

THE THERMODYNAMICS OF THE REAL FLUIDS: Maxwell Relations and its relevance SELF STUDY MODULE

Objective

The objective of this module is to derive the Maxwell relations as a basis for estimating properties of the real fluids. The equation of state and internal energy components of the real fluids are also consolidated here for completeness.

Reading assignment

Read Chapter 6 Sandler's Thermodynamics, 4th edition.

Remember

This section is borrowed from the self study module on the thermodynamic landscape, U, H, A, G. We will derive the energy introduced into a fluid confined in a piston and cylinder assembly by an impeller performing reversible shaft work, subject to different constraints. We will start from the most general form of the Energy balance and the entropy balance to find the answers under different constraints.

$$\frac{dU}{dt} = \sum_{\text{all streams}} \dot{m}_i \hat{H}_i + \dot{Q} + \dot{W}_s - P \frac{dV}{dt}$$

$$\frac{dS}{dt} = \sum_{\text{all streams}} \dot{m}_i \hat{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{\text{generated}}$$

Case 1: The system is closed, the process is adiabatic and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s$$

The entropy balance indicates that

$$\frac{dS}{dt} = 0$$

This result indicates that for a reversible and adiabatic process, entropy is constant.

Case 2: The system is closed, the process is adiabatic and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{W}_s - P \frac{dV}{dt}$$

At constant pressure, it is possible to rearrange the expression as

$$\frac{dH}{dt} = \dot{W}_s$$

Similar to case 1,

$$\frac{dS}{dt} = 0$$

Case 3: The system is closed, the process is isothermal and the system is at constant volume

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s$$

While the entropy balance yields

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} \text{ or } \dot{Q} = T \frac{dS}{dt} \text{ when this expression for } \dot{Q} \text{ is substituted in the energy balance,}$$

keeping in mind that the temperature is constant, the rearrangement gives

$$\frac{dA}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, $A=U-TS$

It is important to note here that we derive this expression for any fluid. The fact that at constant temperature U is also constant is valid only for the ideal gases, not for the real fluids.

Therefore we keep U in our derivations.

Case 4: The system is closed, the process is isothermal and the system is at constant pressure

The energy balance simplifies to

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s - P \frac{dV}{dt}$$

While the entropy balance yields

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} \text{ or } \dot{Q} = T \frac{dS}{dt} \text{ when this expression for } \dot{Q} \text{ is substituted in the energy balance,}$$

keeping in mind that the temperature and pressure are constant, the rearrangement gives

$$\frac{dG}{dt} = \dot{W}_s$$

Where A is the Helmholtz free energy defined by, $G=U+PV-TS$

It is important to note here that we derive this expression for any fluid. The fact that at constant temperature U is also constant is valid only for the ideal gases, not for the real fluids.

Therefore, we keep U in our expressions.

Now let's combine all of the cases along with their constraints in the table below. Realize that your independent variables are S, T, P and V and your dependent variables are U, H, A and G.

S and V constant $\frac{dU}{dt} = \dot{W}_s$	S and P constant $\frac{dH}{dt} = \dot{W}_s$ H=U+PV
T and V constant $\frac{dA}{dt} = \dot{W}_s$ A=U-TS	T and P constant $\frac{dG}{dt} = \dot{W}_s$ G=U+PV-TS

Derive

The analysis presented above gave us a perspective using Joule's experiment as a tool. Joules experiment was a classic revealing the relationship between work and total energy. We studied an ideal gas confined in a piston and cylinder assembly and realized that under different constraints, the amount of energy exchanged with the environment is different. The special constraint pairs gave rise to new forms of energy as defined above. We will use these energies and their relationships to generate a set of equations that will allow us to determine the real fluid properties.

The internal energy

We have already learned that the internal energy carries information about vibrational, rotational, and translational degrees of freedom of a molecule. For the ideal gases, we also learned that the internal energy is only a function of temperature.

$$\frac{dU}{dT} = n C_v^*$$

In this module, we will ask the question of what happens if we do not have an ideal gas.

The assumptions of the ideal gas law

The ideal gas law has the following assumptions:

1. The volume occupied by the molecules, in comparison to the total volume, is negligible
2. The molecules do not interact.

Using this starting point, Lord Kelvin discovered the absolute zero, by plotting PV (a measure of energy) of a gas as a function of T. This plot had two features. The first feature of the plot, was that it was a straight line with a slope equal for all the gases investigated. The slope is what we call R, the universal gas constant. Universal indicates that the constant is valid for all of the gases under the conditions that they behave ideally. The second feature was the intercept of the Temperature axis. This temperature signified the condition where net energy is zero.

The van der Waals Equation of State

Let us now remove the assumptions of the ideal gas law one by one:

1. There is a finite volume that the molecules occupy. In fact, this is even more important when we move close to the liquid state. Let's call this volume b , such that the volume of voids that is calculated by the ideal gas law becomes $(V - b)$ and the new equation of state is $P(V - b) = RT$
2. We will also remove the second assumption by adding a term that represents the molecular interactions. For the discussion we will conduct here, the interaction parameter we chose will be $\frac{a}{V^2}$, this parameter will correct the local pressures sensed by the molecules, for the attractive interactions.

As a result, our new equation of state took the following form:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

This is the van der Waals equation of state. It will be the basis of our discussions. The van der Waals (vdW) equation of state (EOS) is a cubic polynomial in terms of \underline{V} . There is a group of equations of state called cubic equations due to the fact that in all of these equations, the highest power of \underline{V} is three, but the function does not have to be a polynomial. Now, in the Figure below, you see a plot of two isotherms emanating from VDW EOS. One of the isotherms (orange colored) is at the critical temperature, and the other one (blue) is at a temperature lower than the critical temperature, such that the vapor and liquid coexistence can be experienced.

The cubic equation of state exhibit three extrema: a maximum, a minimum, and a saddle point at which the concave curve and convex curve meet. These extrema are represented by the following mathematical equalities at the critical point.

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = 0 = -\frac{RT}{(\underline{V} - b)^2} + 2\frac{a}{\underline{V}^3}$$

$$\left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T = \frac{2RT}{(\underline{V} - b)^3} - 6\frac{a}{\underline{V}^4} = 0$$

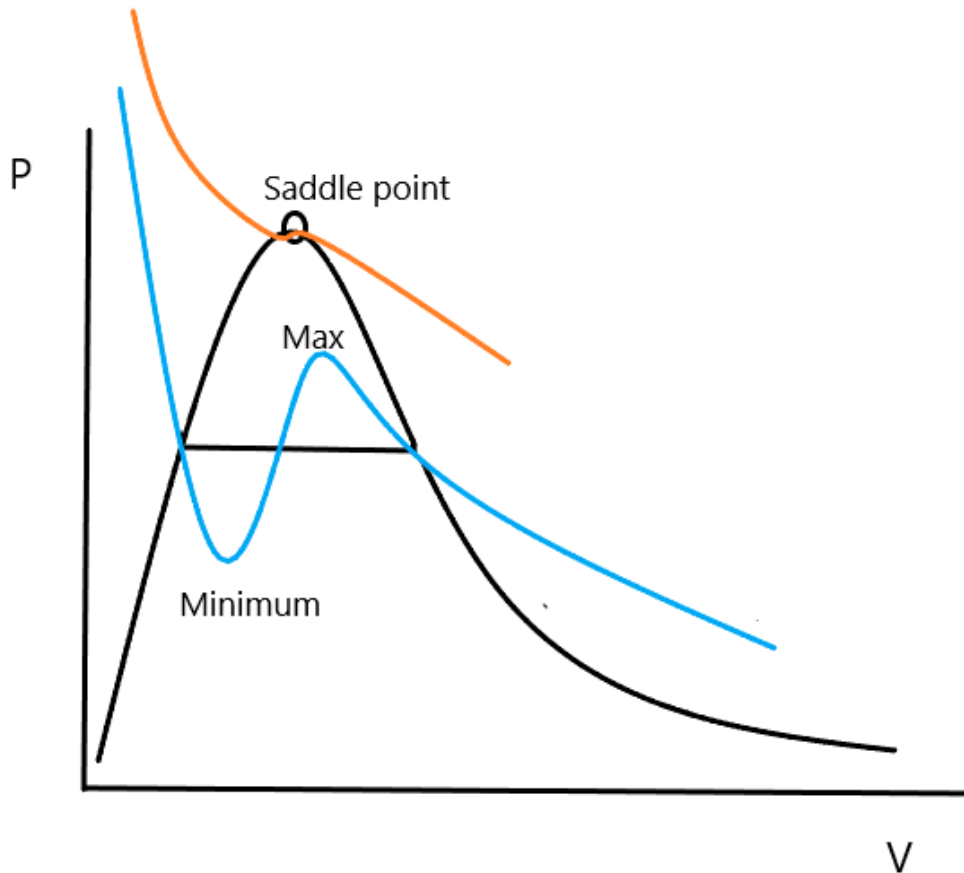
These two identities give us a set of equations that we can calculate and b

$$a = \frac{9\underline{V}_c RT_c}{8}$$

$$b = \frac{\underline{V}_c}{3}$$

Substitute these values to vdW to obtain the critical pressure.

$$P_c = \frac{a}{27b^2}$$



As seen, there is a horizontal line connecting the vapor equilibrium curve with that of the liquid equilibrium curve. The locus of this curve was decided such that the area remaining above the curve and below are equal.

We have removed the ideal gas assumptions from the equation of state. Now we will do the same for the internal energy.

Internal Energy of a Real Fluid

So far, we used The following identity to estimate the internal energy of the ideal gas

$$\frac{dU}{dT} = n C_v^*$$

For the real fluids, this expression will take the following form

$$\left(\frac{\partial U}{\partial T}\right)_V = n C_v$$

Notice the difference between these two expressions. The total derivative indicating U is only a function of temperature for an Ideal Gas is replaced with a partial derivative, indicating that U depends on more than one variable. In this section we will learn these parameters and their interrelationships.

In order to estimate the thermodynamic behavior of the real fluid, we need to start from the energy balance and the entropy balance. This time we will have a real fluid confined in a piston and cylinder assembly, under closed system configurations, and there is no shaft work. The energy balance reduces to

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt}$$

Similarly, entropy balance reduces to (for situations that the entropy generation is not considered)

$$\frac{dS}{dt} = \frac{\dot{Q}}{T}$$

Hence, substitution yields,

$$\frac{dU}{dt} = T \frac{dS}{dt} - P \frac{dV}{dt}$$

We can eliminate the dt terms to have the most general expression of the internal energy:

$$dU=TdS-PdV$$

This expression tells us that U is a function of entropy and volume, $U(S,V)$. This is the most fundamental level of defining the internal energy coordinate system. But similar to mathematics, where we change the variables in order to ease the calculations, we can do the same in thermodynamics. As we have seen so far, entropy is a difficult state variable to control or measure. Therefore, we will switch the coordinates to T, V instead (however, will always remember that internal energy is a function of entropy and volume, at the fundamental level) . The coordinate transformation will require defining entropy, S, as a function of T and V, $S(T,V)$. Then we will substitute this function in the definition of internal energy equation.

$$\text{If } S(T,V) \text{ then, } dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\text{Now, we need to define } \left(\frac{\partial S}{\partial T}\right)_V \text{ and } \left(\frac{\partial S}{\partial V}\right)_T.$$

Starting from $dU=TdS-PdV$, dividing both sides by dT and keeping volume constant, in other words, $dV=0$ gives us

$$\left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

Remember

$$\left(\frac{\partial U}{\partial T}\right)_V = n C_v$$

Therefore

$$\left(\frac{\partial S}{\partial T}\right)_V = n \frac{C_v}{T}$$

Being able to replace $\left(\frac{\partial S}{\partial V}\right)_T$ will require a little bit more effort. We will bring the PVT equivalent of this term from the Helmholtz free energy based Maxwell relations.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

With this substitution, we obtain an equation for the entropy:

$$dS = n \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

Substituting this will give us the relationship for the internal energy:

$$dU = T \left[n \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \right] - P dV$$

rearranging gives:

$$dU = nC_v dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

This is the equation we should use to determine the internal energy change.

Example

Determine the internal energy change for an ideal gas.

Solution

The equation of state for an ideal gas is given by $P = nRT/V$. We have to determine the function $T \left(\frac{\partial P}{\partial T}\right)_V - P$ for the ideal gas.

$$\left(\frac{\partial P}{\partial T}\right)_V = nR/V$$

Upon substitution, we obtain

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{nRT}{V} - P = 0$$

Hence, for an ideal gas $dU = nC_v dT$

Example

Derive the function for internal energy change for a van der Waals equation of state.

Solution

Van Der Waals equation of state is given by $P = nRT/V$. We have to determine the function

$T\left(\frac{\partial P}{\partial T}\right)_V - P$ for the ideal gas.

$$\left(\frac{\partial P}{\partial T}\right)_V = nR/V$$

Upon substitution, we obtain

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{nRT}{V} - P = 0$$

Hence, for an ideal gas $dU = nC_v dT$

Maxwell relationships

Maxwell's relationships define how the thermodynamic independent parameters, T, S, P and V are related to each other. You may have already noticed from the example we used in the beginning of this document that we had four different forms of energy U, H, A and G. Each simplified a situation under a particular constraint so that we knew how much shaft work was done, through the changes in these energies. Now we will use these energies and their dependency on the variables T, S, P and V to establish relationships between the independent variables.

I will derive the relationship based on U function, and will leave the rest as an exercise for you (and if you attended the lecture, you know what to do). The internal energy at the fundamental level, (i.e. by the combination of the first and second laws) is a function of S and V.

$$U=U(S, V)$$

Therefore its derivative should look like

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

We started this course by taking energy as a conserved quantity. As such, the differential equation above is an exact differential, which allows the commutation of the differentiation operators. In other words,

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$$

There is a second step: We also know that $dU=TdS-PdV$

if we compare

Prof. Dr. Deniz Uner
Chemical Engineering. Middle East Technical University, Ankara

$dU = TdS - PdV$ and $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$, we notice that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

So let us substitute these equalities in $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$ to obtain,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

This last equality is the Maxwell relationship. It relates T, V, P and S to each other.

enthalpy

We will relate T, V, P and S to each other starting from the equation for H.

$$H = U + PV$$

$$dH = dU + d(PV) = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

Exercise: Using the tools of mathematics, derive the following relationships

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Helmholtz Free Energy

We will relate T, V, P and S to each other starting from the equation for A.

$$A=U-TS$$

$$dA= dU - d(TS) = TdS-PdV-TdS-SdT$$

$$dA= -SdT-PdV$$

Exercise: Using the same tools of mathematics we used above for internal energy based derivations, derive the following relationships

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P$$

The corresponding Maxwell relationship is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Gibbs Free Energy

We will relate T, V, P and S to each other starting from the equation for G.

$$G=H-TS$$

$$dG= dH - d(TS) = TdS+VdP-TdS-SdT$$

$$dG= -SdT+VdP$$

Exercise: Using the same tools of mathematics we used above for internal energy based derivations, derive the following relationships

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

The corresponding Maxwell relationship is

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$