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THE THERMODYNAMICS OF THE REAL FLUIDS: Internal Energy Change SELF STUDY MODULE

Objective

The objective of this module is to derive the equations for the internal energy of a real fluid. Upon successful completion of this module, the student should be able to estimate the internal energy change of a real fluid using van der Waals equation of state.

Reading assignment

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

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 particle 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.

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

Now, we need to define $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$ and $\left(\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{T}}$.

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

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = T\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}}$$

Remember

$$\left(\frac{\partial U}{\partial T}\right)_{V} = n\,C_v$$

Therefore

$$\left(\frac{\partial \mathrm{S}}{\partial \mathrm{T}}\right)_{\mathrm{v}} = n\frac{C_v}{T}$$

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

$$\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$$

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

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

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

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

rearranging gives:

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

This is the equation we should use to determine the internal energy change. The multiplier of the dV term is called the departure function to indicate the departure from the ideal gas behavior.

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

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

Upon substitution, we obtain

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

Hence, for an ideal gas $\mathbf{dU = n}\boldsymbol{C_v}\mathbf{dT}$

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 $P = \frac{RT}{(\underline{V}-b)} - \frac{a}{\underline{V}^2}$. equivalently this equation can be written as $P = \frac{n\,RT}{(V-b)} - \frac{n^2\,a}{V^2}$. We have to determine the function $T\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P$ for the van der Waals fluid.

$$\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = nR/(V-b)$$

Upon substitution, we obtain

$$T\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - P = \frac{n^2 a}{V^2}$$

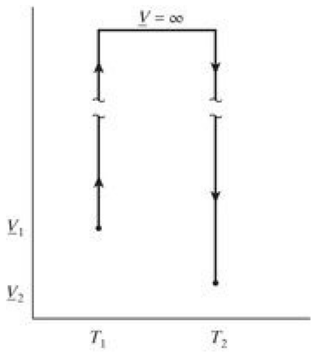
Hence, for a van der Waals fluid $\mathbf{dU} = \mathbf{n}\boldsymbol{C_v}\mathbf{dT} + \boldsymbol{\frac{n^2 a}{V^2}\,dV}$

The state postulate

In order to determine the internal energy change of a fluid, between two arbitrary points of (T_1, V_1) and (T_2, V_2) we will use the state postulate: The value of the state functions depend only on the state of the system, but not the path taken.

Hence, we will carry out the evaluation process as follows. We will bring the fluids to an ideal gas state, by first integrating the V function. Fluids under their ideal gas conditions can have very large volumes, such as $V= \infty$. Under these conditions, the fluid will behave like an ideal gas, hence we can use the ideal gas heat capacities to evaluate the T function, finally we will bring the fluids back to the real fluid conditions from $V= \infty$ to the real value.

Graphically this process looks like as follows



The algebra of this process is as follows:

$$\int_{U_1}^{U_2} \mathrm{dU} = \int_{V_1}^{\infty} \frac{n^2 a}{V^2}\, dV + \int_{T_1}^{T_2} \mathrm{n} C_v^* \mathrm{dT} + \int_{\infty}^{V_2} \frac{n^2 a}{V^2}\, dV$$

Notice that the heat capacity now has its *, indicating that it is the ideal gas heat capacity.

Calculate

1. Using the van der Waals equation of state, determine the internal energy change of steam between (1 MPa, 200 °C) and (4 MPa, 400 °C). You need to determine the volumes first from vdW EOS and proceed with the internal energy calculations.
2. Compare your estimations with the values you would obtain from the steam tables.
3. Given that you have the internal energy change and the values of P and V, determine ΔH between these states.
4. Also determine ΔS, ΔA and ΔG.

Evaluate yourself

Check if you have answers to the following questions:

1. Why do we need these four different forms of energy, i.e., U, H, G and A?
2. What is the difference between internal energy and enthalpy?

3. What is the difference between Helmholtz free energy and Gibbs Free Energy?

4. Why Helmholtz Free Energy and Gibbs Free Energy are called free energies? What makes them free? Is there a bound energy?

5. Why is entropy an independent variable in the thermodynamic landscape?