In this lecture, we will discuss fluids beyond the ideal gas limit. This means we need to account for interactions between molecules. Unlike the case of solid, we cannot remove the interactions between different degrees of freedom simply from a coordinate transformation. Instead, techniques have been developed to account for the interactions as a perturbation to the non-interacting system.

Reading assignment: Reif §10.3-10.5.

1 Ideal gas model review

In the limit of temperature going to infinity and density goes to zero, all gases can be well described by the ideal gas model with the well-known equation of state,

\[ pV = Nk_B T \] (1)
For simplicity, we are considering mono-atomic gas molecules and \( N \) is the total number of gas molecules. Eq. (1) is not the most fundamental form of the equation of state, in the sense that from it we cannot derive all thermodynamic properties of the ideal gas.

One of the fundamental form of the equation of state is,

\[
A(T,V,N) = -Nk_B T \left[ \ln \left( \frac{V}{N\Lambda^3} \right) + 1 \right] = Nk_B T \left[ \ln (\rho\Lambda^3) - 1 \right]
\]

(2)

where \( \Lambda \equiv h/\sqrt{2\pi mk_BT} \) is the de Broglie wavelength at temperature \( T \) and \( \rho \equiv N/V \) is the density. From Eq. (2) we can derive Eq. (1) easily by following the definition of pressure,

\[
p \equiv - \left( \frac{\partial A}{\partial V} \right)_{N,T} = -\frac{Nk_B T}{V}
\]

(3)

However, it is impossible to derive Eq. (2) from Eq. (1) alone.

We can give it a try by writing,

\[
A(T,V_1,N) - A(T,V_0,N) = \int_{V_0}^{V_1} \frac{\partial A}{\partial V} dV = - \int_{V_0}^{V_1} p \, dV
\]

(4)

Using Eq. (1) we have

\[
A(T,V_1,N) - A(T,V_0,N) = -Nk_B T \int_{V_0}^{V_1} \frac{1}{V} dV = -Nk_B T \ln \frac{V_1}{V_0}
\]

(5)

In other words,

\[
A(T,V,N) = -Nk_B T \ln \frac{V}{h(N,T)}
\]

(6)

where \( h \) is some arbitrary function of \( N \) and \( T \). Hence the result is consistent with Eq. (2), but more information (such as heat capacity) is needed to uniquely determine the function \( h(N,T) \).
2 Van der Waals model

With decreasing temperature and increasing density, all gases exhibit deviation from the ideal gas model. The Van der Waals model is an interesting phenomenological model that tries to capture the main physical effects responsible for the deviation from the ideal gas model. It tries to capture two main features of the interactions between two gas molecules. First, two molecules repel each other strongly when they get too close to each other. (This is mainly caused by the electrons on both molecules that are forbidden to take the same quantum state according to the Pauli’s exclusion principle.) Hence we can think of molecules as tiny solid spheres each having a non-zero exclusion volume. Second, two molecules attract each other when they are far apart. (This is caused by the fluctuating electric dipole moment of each molecule. The interaction is called Van der Waals interaction and interaction energy scales as $r^{-6}$ where $r$ is the distance between two molecules.)

The $p$-$V$ relation of the Van der Waals model of a non-ideal gas is,

$$\left( p + \frac{N^2 a}{V^2} \right) (V - Nb) = N k_B T \tag{7}$$

where $a > 0$ and $b > 0$ are two empirical constants. Equivalently, we have

$$p = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2} \tag{8}$$

$b$ can be thought of as the exclusion volume of each gas molecule, so that the available volume for the gas molecules to wiggle around is reduced to $V - Nb$. $a$ is supposed to capture the mutual attraction between the molecules, which should reduce the pressure exerted on the wall of the gas tank. Because the attraction is between every pair of molecules, the reduction of the pressure should be proportional to the square of density (in the limit of low density), hence the term $-N^2a/V^2$.

A fundamental form of the equation of state of the Van der Waals model is

$$A(T, V, N) = -N k_B T \left[ \ln \left( \frac{V - Nb}{N A^3} \right) + 1 \right] - \frac{N^2 a}{V} \tag{9}$$

Again, we can derive Eq. (8) from Eq. (9) but not vice versa.

3 Virial expansion

The Van der Waals model captures several important physical aspects of a real fluid (such as the transition between the liquid and vapor phases below a critical temperature, to be discussed later). However, the behavior of a real fluid is not necessarily described very
accurately by the (two-parameter) Van der Waals model. The Virial expansion is a more systematic approach to describe the deviation of a real gas from an ideal gas. Define particle density \( \rho \equiv N/V \), then the ideal gas satisfies the relation

\[
\frac{p}{k_B T} = \rho
\]  

(10)

One way to generalize this (ideal gas) law is to add higher order terms of \( \rho \) to the right hand side. The resulting expression is called the **Virial expansion**.

\[
\frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots
\]

(11)

where \( B_2(T), B_3(T), \cdots \) are called **Virial coefficients**. In the limit of \( \rho \to 0 \), the leading term (\( \rho \)) dominates the right hand side, and the ideal gas is recovered, as it should.

The Van der Waals equation of state, Eq. (8) can be rewritten in the form of Virial expansion.

\[
\begin{align*}
p &= \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \\
\frac{p}{k_B T} &= \frac{N}{V - Nb} - \frac{N^2 a}{V^2 k_B T} \\
&= \frac{\rho}{1 - b\rho} - \frac{a}{k_B T \rho^2} \\
&= \rho (1 + b\rho + b^2 \rho^2 + b^3 \rho^3 + \cdots) - \frac{a}{k_B T \rho^2} \\
&= \rho + \left( b - \frac{a}{k_B T} \right) \rho^2 + b^2 \rho^3 + b^3 \rho^4 + \cdots
\end{align*}
\]

(12)

Hence

\[
\begin{align*}
B_2(T) &= b - \frac{a}{k_B T} \\
B_3(T) &= b^2 \\
B_4(T) &= b^3 \\
&\vdots
\end{align*}
\]

(13) \hspace{1cm} (14) \hspace{1cm} (15)

Of course, the Virial coefficients of a real gas does not need to have the same form as above, which only holds for the Van der Waals model.

Q: Can we find the Helmholtz free energy \( A(N, V, T) \) (i.e. the fundamental equation of state) of a non-ideal gas given its Virial expansion coefficients?

A: The answer is yes. This may sound strange because in the previous two sections we said that from the \( p-V \) relation alone it is impossible to completely determine the \( A(N, V, T) \)
function. However, now that the $A(N,V,T)$ function for an ideal gas is already known, we can use it to our advantage to determine the $A(N,V,T)$ function for a non-ideal gas.

All we need to do is to determine the Helmholtz free energy difference between the non-ideal (real) gas and the ideal gas, i.e.,

$$\Delta A(N,V,T) \equiv A\text{real.gas}(N,V,T) - A\text{ideal.gas}(N,V,T)$$

(16)

$$\Delta A(T,V_1,N) - \Delta A(T,V_0,N) = -\int_{V_0}^{V_1} (p_{\text{real.gas}} - p_{\text{ideal.gas}}) dV$$

$$= -\int_{V_0}^{V_1} k_B T \left( \frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV$$

$$= \int_{V_1}^{V_0} k_B T \left( \frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV$$

(17)

Notice that at constant $N$ and $T$, a real gas goes to the ideal gas limit as $V \to \infty$. Hence

$$\lim_{V \to \infty} \Delta A(T,V,N) = 0$$

(18)

$$\Delta A(T,V_1,N) = \int_{V_1}^{V_0} k_B T \left( \frac{B_2 N^2}{V^2} + \frac{B_3 N^3}{V^3} + \cdots \right) dV$$

(19)

$$\Delta A(T,V,N) = N k_B T \left( \frac{B_2 N}{V} + \frac{B_3 N^2}{2V^2} + \frac{B_4 N^3}{3V^3} + \cdots \right)$$

(20)

$$= N k_B T \left( B_2 \rho + \frac{1}{2} B_3 \rho^2 + \frac{1}{3} B_4 \rho^3 + \cdots \right)$$

(21)

Hence the Helmholtz free energy of a real gas described by the Virial coefficients $B_2(T), B_3(T), \cdots$ is,

$$A(T,V,N) = N k_B T \left[ \ln (\rho A^3) - 1 + B_2(T) \rho + \frac{1}{2} B_3(T) \rho^2 + \frac{1}{3} B_4(T) \rho^3 + \cdots \right]$$

(22)

Adding this to the ideal gas Helmholtz free energy, we obtain the Helmholtz free energy of a real gas in terms of Virial expansion coefficients.

Q: What is the energy $E$ of the gas? [Hint: $S \equiv -(\frac{\partial A}{\partial T})_{V,N}$, $E = A + TS$.]

Q: What is the chemical potential of the gas?


4 Virial coefficients from molecular interactions

So far all of our discussions are still phenomenological. For example, we can consider the Virial coefficients \( B_2(T), B_3(T), \cdots \) as empirical functions to characterize the experimental \( p-V \) curves of a non-ideal gas. However, to gain a fundamental understanding of the behavior of a non-ideal gas, we would like to be able to derive the Virial coefficients from the interaction potentials between the gas molecules.

We can often assume that the potential energy of a (non-ideal) gas can be written as a sum over all pair-wise interactions between the gas molecules

\[
U_{\text{int}}(\{r_i\}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}),
\]

(23)

where \( r_{ij} = |r_i - r_j| \) is the distance between molecules \( i \) and \( j \). The function \( \phi(r) \) describes the interaction energy between two molecules as a function of their separation distance \( r \). Typically, \( \phi \rightarrow +\infty \) as \( r \rightarrow 0 \), \( \phi \rightarrow 0 \) as \( r \rightarrow \infty \), and \( \phi \) exhibits a minimum between these two limits, as shown below.

\[
\phi(r) - \text{pair potential}
\]

\[
f(r) = e^{-\beta \phi(r)} \left[ e^{\beta \phi(r)} - 1 \right]
\]

In this section, we will show that the Virial coefficients can indeed be expressed in terms of function \( \phi(r) \). Specifically, the second Virial coefficient is

\[
B_2(T) = -2\pi \int_0^\infty \left[ e^{-\beta \phi(r)} - 1 \right] r^2 \, dr
\]

(24)

Higher order Virial coefficient can also be derived (Barker 1964).

This means that the \( p-V \) curve measurements can tell us something about the inter-molecular interaction and vice versa.
First, we can write down the explicit expression of the Hamiltonian for a tank of gas with inter-molecular potential function \( \phi(r) \),

\[
H(\{q_i\}, \{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{r_i\})
\]

\[
= \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(|r_i - r_j|) + \sum_{i=1}^{N} U^\text{ext}(r_i)
\]

(25)

where \( U^\text{ext}(r_i) \) is introduced to describe the confining effect of the gas container.

In order to derive the second Virial coefficient \( B_2 \) (or for anything else really), we start with the partition function in the canonical ensemble.

\[
Z = \frac{1}{N!h^{3N}} \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta \left( \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{r_i\}) \right)}
\]

The integrals over the momenta can be performed analytically (just in the case of the ideal gas), so that,

\[
Z = \frac{1}{N!\Lambda^{3N}} \int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta U(\{r_i\})}
\]

(26)

Define

\[
Z_u \equiv \int d^3r_1 d^3r_2 \cdots d^3r_N e^{-\beta U(\{r_i\})}
\]

then

\[
Z = \frac{Z_u}{N!\Lambda^{3N}}
\]

(27)

Recall that for an ideal gas, \( Z_u = V^N \), hence \( Z = \frac{V^N}{N!\Lambda^{3N}} \), leading to Eq. (2).

To get rid of the inconvenient potential from the container \( U^\text{ext}(r) \), we can assume the gas molecules are subjected to the periodic boundary conditions (PBC) in a cube of length \( L \)

\[
V = L^3
\]

(28)
When there is no interaction between atoms, this directly give us $Z_u = V^N$. When there is pair interaction between gas molecules

$$U\{r_i\} = \sum_{i<j} \phi(r_{ij}) , \quad r_{ij} = |r_i - r_j|$$

(29)

Therefore

$$Z_u = \int d^3r_1 d^3r_2 \cdots d^3r_N \exp(-\beta U)$$

(30)

$$\exp(-\beta U) = \prod_{i<j} \exp(-\beta \phi(r_{ij}))$$

(31)

$$= \prod_{i<j} (1 + f(r_{ij}))$$

(32)

where we have defined $f(r_{ij}) \equiv e^{-\beta \phi(r_{ij})} - 1$.

Next we expand the product and write down all the terms...

$$\prod_{i<k<l\leq N} (1 + f(r_{ij})) = 1 + \sum_{i<j} f(r_{ij}) + \sum_{i<j} \sum_{k<l} f(r_{ij}) f(r_{kl}) + \cdots$$

$$\frac{Z_u}{V^N} = \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \cdot 1$$

$$+ \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \cdot \sum_{i<j} f(r_{ij})$$

$$\quad + \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \cdot \sum_{i<j} \sum_{k<l} f(r_{ij}) f(r_{kl})$$

$$\quad + \cdots$$

($\# \text{ of pairs } (i,j) = \frac{N(N-1)}{2}$)
\[ \frac{Z}{V N} = 1 + \frac{N(N-1)}{2V^2} \int d^3l_1 d^3l_2 \, f(l_1) + \cdots \]
\[ = 1 + \frac{N(N-1)}{2V} \int d^3x \, f(y) + \cdots \quad r=|x| \]
\[ = 1 + \frac{N(N-1)}{2V} \int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots \]
\[ \bar{Z} = \frac{Z}{N! A^3} = \frac{V N}{N! A^3} \left( 1 + \frac{N(N-1)}{2V} \int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots \right) \]
\[ = \bar{Z}^{\text{idem, gas}} \cdot \left( 1 + \frac{N(N-1)}{2V} \int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots \right) \]
\[ A = -k_B T \ln \bar{Z} \]
\[ \Delta A = A - A^{\text{idem, gas}} = -k_B T \ln \left( 1 + \frac{N(N-1)}{2V} \int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots \right) \]
\[ = -\frac{N k_B T (N-1)}{2V} \int_0^\infty dr \cdot 4\pi r^2 f(r) + \cdots \]
\[ \approx -N k_B T \rho \int_0^\infty 2\pi r^2 f(r) + \cdots \quad (N-1 \approx N \quad \text{as} \ N \to \infty) \]

Compare this with earlier expression

\[ \Delta A(T, V, N) = N k_B T \left( B_2(T) \rho + \frac{1}{2} B_3(T) \rho^2 + \cdots \right) \quad (33) \]

We have

\[ B_2(T) = -2\pi \int_0^\infty f(r) r^2 dr \]
\[ = -2\pi \int_0^\infty \left[ e^{-\beta \phi(r)} - 1 \right] r^2 dr \quad (34) \]

Higher order Virial coefficient can be obtained similarly — the approach is called cluster expansion. The math will become horrendous by the time you get to the 5th Virial coefficient but it can be done [2].
5 Liquid-gas phase transition

The Van der Waals model is important because it is a simple model that captures the transition between the liquid and gas phases (vaporization and condensation). This can be seen by plotting the Helmholtz free energy and pressure of the Van der Waals model as a function of $V$ at constant $T$. (Download plotvanderwaals.m from coursework.)

$$A(T, V, N) = -Nk_B T \left[ \ln \left( \frac{V - Nb}{N} \left( \frac{2 \pi m k_B T}{h^2} \right)^{3/2} \right) + 1 \right] - \frac{N^2 a}{V}$$

$$p = -\left( \frac{\partial A}{\partial V} \right)_{T,N} = \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2}$$

The model exhibits two different behaviors when $T$ is above or below a critical temperature $T_c$, where $k_B T_c = \frac{8a}{27b}$. When $T > T_c$, the Van der Waals model behaves like one homogeneous fluid. When $T < T_c$, the model exhibits a distinction between two phases: a gas phase at large $V$ and a liquid phase at small $V$, and a phase transition between the two.
Observations: There exist a critical temperature $T_c$.

- When $T > T_c$, the $A(V)$ curve is convex ($\frac{\partial^2 A}{\partial V^2} > 0$) everywhere. Correspondingly, the $p(V)$ curve has negative slope everywhere.

- When $T < T_c$, the $A(V)$ curve has concave regions ($\frac{\partial^2 A}{\partial V^2} < 0$). Correspondingly, the $p(V)$ curve has positive slope there.

A **convex** free energy is required for the **stability** of a homogeneous phase.

Consider a tank of gas with volume $V_0$ that has reached thermal equilibrium.

Now let us introduce a piston that separate the gas tank into two halves.

The gases on both sides of the piston can be described by the same $p(V)$ curve.

Initially, both of them have the same volume $V_1 = V_2 = V_0/2$.

Hence they have the same pressure $p_1 = p_2$.

Now imagine a small perturbation on the position of the piston, such that

$$V_1 = \frac{V_0}{2} + \delta V, \quad V_2 = \frac{V_0}{2} - \delta V, \quad \delta V > 0$$

If $\frac{\partial^2 A}{\partial V^2} > 0$, $\frac{\partial p}{\partial V} < 0$, then $p_1 < p_2$. Therefore, there is a net force to the left, which pushes the piston back to its original position. In this case, we say that the system is **stable** against the perturbation.

What happens if $\frac{\partial^2 A}{\partial V^2} < 0$, $\frac{\partial p}{\partial V} > 0$?

Then we will have $p_1 > p_2$. There is a net force to the right, pushing the piston further away from its original positions.

In this case, the system is **unstable** against the perturbation.
Q: Is this really bad if the position of the piston is unstable?

Yes! The piston is only imaginary. If $\frac{\partial p}{\partial V} > 0$, then a spontaneous density fluctuation somewhere inside the gas tank will always get amplified. The denser region will get even denser, the more dilute region will get even more dilute. In other words, the original homogeneous phase is unstable against spontaneous separation into two phases — a denser liquid phase and a more dilute gas phase.

Even if locally $\frac{\partial^2 A}{\partial V^2} > 0$, the phase is not necessarily stable.

For example, consider point $m$, whose volume is $V_m$. According to the $A(V)$ curve, the free energy at $V_m$ is $A(V_m)$.

Now consider a common tangent line touching the $A(V)$ curve at $V_\alpha$ and $V_\beta$. Let $V_m = (1 - \lambda)V_\alpha + \lambda V_\beta$ ($\lambda > 0$).

Claim: A gas at volume $V_m$ (density $\rho_m = N/V_m$) is thermodynamically unstable against separation into two phases: one phase having density $\rho_\alpha = N/V_\alpha$, the other phase having density $\rho_\beta = N/V_\beta$.

From Eq. (35), the Helmholtz free energy per molecule of the Van der Waals model can be expressed as a function of density $\rho = N/V$,

$$\frac{A(T, V, N)}{N} = -k_B T \left[ \ln \left( \frac{1}{\rho A^3} - \frac{b}{A^3} \right) + 1 \right] - \rho a$$

Let us compute the free energy of a mixture of two phases (at density $\rho_\alpha$ and $\rho_\beta$) and compare it with the free energy of a homogeneous phase (at density $\rho_m$).

Let $\tilde{N}_\alpha, \tilde{N}_\beta$ be the number of molecules in phase $\alpha, \beta$.

Let $\tilde{V}_\alpha, \tilde{V}_\beta$ be the volume occupied by phase $\alpha, \beta$.
\[
\tilde{N}_\alpha + \tilde{N}_\beta = N \\
\tilde{V}_\alpha + \tilde{V}_\beta = V_m
\]

\[
\frac{\tilde{N}_\alpha}{\tilde{V}_\alpha} = \frac{N_\alpha}{V_\alpha} = \rho_\alpha
\]

\[
\frac{\tilde{N}_\beta}{\tilde{V}_\beta} = \frac{N_\beta}{V_\beta} = \rho_\beta
\]

Hence

\[
\tilde{N}_\alpha = (1 - \lambda) N \\
\tilde{V}_\alpha = (1 - \lambda) V_\alpha \\
\tilde{N}_\beta = \lambda N \\
\tilde{V}_\beta = \lambda V_\beta
\]

(36)

The Helmholtz free energy of the two phase mixture is

\[
A(T, \tilde{V}_\alpha, \tilde{N}_\alpha) + A(T, \tilde{V}_\beta, \tilde{N}_\beta) \\
= (1 - \lambda) A(T, V_\alpha, N) + \lambda A(T, V_\beta, N) \\
< A(T, V_m, N) \quad \text{(free energy of the homogeneous phase)}
\]

(37)

Hence the fluid (starting from a homogenous phase at density \(\rho_m\)) can lower its Helmholtz free energy by breaking into two phases (with densities \(\rho_\alpha\) and \(\rho_\beta\)). From second law of Thermodynamics, this shall happen spontaneously and is an irreversible process.

Hence for \(T < T_c\), the Van der Waals fluid consists of a single phase only if \(V \leq V_\alpha\) (liquid) or \(V \geq V_\beta\) (gas). It is a mixture of two phases if \(V_\alpha < V < V_\beta\).

For \(T > T_c\), the Van der Waals fluid consists of a single phase at all volume (or density).

References