

Perturbations about the Ideal Gas

Classical Hamiltonian is

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + U(\{\vec{q}\})$$

for the set conjugate coordinates of momentum, \vec{p}_i and position \vec{q}_i vectors for particle i . Classical partition function would be

$$Z_c = \frac{1}{N!} \sum_{cells} e^{-\beta H}$$

for cells of volume h^3 in the $6N$ dimensional phase space. For small cells this can be replaced with an integral

$$\sum_{cells} \rightarrow \frac{1}{h^3} \int dq_x dq_y dq_z \int dp_x dp_y dp_z$$

and so the partition function becomes

$$Z_c(T, V, N) = \frac{1}{N! h^{3N}} \int \prod_i d^3 q_i d^3 p_i e^{-\beta H(\{\vec{q}\}, \{\vec{p}\})}$$

Ideal Gas

For the ideal gas, $U = 0$ and the partition function is given by

$$\begin{aligned} Z_{ideal} &= \frac{V^N}{N! h^{3N}} \prod_i \left[\int d^3 p_i e^{-\beta p_i^2 / 2m} \right] \\ &= \frac{V^N}{N! h^{3N}} \left[\int_0^\infty dp e^{-\beta p^2 / 2m} \right]^{3N} \\ &= \frac{V^N}{N! h^{3N}} \left[\left(\frac{2m\pi}{\beta} \right)^{1/2} \right]^{3N} \\ &= \frac{1}{N!} \left[\frac{V}{\lambda_T^3} \right]^N \end{aligned}$$

from which expressions for pressure, entropy etc can be found using the bridge equation.

Configurational Integral

In the interacting case with interaction potential $U(\vec{q}_1, \dots, \vec{q}_N)$ the total partition function becomes

$$Z_c = \frac{1}{N! h^{3N}} \prod_i \int d^3 p_i e^{-\beta \sum p_i^2 / 2m} \int \prod_i d^3 q_i e^{-\beta U(\{\vec{q}\})}$$

which is written as follows, for the configurational integral Q

$$Z_c(T, V, N) = Z_{ideal} Q$$

with

$$Q = \frac{1}{V^N} \int \prod_{i=1}^N d^3 q_i e^{-\beta U(\vec{q}_1, \dots, \vec{q}_N)}$$

Virial Expansion

Assuming 2-body interactions, and a central potential between particles, the interaction potential can be written

$$U(\{\vec{q}\}) = \sum_{i < j} \phi_{ij}$$

configurational integral is given by

$$Q = \frac{1}{V^N} \int \prod_i d^3 q_i \prod_{i < j} F_{ij}, \quad \text{where } F_{ij} = e^{-\beta \phi_{ij}}$$

which can be interpreted as a spatial average, and approximated by replacing the average of the product by the product of the averages

$$Q = \langle \prod_{i < j} F_{ij} \rangle \approx \prod_{i < j} \langle F_{ij} \rangle = \langle F \rangle^{N(N-1)/2}$$

since there are N choose 2 interaction forces to consider. Make the replacement $F_{ij} = 1 + f_{ij}$ and take $i, j = 1, 2$

$$\langle F \rangle \equiv \langle F_{12} \rangle = 1 + \frac{1}{V^N} \int \prod_i d^3 q_i f_{12} = 1 + \frac{1}{V^2} \int d^3 q_1 d^3 q_2 f_{12}$$

Change to centre of mass coordinates

$$\vec{r} = \vec{q}_1 - \vec{q}_2, \quad \vec{R} = \frac{1}{2}(\vec{q}_1 + \vec{q}_2)$$

the Jacobian is given by (component wise)

$$\left| \begin{array}{cc} \frac{\partial r_k}{\partial q_{1k}} & \frac{\partial r_k}{\partial q_{2k}} \\ \frac{\partial R_k}{\partial q_{1k}} & \frac{\partial R_k}{\partial q_{2k}} \end{array} \right| = 1 \quad \text{so} \quad d^3 q_1 d^3 q_2 = d^3 r d^3 R$$

and there is no dependence on \vec{R} so

$$\langle F_{12} \rangle = 1 + \frac{1}{V} \int d^3 r [e^{-\beta \phi(r)} - 1]$$

which gives for the configurational integral

$$Q = \left(1 - \frac{2B_2}{V} \right)^{N(N-1)/2}$$

with the second virial coefficient

$$B_2 = -\frac{1}{2} \int d^3 r [e^{-\beta \phi(r)} - 1]$$

and again thermodynamic quantities can be found using bridge equation

$$F = F_{ideal} - kT \ln Q \approx F_{ideal} + \frac{N^2 kT}{V} B_2$$

and equation of state

$$\frac{P}{kT} = \rho + B_2 \rho^2$$

which is equivalent to van der Waals equation of state

$$(P + \rho^2 a_0) = \frac{NkT}{V - Nb_0}$$