Interacting Gases

and Fluids

Next in our survey of interacting systems, we consider a single-component classical monatomic gas. Here

\[ H = \frac{1}{K} \sum_{i} \frac{p_i^2}{2m} + U(\vec{x}_1, \ldots, \vec{x}_N) \]

Partition function is

\[ Q_N(V, T) = \frac{1}{N! \hbar^{3N}} \int d^{3N} x \int d^3 p \exp \left( -\frac{K + U}{k_B T} \right) \]

Now since gas is classical, we can write

\[ \exp \left( -\frac{K + U}{k_B T} \right) = \exp \left( -\frac{K}{k_B T} \right) \exp \left( -\frac{U}{k_B T} \right) \]

The so integral separates into a config part and a momentum part. Momentum part can be solved exactly:

\[ \frac{1}{N! \hbar^{3N}} \int \left( \frac{-K}{k_B T} \right)^{3/2} d^{3N} p = \frac{1}{N! \hbar^{3N}} \int d^3 p_i \exp \left( -\frac{p_i^2}{2mk_B T} \right) \cdot \frac{1}{\hbar^{3N}} \]

\[ = \frac{1}{N! \hbar^{3N}} \left[ \int d^3 p \exp \left( -\frac{p^2}{2mk_B T} \right) \right]^N \]

since each integral is the same

\[ \lambda = \frac{\hbar}{(2\pi mk_B T)^{1/2}} \]

(We calculated this before in discussing ideal gases)
So \( Q_N (V, T) = \frac{1}{N! \chi^{3N}} Z_N (V, T) \)
\[
Z_N (V, T) = \int \exp \left( -\frac{U}{k_B T} \right) dx_1 \ldots dx_N
\]

If \( U = 0 \) then \( Z_N = V^N \) and we can rewrite as
\[
\frac{Z_N}{V} = V^{N-1}
\]

\( Z_N \) usually called configurational integral.

Common case:
\[
U(x_1, \ldots, x_N) = \sum_{i > j} u(r_{ij})
\]

where \( r_{ij} = |x_i - x_j| \) and \( u(r) = \) "pair potential"

E.g. \( u(r) = 4 \pi \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \)

"Lennard-Jones potential"

(named after Lennard-Jones, not Lennard and Jones).

Another example: \( u(r) = \frac{(Ze)^2}{r} \)

Coulomb potential (with compensating negative background) — sometimes called the one-component plasma.
How to treat the non-ideal case? ($u \neq 0$)

- **Various methods:**

  (a). Analytical
  - Cluster expansions
  - Integral equation methods

  (b). Numerical
  - Monte Carlo simulation
  - Molecular dynamics

(c). Which

I will not touch on a couple.

**Cluster expansion (and second virial coefficient)**

Doesn't work very well for dense liquids, such as water.

Basically, we need to calculate

\[
\int d^3x_1 \ldots d^3x_N \exp \left( - \frac{U}{k_B T} \right)
\]

\[
= \int d^3x_1 \ldots d^3x_N \prod_{i > j} \exp \left( - \frac{u_{ij}}{k_B T} \right)
\]

Now we note that $e^{-u_{ij}/k_B T} \rightarrow 1$ at large separations

(since $u_{ij} \rightarrow 0$).

So write $e^{-\beta u_{ij}} = 1 + f_{ij}$ where $f_{ij} = e^{-1}$

Note that $f_{ij} \rightarrow 0$ for large $r_{ij}$
\[ E_N = \sum_{i<j} \int d^3 \mathbf{x}_1 \ldots d^3 \mathbf{x}_N \]

\[ = \frac{N(N-1)N^2}{2} \int f_{ij} \mathbf{\dot{d}x}_1 \mathbf{\dot{d}x}_2 \]

\[ = \frac{N(N-1)N^2}{2} \sqrt{\int f_{ii}(x) d^3 x} \]

\[ \text{So} \quad Z_N = V^N \left[ 1 + \frac{1}{2} \frac{N^2}{2} \int f(x) d^3 x + \frac{1}{2} \left( \frac{N^2}{2} \int f(x) d^3 x \right)^2 + \ldots \right] \]

\[ \bar{w}_{N,T} = V^N \exp \left[ \frac{1}{2} \frac{N^2}{2} \int f(x) d^3 x \right] \]

\[ \ln Z_N = N \ln V + \frac{1}{2} N n \int f(x) d^3 x \]

\[ F = -k_B T \ln Q_N = -k_B T \ln Z_N \]

\[ = k_B T N \ln \frac{V}{N} + 3 N \ln \lambda + N \ln \frac{k_B T \lambda}{k_B} - N \ln V - \frac{1}{2} N \int f(x) d^3 x \]

and finally

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

\[ = \frac{N k_B T}{V} + \frac{1}{2} N k_B T n \int f(x) d^3 x \]

or, collecting terms
Thus we have:

\[
Z_N = \int \cdots \int \prod_{i \neq j} \left( 1 + f_{ij} \right)
\]

\(f_{ij}\) nonzero only if \(i\) close to \(j\)

or

\[
Z_N = \int \cdots \int \left( 1 + \prod_{i \neq j} f_{ij} + \prod_{i \neq j} \prod_{k \neq l} f_{ij} f_{kl} + \cdots \right)
\]

Method: (i). Write out \(Z = \sum_{N=1}^{\infty} Z_N Q_N\) in a similar form

(ii) \(\frac{PV}{k_B T} = -k_B T \ln Z\)

(iii) Collect terms. Find\(\frac{PV}{k_B T}\) is a power series in \(n = \frac{V}{N}\)

Specifically, with \(n = \frac{V}{N}\),

\[
\frac{PV}{k_B T} = \sum_{l=1}^{\infty} a_2 (l) \left( \frac{\lambda^3}{n} \right)^l
\]

\(a_2 (l) = l^{th}\) virial coefficient

\(a_1 = 1\) \(
\Rightarrow\) ideal gas

\[
a_2 = -\frac{2\pi}{\lambda^3} \int_{0}^{\infty} \left[ \frac{e^{-u(r)/k_B T} - 1}{r^2} \right] r^2 dr
\]

\[
= -\frac{1}{2\lambda^3} \int s(r) r^2 dr
\]
Higher terms don't have simple expression

Not too useful, but we can get some info from this:

E.g. hard sphere potential: \( u = \int_0^\infty r < \sigma \)

Then \( e^{-u/k_B T} \)

\[ e^{-1} = -1 \quad r < \sigma \]

So \( r > \sigma \)

\[ \frac{2n}{\lambda^3} \int_0^\sigma r^2 \, dr = \frac{2n \sigma^3}{3 \lambda^3} > 0 \]

So \( P > P_{\text{ideal}} \)

For \( u = \varphi^{12}/r - \varphi^{6}/r \)

\( P < P_{\text{ideal}} \) (result of attractive potential)

Exact results: Van der Waals eq

\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]

Except for the \( b \), this is a usual eq. of state with an attractive second virial coefficient.
Important concepts in fluids:

Pair correlation function:

\[ g(r) = \text{relative probability density of finding an atom at } r, \text{ given that there is an atom at the origin} \]

Ideal gas: \( g(r) = 1 \); doesn't matter since atoms don't interact.

Real fluid (say liquid argon):

\[ g(r) \]

How do we know this?

Can measure the Fourier transform, \( S(k) \), known as the structure factor:

\[ S(k) \propto \omega \int d^3r \left[ g(r) - 1 \right] e^{ik \cdot r} \]

Const. is chosen so that \( S(k) \to 1 \) as \( k \to \infty \)

Typically, \( \frac{S(1)}{S(k)} \)

\[ k \]
Can measure by either X-ray or neutron diffraction:

Other ways of calculating props of liquids:

Molecular dynamics

Just solve $F_i = m \ddot{x}_i$ for each atom numerically.

Total kinetic energy $= \frac{3}{2} N k_B T$.

Gives results similar to Monte Carlo but also gives dynamics.