gas is rarefied.

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V = - T \frac{\partial^2 F}{\partial T^2} = ? \]

\[ F = - N T \, \epsilon_u \left[ \frac{e^u}{N} \left( \frac{m T}{2 \pi h^2} \right)^{3/2} \right] \]

\[ \Rightarrow C_v = \frac{3}{2} N \text{ const} \]

This is an example of equipartition law. Each degree of freedom contributes \( \frac{1}{2} \) to the specific heat.