Important Points from the Previous Lecture

The fundamental relation can be written as the Euler equation:

$$U = TS - PV + \mu_1 N_1 + \ldots + \mu_m N_m$$

We derived the Gibbs-Duhem relation:

$$\boxed{SdT - VdP + N_1 d\mu_1 + \ldots = 0} \qquad U \cdot d\left(\frac{1}{T}\right) + V \cdot d\left(\frac{P}{T}\right) - N \cdot d\left(\frac{\mu}{T}\right) = 0$$

From the Gibbs-Duhem relation and the equations of state for an ideal gas, we obtained the fundamental relation for an ideal gas:

$$s = cR\ln(u) + R\ln(v) + const$$

Important Points from the Previous Lecture

Two methods of reconstruction of the fundamental relation

1. Equations of state, e.g. T(U,V,N) → Gibbs-Duhem gives μ(U,V,N) → Substitution into the Euler equation → Fundamental relation

2. If there is no need to derive an explicit expression for the chemical potential **μ,** then the following expression for the molar entropy ***s*** can be integrated directly to obtain the fundamental relation in the entropy representation (its molar form)

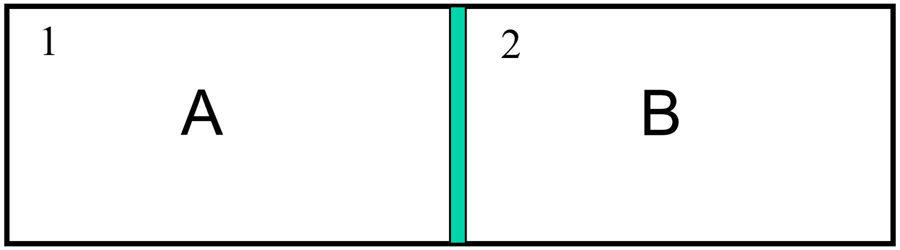
$$\boxed{ds = \frac{1}{T}du + \frac{P}{T}dv}$$

This expression is based on:

$$\frac{\partial s}{\partial u} = \frac{1}{T} \qquad \frac{\partial s}{\partial v} = \frac{P}{T}$$

Ideal Gas Mixtures – the Entropy of Mixing

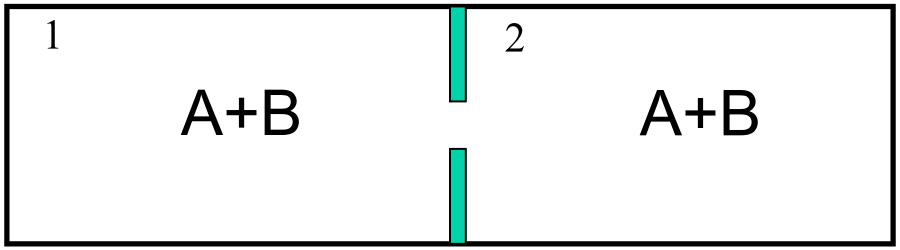
Consider an example: two types of ideal gas, A and B, are initially separated by an impermeable diathermal partition. We also assume that pressure in the left and right compartments are the same.



$T_1 = T_2 \qquad P_1 = P_2$

$V_0 = V_1 + V_2$

Then, a hole is created in the partition, and the gases intermix



Question: What is the change of entropy in the mixing process?

Ideal Gas Mixtures – the Entropy of Mixing

Before Mixing

$$S_A + S_B = cRN_A \ln\left(\frac{U_A}{N_A}\right) + RN_A \ln\left(\frac{V_1}{N_A}\right) + cRN_B \ln\left(\frac{U_0 - U_A}{N_B}\right) + RN_B \ln\left(\frac{V_2}{N_B}\right) + C$$

After Mixing

⇩ ⇩

$$S_{A+B} = cRN_A \ln\left(\frac{U_A}{N_A}\right) + RN_A \ln\left(\frac{V_0}{N_A}\right) + cRN_B \ln\left(\frac{U_0 - U_A}{N_B}\right) + RN_B \ln\left(\frac{V_0}{N_B}\right) + C$$

Change of entropy

$$S_M = S_{A+B} - S_A - S_B = RN_A \ln\left(\frac{V_0}{N_A}\right) + RN_B \ln\left(\frac{V_0}{N_B}\right) - RN_A \ln\left(\frac{V_1}{N_A}\right) - RN_B \ln\left(\frac{V_2}{N_B}\right)$$

Ideal Gas Mixtures – the Entropy of Mixing

$$S_M = RN_A \ln\left(\frac{V_0}{N_A}\right) + RN_B \ln\left(\frac{V_0}{N_B}\right) - RN_A \ln\left(\frac{V_1}{N_A}\right) - RN_B \ln\left(\frac{V_2}{N_B}\right)$$

⇩

$$S_M = -RN_A \ln\left(\frac{V_1}{V_0}\right) - RN_B \ln\left(\frac{V_2}{V_0}\right) > 0$$

Using an “equation of state” of the ideal gas: $PV = NRT$ *and* $P_A = P_B = P_{A+B}$

We obtain: $S_M = -RN_A \ln\left(\frac{N_A}{N}\right) - RN_B \ln\left(\frac{N_B}{N}\right)$ where $N = N_A + N_B$

S_M is called the entropy of mixing.
Entropy increases upon mixing.

Ideal Gas Mixtures – the Entropy of Mixing

For a multi-component ideal gas, the entropy of mixing is:

$$S_M = -R \sum N_j \ln\left(\frac{N_j}{N}\right) > 0$$

Recall the example of a chemical reaction in an ideal gas. The fundamental relation we considered in that example had a term proportional to the entropy of mixing.

$S = N^*\ln(U) - \Sigma N_i^*\ln(N_i/N)$

This term was important as it influenced the equilibrium mole numbers in the reaction. Since there was no energy cost associated with the reaction (note that all energy is kinetic in this example), this example shows that chemical reactions (and other processes) can be driven not only but internal energy costs but also by entropy!

Van Der Waals Fluid

Ideal Van der Waals fluid is described by the following equation of state:

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

where R is the universal gas constant $R = N_A k_B$

a and b are material-specific constants, v is molar volume

Van Der Waals Fluid - Motivation

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

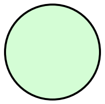
Assumptions:

- Each mole of fluid occupies effective volume of b/N_A

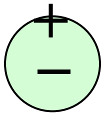
- There are weak attractive forces among the gas particles which lead to a decrease of pressure exerted by the particles on the walls of the gas container (the second term in the equation arises from these weak attractive force, called the Van der Waals force).

Van der Waals forces are electrostatic in nature and arise due to dipole-dipole interactions between particles

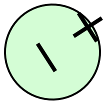
Van der Waals Fluid – Dipolar Forces



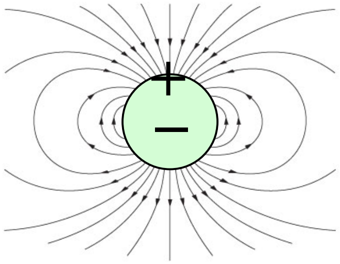
- neutral molecule with zero electric dipole moment



- due to charge fluctuations inside the molecule, electric dipole moment is induced

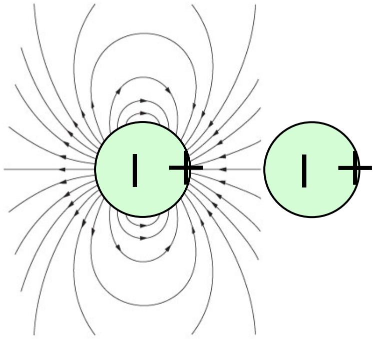


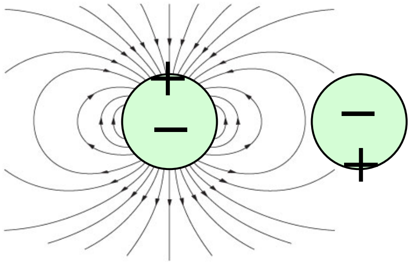
- both direction and magnitude of the dipole moment fluctuate in time



- The dipole generates electric field that polarizes (induces electric dipole moments) molecules around it

Van der Waals Fluid – Dipolar Forces are Attractive

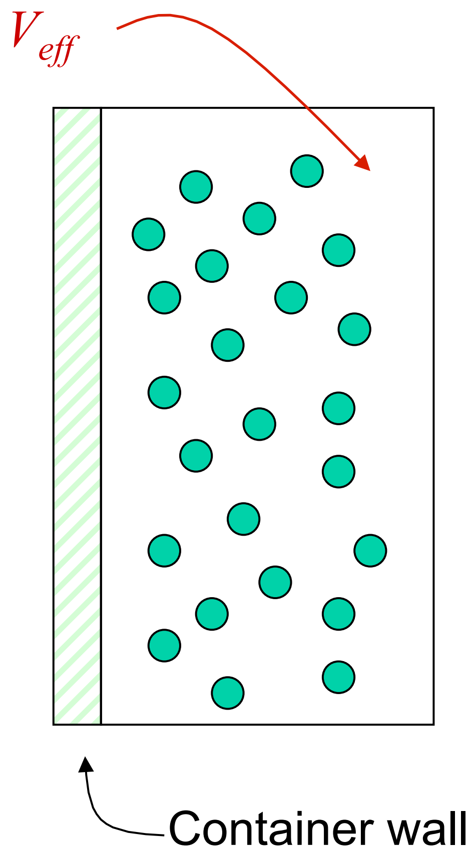




The pictures above show a couple of examples of polarization induced by molecule 1 in molecule 2 for two different positions of molecule 2 with respect to the direction of the dipole moment of molecule 1

Note in both cases the electrostatic energy of interaction of the four electric charges shown is negative. This means that the electrostatic forces acting between molecules are attractive.

Van der Waals Fluid – Pressure Reduction



In the absence of inter-molecular attractive forces (e. g. ideal gas case), the pressure acting on the wall is P_0.

For ideal gas, $P = n\,R\,T$, where $n = N/V=1/v$ is the particle density, $P_0 \sim n$.

Pressure is force per area, so $P_0 \sim n\,F$, where F is the average force exerted by a individual gas molecule on the wall.

Consider a molecule near the wall. The attractive force f_m acting on it from other gas molecules pulls it away from the wall. This attractive force is proportional to the number of molecules in some effective volume, V_{eff}, so $f_m = an$ (a=$const$).

Therefore, the force per molecule acting on the wall is now $F - f_m = F - a\,n$, and pressure is $P \sim n\,(F - f_m) = P_0 - a\,n^2$.

Van der Waals Fluid –Origin of Pressure Reduction

Now, since $P \sim n\,(F - f_m) = P_0 - a\,n^2 = P_0 - a\,(1/v)^2$.

This is almost the same as the VdW "equation of state": $P = \dfrac{RT}{v-b} - \dfrac{a}{v^2}$

The equation $P = P_0 - a\,(1/v)^2$ becomes the VdW equation of state if we start with the ideal gas expression for P_0:

$$P_0 = \frac{RT}{v}$$

and use the fact that molecules have finite volume: $v \rightarrow (v-b)$.

Van der Waals Fluid – Two Equations of State

We can solve this problem in the same way as the ideal gas problem.

One “equation of state” is:

$$\frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}$$

Another equation of state is of the form:

$$\frac{1}{T} = f(u,v)$$

The fundamental relation can be obtained by integration of:

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

Van der Waals Fluid –Equations of State are not Independent

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

To guess the right form of the second equation of state, let us use the theorem of differential analysis that the mixed second-order derivatives of a differentiable function should be equal:

$$\frac{\partial^2 s}{\partial v \partial u} = \frac{\partial^2 s}{\partial u \partial v} \qquad \Longrightarrow \qquad \frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v$$

Van der Waals Fluid –Equations of State are not Independent

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial u}\left(\frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}\right)_v = -\frac{a}{v^2}\frac{\partial}{\partial u}\left(\frac{1}{T}\right)_v$$

This can be rewritten as:

$$\frac{\partial}{\partial(1/v)}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial(u/a)}\left(\frac{1}{T}\right)_v$$

Van der Waals Fluid – the Second Equation of State

$$\frac{\partial}{\partial(1/v)}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial(u/a)}\left(\frac{1}{T}\right)_v$$

The simplest function satisfying the above condition is $(1/v+u/a)$

Any function $1/T=f(1/v+u/a)$ satisfies the above differential equation

By analogy with the equation of state of ideal gas: $1/T=cR/u$, we write:

$$\frac{1}{T} = \frac{cR}{u+a/v}$$

Van der Waals Fluid – the Equations of State

One equation of state is:

$$\frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}$$

Another equation of state is of the form:

$$\frac{1}{T} = \frac{cR}{u + a/v}$$

The fundamental relation can be obtained by integration of:

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

Van der Waals Fluid - the Fundamental Relation

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$

or:

$$ds = \frac{cR}{u + a/v}du + \left(\frac{R}{v-b} - \frac{a}{v^2}\frac{cR}{u+a/v}\right)dv$$

You can check that the expression for s below satisfies the equation for ds above:

$$\boxed{s = R\ln(v-b) + cR\ln(u + a/v) + const}$$

The actual integration are not trivial (but not too difficult) and we will discuss the general rules for such integration in the next lecture.

Van Der Waals Fluid – Physical Interpretation of Entropy

$$s = R\ln(v-b) + cR\ln(u + a/v) + const$$

Decrease of entropy because fewer position states are available (in VdW fluid particles cannot occupy the same space)

Increase of entropy because more velocity states are available for the same internal energy due to attractive interactions among particles. Why?

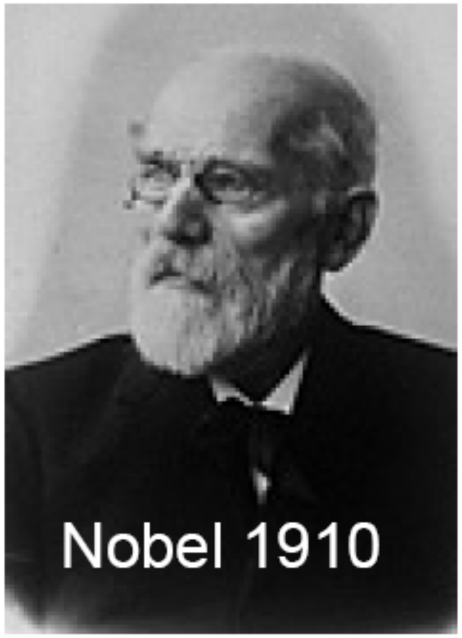
In ideal gas, each particle can have velocity from zero to $\sqrt{\dfrac{2U}{m}}$

U = Pure kinetic energy

In VdW fluid, each particle can have velocity from zero to ~ $\sqrt{\dfrac{2\left(U + N\dfrac{a}{b}\right)}{m}}$

Therefore, the number of velocity states is larger in VdW fluid than in ideal gas

Van der Waals



VdW model was developed in the 1870th

It had great success in qualitative description of real gases, including liquid-gas phase transitions

In his Nobel lecture in 1910 he emphasized that his theory must be successful because of the atomistic nature of matter.

Even in 1910 atoms were not yet widely recognized as being real!