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

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

and so the partition function becomes

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

Ideal Gas

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

$$Z_{ideal} = \frac{V^N}{N! h^{3N}} \prod_i \left[\int d^3 p_i e^{-\beta p_i^2 / 2m} \right]$$

$$= \frac{V^N}{N! h^{3N}} \left[dp e^{-\beta p^2 / 2m} \right]^{3N}$$

$$= \frac{V^N}{N! h^{3N}} \left[\left(\frac{2m\pi}{\beta} \right)^{1/2} \right]^{3N}$$

$$= \frac{1}{N!} \left[\frac{V}{\lambda_T^3} \right]^N$$

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

Configurational Integral

In the interacting case with interaction potential $U(\vec{q_1}, ..., \vec{q_N})$ 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

$$Q = \frac{1}{V^N} \int \prod_{i=1}^N d^3 q_i e^{-\beta U(\vec{q_1}, ..., \vec{q_N})}$$

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

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

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

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

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

$$\vec{r} = \vec{q_1} - \vec{q_2}, \qquad \vec{R} = \frac{1}{2}(\vec{q_1} + \vec{q_2})$$

the Jacobian is given by (component wise)

$$\begin{vmatrix} \frac{\partial r_k}{\partial q_{1k}} & \frac{\partial r_k}{\partial q_{2k}} \\ \frac{\partial R_k}{\partial q_{1k}} & \frac{\partial R_k}{\partial q_{2k}} \end{vmatrix} = 1 \qquad \text{so} \qquad d^3 q_1 d^3 q_2 = d^3 r d^3 R$$

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

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