

Van der Waals' gas

As the concentration of particles in a gas increases, the interactions become more and more important (eventually the gas condenses to a liquid)

// So far, even when considering quantum gases, we did not deal with interactions

$$H(p_1, \dots, p_N, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U$$

$$U = \sum_{i < j} U(\vec{r}_i - \vec{r}_j)$$

Compute the partition function

$$Z = \frac{1}{(2\pi\hbar)^{3N}} \int e^{-\frac{H_{kin} + U}{T}} d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N$$

// We assume here that all the molecules are classical and distinguishable

In an ideal gas ($U=0$)

$$Z_{ideal} = \frac{1}{(2\pi\hbar)^{3N}} V^N \int e^{-\frac{H_{kin}}{T}} d\vec{p}_1 \dots d\vec{p}_N$$

$$F = F_{ideal} - T \ln \left(\frac{1}{V^N} \int e^{-\frac{U}{T}} d\vec{r}_1 \dots d\vec{r}_N \right)$$

add and subtract a unity in the integrand

$$\cdot \left[1 \cdot e^{-\frac{U}{T}} \right] = V^N + 1$$

add and subtract

$$F = F_{\text{ideal}} - T \ln \left[\frac{1}{V^N} \int (e^{-\frac{U}{T}} - 1) d\vec{r}_1 \dots d\vec{r}_N + 1 \right]$$

1) That form is convenient for treating the interaction perturbatively

Let us neglect the interaction except those cases when two particles are very close to each other.

The number of ways to pick 2 coordinates out of $\vec{r}_1, \dots, \vec{r}_N$ is $\frac{1}{2} N(N-1)$. Then we will use the smallness of the correction to unity and expand the log

$$\frac{1}{2} N(N-1) \int (e^{-\frac{U_{12}}{T}} - 1) d\vec{r}_1 \dots d\vec{r}_N$$

$$F \approx F_{\text{ideal}} - \frac{TN^2}{2V^2} \int (e^{-\frac{U_{12}}{T}} - 1) d\vec{r}_1 d\vec{r}_2$$

Instead of integrating wrt \vec{r}_1 and \vec{r}_2 , let's integrate wrt $\vec{\rho} = \vec{r}_1 - \vec{r}_2$ and $\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}$.

1) The Jacobian of this transformation of variables = 1 (you may check it)

$$\text{Then } F = F_{\text{ideal}} + \frac{N^2 T}{V} B(T)$$

$\wedge \quad - \frac{U_{12}(\vec{\rho})}{T} \quad \dots$

ideal

$$B(T) = \frac{1}{2} \int (1 - e^{-\frac{U_{12}(\vec{r})}{T}}) d\vec{r}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = P_0 + \frac{N^2 T}{V^2} B(T)$$

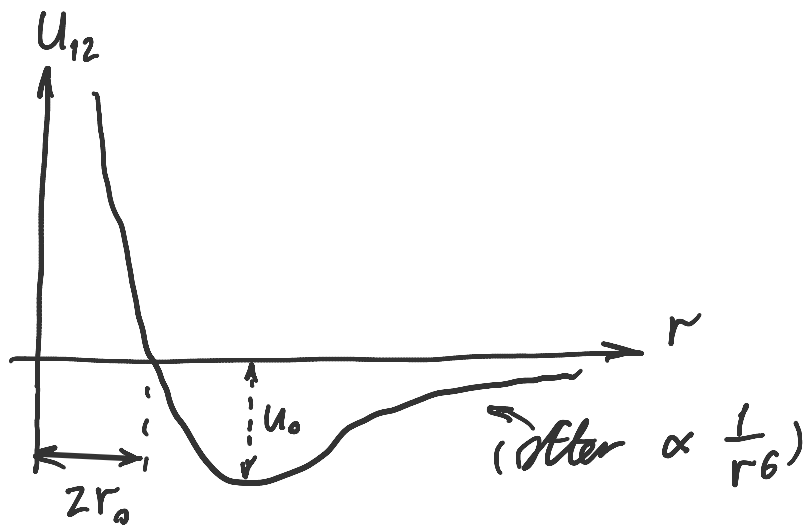
Here $P_0 = \frac{NT}{V}$

$$P = \frac{NT}{V} + \frac{N^2 T}{V^2} B(T)$$

The exact expression will involve an expansion in the density $\frac{N}{V}$ Virial expansion

$$P = \frac{NT}{V} \left(1 + \frac{N}{V} B(T) + \frac{N^2}{V^2} C(T) + \dots \right)$$

B, C, \dots — virial coefficients





$$\vec{p}' \uparrow \text{ induced } p' \propto \frac{p}{r^3}$$

Interaction between \vec{p} and \vec{p}' is $\propto \frac{1}{r^3}$. The interaction energy $\propto \frac{1}{r^6}$

In general we cannot compute the exact equation of state; one may find an interpolation formula.

We will require $\frac{U_0}{T} \ll 1$

$$B = \frac{1}{2} \int (1 - e^{-\frac{U_{12}(\vec{p})}{T}}) d\vec{p} =$$

$$= 2\sqrt{\pi} \int_0^{2r_0} \underbrace{\left(1 - e^{-\frac{U_{12}}{T}}\right)}_I r^2 dr + 2\sqrt{\pi} \int_{2r_0}^{\infty} \underbrace{\left(1 - e^{-\frac{U_{12}}{T}}\right)}_{II} r^2 dr$$

Assume U_{12} is very large for $r < 2r_0$ (hard balls) and neglect $e^{-\dots}$ in this region

$$\text{Then } I = 2\sqrt{\pi} \frac{(2r_0)^3}{3} = \frac{16\sqrt{\pi} r_0^3}{3}$$

$$\text{In } II \quad U_{12} \ll T; \quad 1 - e^{-x} \approx x$$

Also, $U_{12} < 0$

$$II = -\frac{2\sqrt{\pi}}{T} \int_{2r_0}^{\infty} |U_{12}| r^2 dr = -\frac{2a}{T}$$

$$\text{Then } B(T) = b - \frac{a}{T}$$

$$F = F_{\text{ideal}} + \frac{N^2(Tb - a)}{V}$$

H.O.

$$F = F_{\text{ideal}} + \frac{N^2 a}{V}$$

The free energy of an ideal gas the form $F_{\text{ideal}} = -NT \ln \frac{eV}{N} + Nf(T)$, where $f(T)$ is some function

$$(\text{In fact, } F = -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi} \right)^{\frac{3}{2}} \right])$$

Because volume V significantly exceeds

NB:

$$\begin{aligned} \ln(V - Nb) &= \ln V + \ln \left(1 - \frac{Nb}{V} \right) \approx \\ &\approx \ln V - \frac{Nb}{V} \end{aligned}$$

Using this, we'll rewrite F as

$$\begin{aligned} F &= Nf(T) - NT \ln \frac{e(V - Nb)}{N} - \frac{N^2 a}{V} = \\ &= F_{\text{ideal}} - NT \ln \left(1 - \frac{Nb}{V} \right) - \frac{N^2 a}{V} \end{aligned}$$

$$P = - \frac{\partial F}{\partial V} = \frac{NT}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = NT$$