

ChatGPT-4 & Questions from a Materials Thermodynamics Course

Question 4: Stability Callen 8.3-3

TLL Question 4:

1. Show that the van der Waals equation of state does not satisfy the criteria of intrinsic stability for all values of the parameters. Sketch the curves of P v. V for constant T (isotherm) and show the region of local instability. The van der Waals equation of state is given below.

$$P = R^*T((v - b) - a*v^{-2})$$

where P =pressure; T =temperature; v =molar volume; a & b are constants.

ChatGPT4 answer:

The intrinsic stability of a thermodynamic system is governed by two conditions:

The compressibility should be positive, i.e., $(\partial P/\partial V)_T < 0$. This implies that when the volume of a system decreases (under constant temperature), the pressure should increase.

The heat capacity at constant pressure should be positive, i.e., $(\partial E/\partial T)_V > 0$. This implies that when you add heat to the system (at constant volume), the temperature should increase.

Let's start by checking the first condition for the Van der Waals equation of state:

$$P = RT/(v - b) - a/v^2.$$

Taking the derivative with respect to volume at constant temperature yields:

$$(\partial P/\partial V)_T = -RT/(v - b)^2 + 2a/v^3.$$

For this to be negative (i.e., for the system to be stable), the following inequality must be satisfied:

$$-RT/(v - b)^2 + 2a/v^3 < 0.$$

Rearranging gives:

$$RT/(v - b)^2 > 2a/v^3.$$

We can't guarantee that this inequality will be true for all values of P , V , T , a , and b , and indeed, there are regions where it does not hold, indicating regions of instability.

As for the isotherm, when you graph P vs V for constant T using the Van der Waals equation, you get an "S" shaped curve. The middle portion of this curve (the region of the "S" shape that slopes upward) corresponds to the region of instability. This is because in this region, the pressure decreases as the volume decreases, violating the first condition of stability. These areas of instability are associated with the liquid-gas phase transition.

Therefore, while the Van der Waals equation of state captures the behavior of real gases better than the ideal gas law, it does not satisfy the criteria of intrinsic stability for all values of the parameters.

Remember, to fully satisfy the conditions of intrinsic stability, we would also need to check the second condition related to heat capacity, which is beyond the scope of this analysis.

TLL follow-up:

I think you have incorrectly written the partial derivative in condition #2 above. You write: "the heat capacity at constant pressure should be positive, i.e., $(\partial E/\partial T)_V > 0$." BUT - it should be: "the heat capacity at constant pressure should be positive, i.e., $(\partial E/\partial T)_P > 0$."

ChatGPT4 answer:

You are absolutely correct, and I apologize for the oversight. The second condition for thermodynamic stability, relating to the heat capacity at constant pressure, should indeed be written as $(\partial E/\partial T)_P > 0$, which means that when heat is added to the system (keeping the pressure constant), the temperature should increase. Thanks for catching that mistake.

TLL follow-up:

Can you check this condition? If not, why not?

ChatGPT4 answer:

To check the second condition of thermodynamic stability related to heat capacity at constant pressure, we would need to compute the derivative of the internal energy E with respect to temperature T at constant pressure, or $(\partial E/\partial T)_P$.

However, the Van der Waals equation of state is an equation that relates the pressure, volume, temperature, and the constants a and b . It does not include an expression for internal energy (E), which means we can't directly compute $(\partial E/\partial T)_P$ from the Van der Waals equation.

The internal energy of a system is dependent on the particular intermolecular forces and degrees of freedom of the system, which are not accounted for in the Van der Waals equation. Therefore, without more information about the specific system (for example, whether it's a monatomic, diatomic, or polyatomic gas), we cannot check the second condition of thermodynamic stability.

In short, the Van der Waals equation of state is a relationship between pressure, volume, and temperature of a substance, and while it accounts for non-ideality by including real gas constants a and b , it does not provide a direct link to the internal energy of the substance, so we can't use it to directly check the condition related to heat capacity at constant pressure.

TLL follow-up:

Is the intrinsic stability of ANY thermodynamic system is governed by the same two conditions? Specifically: positive isothermal compressibility, and positive constant pressure heat capacity ?

ChatGPT4 answer:

Yes, the conditions for intrinsic stability generally apply to any thermodynamic system. To summarize, these conditions are:

Positive Isothermal Compressibility: The system should respond to an increase in pressure by decreasing its volume. Mathematically, this is expressed as $(\partial P/\partial V)_T < 0$, which is equivalent to saying the compressibility factor, defined as $-1*(\partial V/\partial P)_T$, should be positive.

Positive Constant Pressure Heat Capacity: The system should respond to an input of heat by increasing its temperature. Mathematically, this is expressed as $(\partial T/\partial Q)_P > 0$, which is equivalent to saying that the heat capacity at constant pressure ($C_p = \partial Q/\partial T)_P$, should be positive.

These conditions ensure the system is stable and behaves as we would expect in response to changes in pressure or the addition of heat. If a system doesn't meet these conditions, it could have unstable equilibrium states. For example, a negative compressibility would imply that the system expands when pressure is applied, which is not a typical or stable response for a system. Similarly, a negative heat capacity would imply the system decreases its temperature when heat is added, which is also not typical or stable.

These conditions hold generally for any thermodynamic system, but depending on the specific system or the specific thermodynamic potentials used, there could be additional conditions for stability, such as the positivity of specific heat at constant volume, or the convexity conditions on the energy or entropy. However, the above two conditions are the most commonly used.