

Non-Ideal Systems

In general, the only exact results in statistical mechanics can be obtained for a small handful of systems. Nearly all of these are non-interacting, "ideal" collections of particles.

The ideal gas, for example, is a collection of point particles that are not affected by one another in any way. The partition function, equation of state, and other thermodynamic averages can be calculated exactly because the hamiltonian of the system contains only kinetic energy terms. Ideal molecular gases can also be treated relatively simply because the additional rotational and vibrational degrees of freedom do not depend upon the locations of particles.

We can at least formulate the problem in a way that illustrates the difficulties. For N particles we can write the hamiltonian

$$\hat{H} = \sum_{i=1}^N \frac{1}{2m} \hat{p}_i^2 + \sum_{i < j} \hat{v}_{ij}$$

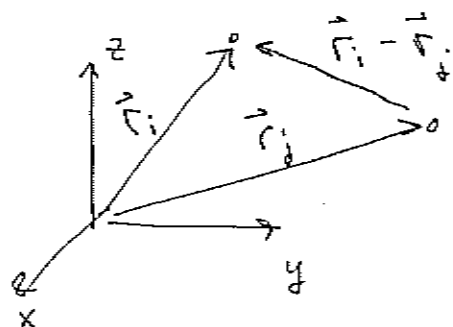
where

$$\hat{p}_i = -i\hbar \nabla_i$$

and

$$\hat{v}_{ij} = v(|\hat{r}_i - \hat{r}_j|)$$

is the potential energy operator that depends only on the relative positions of particles.



The wavefunction of the N particle system is a function of N position vectors:

$$\psi_{\alpha}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$$

and the $\{\psi_{\alpha}\}$ form a complete, orthonormal set of the wavefunctions. The canonical partition function is

$$Z_N = \text{Tr} e^{-\beta \hat{H}} = \int d^3\vec{r} \sum_{\alpha} \psi_{\alpha}^{\dagger}(\vec{r}_1, \dots, \vec{r}_N) e^{-\beta \hat{H}} \psi_{\alpha}(\vec{r}_1, \dots, \vec{r}_N)$$

The problem is that we have no way to solve exactly for the eigenenergies and states of the N -particle interacting hamiltonian. Instead, some approximation must be made.

Cluster expansion

One approach is to write the interaction term in terms of all possible particle combinations and construct a sort of perturbation expansion in terms of configurations. Schematically one obtains something of the form

$$Z_N = \int d^3r_1 d^3r_2 \dots d^3r_N \prod_{i < j} e^{-\beta \psi_{ij}}$$

which can be evaluated in terms of a sum. The sum has the form

$$Z_0 = \sum_{\{m_e\}} \prod_e \frac{1}{m_e!} \left(\frac{V}{\lambda^3} b_e \right)^{m_e}$$

where $\lambda = \left(\frac{2\pi m \hbar^2}{m k_B T} \right)^{1/2}$. The b_e are called "cluster" integrals and can be computed as one, two, ... etc, particle functions:

$$b_1 = \frac{1}{V} \int d^3 r_1 = 1$$

$$b_2 = \frac{1}{2 \lambda^3 V} \int d^3 r_1 d^3 r_2 (e^{-\beta v_{12}} - 1)$$

$$b_3 = \frac{1}{3! \lambda^6 V} \int d^3 r_1 d^3 r_2 d^3 r_3 (e^{-\beta v_{12}} - 1) (e^{-\beta v_{13}} - 1) \times (e^{-\beta v_{23}} - 1) + 2b_2^2$$

Each b_e represents a sum of interactions that can be interpreted graphically:

$$b_1 = \frac{1}{V} [\textcircled{1}]$$

$$b_2 = \frac{1}{2! \lambda^3 V} [\textcircled{1} - \textcircled{2}]$$

$$b_3 = \frac{1}{3! \lambda^6 V} [\begin{array}{c} \textcircled{1} \\ \diagdown \quad \diagup \\ \textcircled{2} - \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \diagup \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \diagdown \quad \diagup \\ \textcircled{2} - \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \diagup \quad \diagdown \\ \textcircled{2} - \textcircled{3} \end{array}]$$

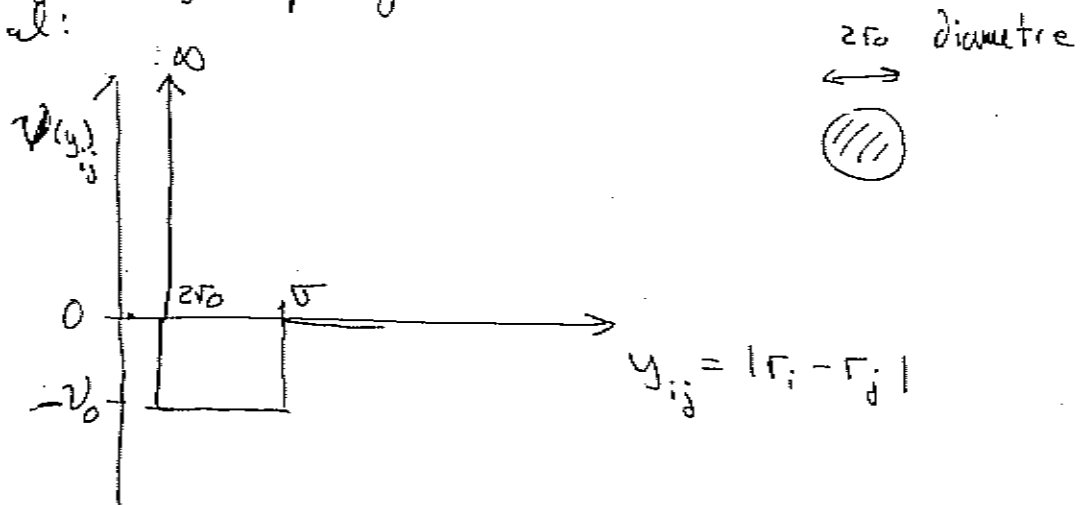
where each $\textcircled{i} - \textcircled{j}$ is a contribution to the integral,

This approach is called a "cluster expansion" (developed by Ursell and Mayer). The same idea can be formulated for the quantum statistics problem, with the same resulting expansion in terms of b_2 . The calculation of the b_2 for a quantum system is more difficult (much more difficult!).

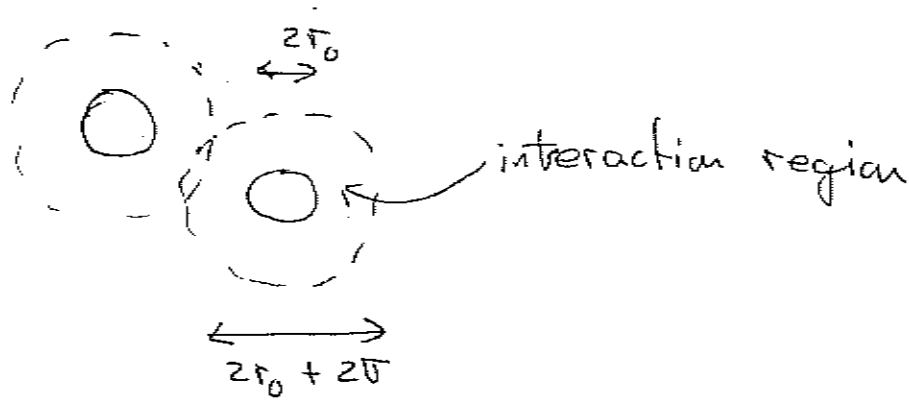
Van der Waals Gas

The van der Waals gas is a classical, weakly interacting non-ideal gas. It is a model which can be solved and is illustrative of how interactions affect thermodynamic quantities and equations of state. It also provides a good description of some real gases!

We begin by defining a crude model interaction potential:



This has a "hard-core repulsion" for $y = 2r_0$ where particles would collide, and an attractive well for particles within a distance σ .



We consider classical particles. The integration over momenta can be done easily for the canonical ensemble:

$$\begin{aligned}
 Z_N &= \frac{1}{h^{3N} N!} \int d^3 p_1 \dots d^3 p_N \int d^3 r_1 \dots d^3 r_N e^{-\beta \left(\frac{1}{2m} p_1^2 + \dots + \frac{1}{2m} p_N^2 \right)} \\
 &\quad \cdot e^{-\beta \sum_{i < j} v_{ij}} \\
 &= \frac{1}{h^{3N} N!} \left(\int d^3 p_1 e^{-\beta \frac{1}{2m} p_1^2} \right) \dots \left(\int d^3 p_N e^{-\beta \frac{1}{2m} p_N^2} \right) \\
 &\quad \cdot \int d^3 r_1 \dots d^3 r_N e^{-\beta \sum_{i < j} v_{ij}}
 \end{aligned}$$

Each momentum integral can be evaluated as

$$\begin{aligned}
 \int d^3 p e^{-\beta \frac{1}{2m} p^2} &= \left(\int dp_x e^{-\beta \frac{1}{2m} p_x^2} \right) \left(\int dp_y e^{-\beta \frac{1}{2m} p_y^2} \right) \left(\int dp_z e^{-\beta \frac{1}{2m} p_z^2} \right) \\
 &= \left\{ \sqrt{\frac{2\pi m}{\beta}} \right\}^3 = (2\pi m k_B T)^{3/2}
 \end{aligned}$$

Thus

$$Z_N = \frac{1}{h^{3N} N!} \int d^3 r_1 \dots d^3 r_N e^{-\beta \sum_{i < j} v_{ij}}$$

where $\lambda = \left(\frac{2\pi\hbar^2}{\mu k_B T} \right)^{1/2}$ as before. (Note: $\frac{1}{\lambda^3}$ is called the "quantum density" and corresponds to the inverse volume of one particle with wavelength λ).

Now if r_0 were zero, and σ were zero, the gas would be ideal and $v_{ij} \rightarrow 0$ so that

$$\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \rightarrow V^N$$

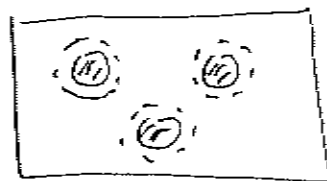
where V is the N particle gas volume.

Instead, the particles are assumed to occupy some volume $v_0 = \frac{4}{3}\pi r_0^3$ defined by the hard core. The simplest approximation is thus to exclude this volume, and replace V by $V - v_0$ for each integration:

$$\int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta \sum_{i,j} v_{ij}} \approx (V - v_0)^N$$

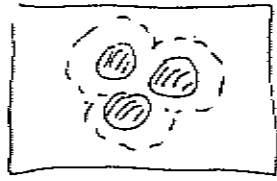
This approximation is too simple however because it neglects how the attractive part of the potential can affect the volume. Consider two extremes:

(A) Separated particles:



\Rightarrow excluded volume is v_0 per particle

(B) Clustered particles:



\Rightarrow excluded volume $< v_0$
per particle.

We therefore break v_{ij} into a "hard core" ^{repulsive} part and an attractive part w :

$$v_{ij} = v_{\text{rep}} + w_{ij}$$

The interaction is simplified ^{using the} average potential approximation. This is an example of a type of approach often used to deal with complicated many body problems.

The idea is to consider interactions affecting a single particle, and replace the real interactions with an effective potential based on some sort of average.

In our case, we examine

$$\sum_{i < j} v_{ij} = \sum_{i < j} v_{\text{rep}} + \sum_{i < j} w_{ij}$$

The repulsive term will give ^{on average} a $(v - v_0)$ correction for each particle, and ~~and~~ we look at the w_{ij} term for a correction to this, again in the form of an average.

Writing,

$$\sum_{i < j} w_{ij} = \sum_i \sum_{j > i} w_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} w_{ij}$$

we see that for any particle i , the actual interaction can be averaged as

$$\frac{1}{2} \sum_{j \neq i} w_{ij} \approx \frac{1}{2} \sum_{j \neq i} \bar{w} = \frac{1}{2} (N-1) \bar{w}$$

where

$$\bar{w} \equiv \langle w_{ij} \rangle$$

which is an average only over the attractive part of the interaction v_{ij} . The many particle potential is thus replaced with an averaged effective single particle potential:

$$\sum_{i < j} v_{ij} \approx \sum_i \left\{ \frac{1}{2} v_{\text{rep}} + \frac{1}{2} (N-1) \bar{w} \right\}$$

This means that the position integral of Z_N can now be evaluated as

$$\begin{aligned} Z_N &= \frac{1}{\lambda^{3N} N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta \sum_{i < j} v_{ij}} \\ &\approx \frac{1}{\lambda^{3N} N!} \left(\int d\mathbf{r}_1 e^{-\beta \frac{1}{2} (v_{\text{rep}} + (N-1) \bar{w})} \right) \dots \\ &\quad \cdot \left(\int d\mathbf{r}_N e^{-\beta \frac{1}{2} (v_{\text{rep}} + (N-1) \bar{w})} \right) \end{aligned}$$

$$= \frac{1}{\lambda^{3N} N!} \left(\int d^3r e^{-\beta \frac{1}{2} (v_{\text{rep}} + (N-1)\bar{w})} \right)^N$$

$$= \frac{1}{\lambda^{3N} N!} \left((v - v_0) e^{-\beta \frac{1}{2} (N-1)\bar{w}} \right)^N$$

$$= \frac{1}{\lambda^{3N} N!} (v - v_0)^N e^{-\frac{1}{2} \beta N(N-1)\bar{w}}$$

$$\stackrel{N \gg 1}{\approx} \frac{1}{\lambda^{3N} N!} (v - v_0)^N e^{-\frac{1}{2} \beta N^2 \bar{w}}$$

where the last step follows for the limit of many particles ($N \gg 1$).

Finally, we follow convention and write

$$\bar{w} \equiv -\frac{2a}{v}$$

$$\text{and } v_0 \equiv Nb$$

where a and b are interaction and excluded volume parameters. Then for the van der Waals' gas,

$$Z_N \approx \frac{1}{\lambda^{3N} N!} (v - Nb)^N \exp\left[\frac{N^2 a}{v k_B T}\right].$$

The free energy can now be obtained directly from $\ln Z_N$. From this we can determine the equation of state relating pressure and temperature.

The free energy is

$$F = -k_B T \ln Z_N \\ = -k_B T \left\{ -\ln(\lambda^{3N} N!) + N \ln(V - bN) + \frac{N^2 a}{V k_B T} \right\}$$

For large N , we can use Stirling's approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N}$$

so that the leading large N term is

$$\ln(\lambda^{3N} N!) \approx N \ln N + N \ln \lambda^3 - N + \frac{1}{2} \ln(2\pi N) \\ \approx N \ln(\lambda^3 N)$$

Thus

$$F \approx -k_B T \left\{ + N \ln\left(\frac{V - bN}{\lambda^3 N}\right) + \frac{N^2 a}{V k_B T} \right\}$$

The pressure is

$$P = \left(-\frac{\partial F}{\partial V}\right)_{T, N} = +k_B T N \left(\frac{V - bN}{\lambda^3 N}\right)^{-1} \frac{1}{\lambda^3 N} + \left(-\frac{N^2 a}{V^2}\right) \\ = +k_B T \frac{N}{V - bN} - \frac{N^2 a}{V^2}$$

Rewriting slightly, we can see

$$\left(P + \frac{N^2}{V^2} a^2\right) (V - bN) = N k_B T$$

which has a modified ideal gas law form. The modifications have simple physical interpretations.

1. Reduced volume due to hard core repulsion;

2. Contribution to pressure from internal attraction: this reduces the external pressure on container walls.

We can also see the effects of interaction on the internal energy. Calculating from standard thermodynamics,

$$U = - \frac{\partial}{\partial \beta} \ln Z_N$$

$$= - \frac{\partial}{\partial \beta} \left\{ N \ln(V - bN) - N \ln(\lambda^3 N) + \frac{N^2 a}{V} \beta \right\}$$

$$= \frac{N}{N \lambda^3} \frac{\partial}{\partial \beta} (N \lambda^3) - \frac{N^2 a}{V}$$

$$= \frac{N}{\lambda^3} 3 \lambda^2 \left(\frac{\partial}{\partial \beta} \sqrt{\frac{2\pi k_B}{m} \beta} \right) - \frac{N^2 a}{V}$$

$$= 3 \frac{N}{\lambda} \frac{1}{2} \lambda^{-1} \frac{2\pi h^2}{m} - \frac{N^2 a}{V}$$

$$= \frac{3N}{2\beta} - \frac{N^2 a}{V}$$

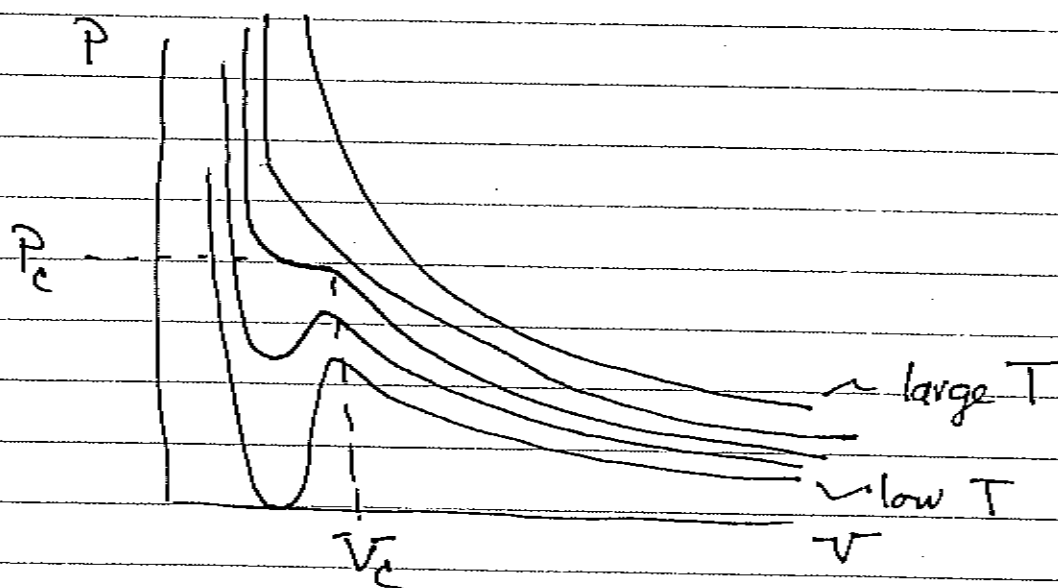
$$= \frac{3}{2} N k_B T - \frac{N^2 a}{V}$$

The average internal energy per particle is therefore

$$\frac{E}{N} = \frac{3}{2} k_B T - \frac{N}{V} a$$

The internal energy is reduced by the attractive interaction.

The difference with the ideal gas is most clear if we examine isotherms of P-V plots:



The gas is "ideal" at high temperatures, but the pressure drops significantly

at lower temperatures. The point (P_c, T_c) defines a critical temperature.

The interaction term aN^2/v is responsible for the deviations from ideal gas behaviour. We will see that the attraction can lead to a change in phase from gas to liquid at a low enough temperature. We return to this point later.

~~We~~