Let us look at:

$$(*) \quad \boxed{S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) \le 2S(U,V,N)}$$

Stability of a system requires that (*) holds.

Illustration:

Consider two systems separated by totally restrictive wall, i.e., no talking between the two systems.

$$\underbrace{\begin{array}{l} \text{System 1 has } S(U,V,N). \\ \text{System 2 has } S(U,V,N). \end{array}}_{\text{System has entropy } 2S(U,V,N)} \left.\vphantom{\begin{array}{l} a \\ b \end{array}}\right\} \text{two identical systems}$$

Now imagine we move a tiny bit of energy from subsystem 1 to subsystem 2.

Subsystem 1 now has entropy $S_1(U-\Delta U, V, N)$.

Subsystem 2 now has entropy $S_2(U+\Delta U, V, N)$.

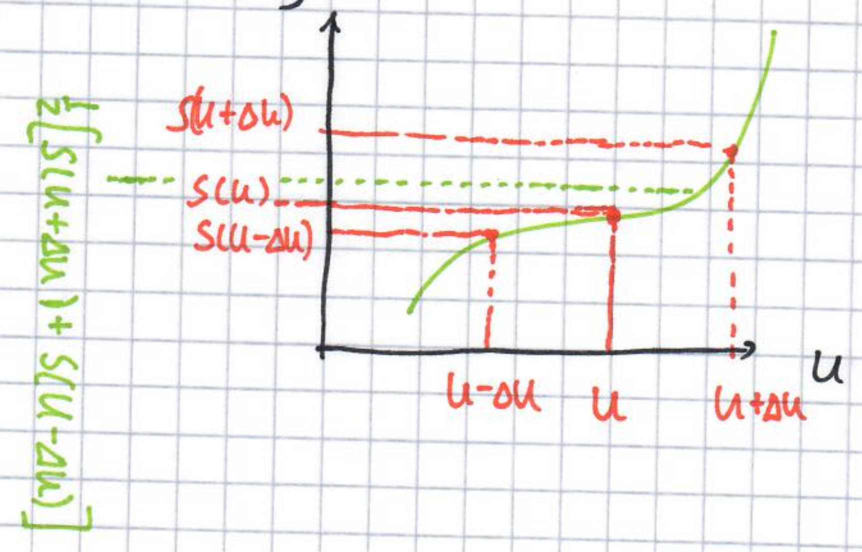
But our "entropy fct." has not changed, i.e.,

we can simply write $S(U-\Delta U, V, N)$

& $S(U+\Delta U, V, N)$

ΔU does not have to be tiny

Now: let's imagine that the system is described by an entropy fct. that has the following dependence on U:



For this S vs. U curve:

$$S(U+\Delta U) + S(U-\Delta U) > 2S(U)$$

I'm suppressing the dependence on V & N.

The resulting entropy would be larger than the initial entropy!

What does this mean?

If the restrictive wall was removed, energy would flow spontaneously across the wall: one subsystem would increase its energy and the other would decrease its energy.

Actually: Even within one subsystem, the system would find it advantageous to transfer energy from region to another, i.e., inhomogeneities would develop (the wall really just helped us to think about this).
→ We would have loss of homogeneity.
Said differently, the system is unstable.
Loss of homogeneity is the hallmark of a phase transition.

Go back to Eq. (*) from page EZ-16:

$$S(U+\Delta U, V+\Delta V, N) + S(U-\Delta U, V-\Delta V, N) < 2S(U,V,N)$$

for system to be stable

Set $\Delta V = 0$ and let $\Delta U \to 0$

$$\Rightarrow \text{limit}_{\Delta U \to 0} \left(\left[S(U+\Delta U, V, N) - S(U,V,N) \right] + \left[S(U+\Delta U, V, N) - S(U,V,N) \right] \right. < 0$$

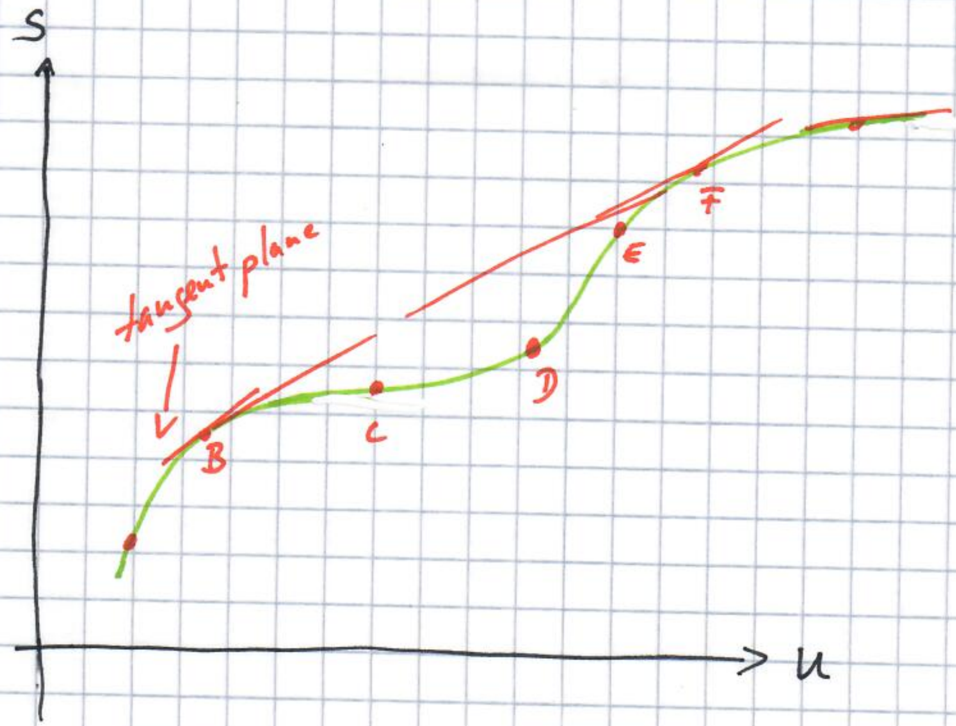
Or: $$\lim_{\Delta U \to 0} \frac{\left[S(U+\Delta U, V, N) - S(U,V,N) \right] + \left[S(U-\Delta U, V, N) - S(U,V,N) \right]}{\Delta U^2} < 0$$

$$\boxed{\left(\frac{\partial^2 S(U,V,N)}{\partial U^2} \right)_{V,N} < 0}$$

Local conditions for stability

Similarly: $$\boxed{\left(\frac{\partial^2 S(U,V,N)}{\partial V^2} \right)_{U,N} < 0}$$

Illustration:



"trajectory BCDEF"

From B through F, the S-U curve corresponds to an unstable situation. ← global criterium

"trajectory CDE"

From C through E, is locally unstable.

Straight line from B to F: line corresponds to phase separation in which part of the system is in state B and part of the system is in state F.

Look at $\underbrace{\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N}}_{-\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_{V,N}} < 0$ ← for stable system

$$= -\frac{1}{T^2}\frac{1}{\left(\frac{\partial U}{\partial T}\right)_{V,N}}$$

$$= -\frac{1}{T^2}\frac{1}{C_V}$$

$\Rightarrow$ C_V must be positive in stable system

For stable system, one can show: $C_P > C_V > 0$; $\kappa_T > \kappa_S > 0$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ isothermal compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$ adiabatic compressibility

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$ heat capacity at constant volume

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$ heat capacity at constant pressure

Reformulate stability criterium in terms of energy instead of entropy.

Stability: Entropy is maximal

Internal Energy is minimal

$$\Rightarrow U(S+\Delta S, V+\Delta V, N) + U(S-\Delta S, V-\Delta V, N) > 2U(S,V,N)$$

Local conditions for stability:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} \overset{(*)}{=} \left(\frac{\partial T}{\partial S}\right)_{V,N} > 0$$ using $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,N} \overset{(*)}{=} -\left(\frac{\partial P}{\partial V}\right)_{S,N} > 0$$ using $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

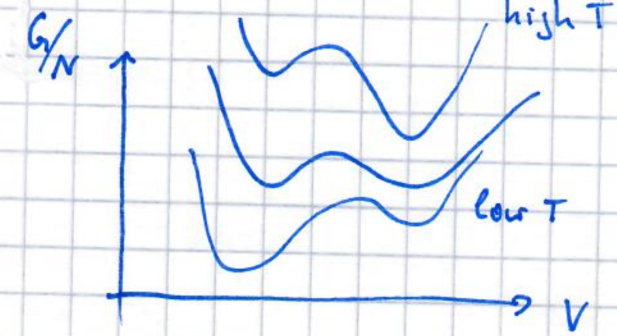
It follows:

Helmholtz free energy: $\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} < 0$ & $\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} > 0$

Enthalpy: $\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,N} > 0$ & $\left(\frac{\partial^2 H}{\partial P^2}\right)_{S,N} < 0$

Gibbs free energy: $\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} < 0$ & $\left(\frac{\partial^2 G}{\partial P^2}\right) < 0$

Recall: for van der Waals equation of state

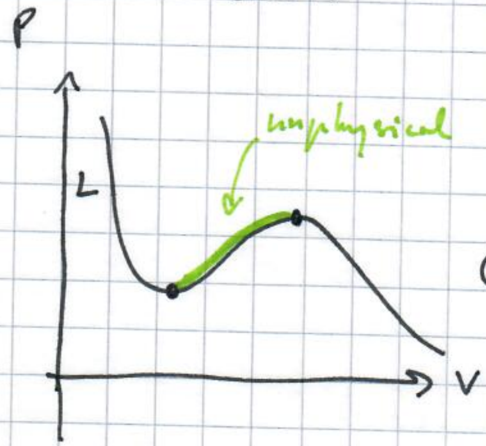


VdW E-o-S has states characterized by $\left(\frac{\partial P}{\partial V}\right)_T > 0$

or $\chi_T < 0$

unstable

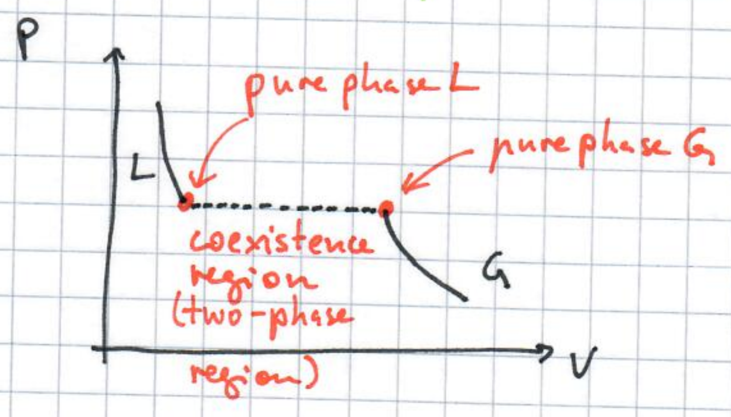
→ unphysical
(system would not want to be in this state)



L: liquid

G: gas

there must be a phase transition



As the system is transformed, at fixed T and P, from the pure phase L to the pure phase G, it absorbs an amount of heat per mole of $T\Delta s$.

The volume per mole changes by Δv.

E2-24

$\rightarrow \Delta u = T\Delta s - P\Delta v$