

Today

I. Thanksgiving Update

II. Last Time

III. Exploring the Van Der Waals Equation of State and Phase Transitions in Detail

II. Justified the van Der Waals equation of state:

$$\left(P + \frac{aN^2}{V^2} \right) (V - bN) = NkT.$$

We plotted its isotherms, saw that starting from large volume and compressing the gas the pressure increased at first and then decreased. This surprise led us to start considering whether perhaps there was an intermediate phase transition before this strange behavior. This led us to start computing the Gibbs free energy.

II. We have

$$dG = -SdT + VdP + \mu dN,$$

Again we fix the amount of material (N) and the temperature:

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V \left(\frac{\partial P}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V - Nb)^2} + \frac{2aN^2}{V^2}.$$

To integrate this with respect to volume it helps to write the first term's numerator $V = (V - Nb) + Nb$, this allows us to do all the integrals...

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T).$$

This expression now allows us to identify the equilibrium phase, which has the lowest Gibbs free energy. Let's consider the case of fixed temperature and investigate $G(P)$.

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The nicest way is to do this parametrically: $x = r \cos \theta$ and $y = r \sin \theta$,
And plot x and y as functions of θ .

We want to plot

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$$

as a function of pressure, but that's gonna be ugly: to this I would
have to solve for V in

$$\left(P + \frac{aN^2}{V^2} \right) (V - bN) = NkT.$$

To avoid all of this mess, we plot parametrically. Luckily both of
these equations are already expressed parametrically in terms of V ,
so all we need to do is make a plot.

III. The result is:

**This triangle,
2-3-4-5-6, is
made up of
unstable states.**

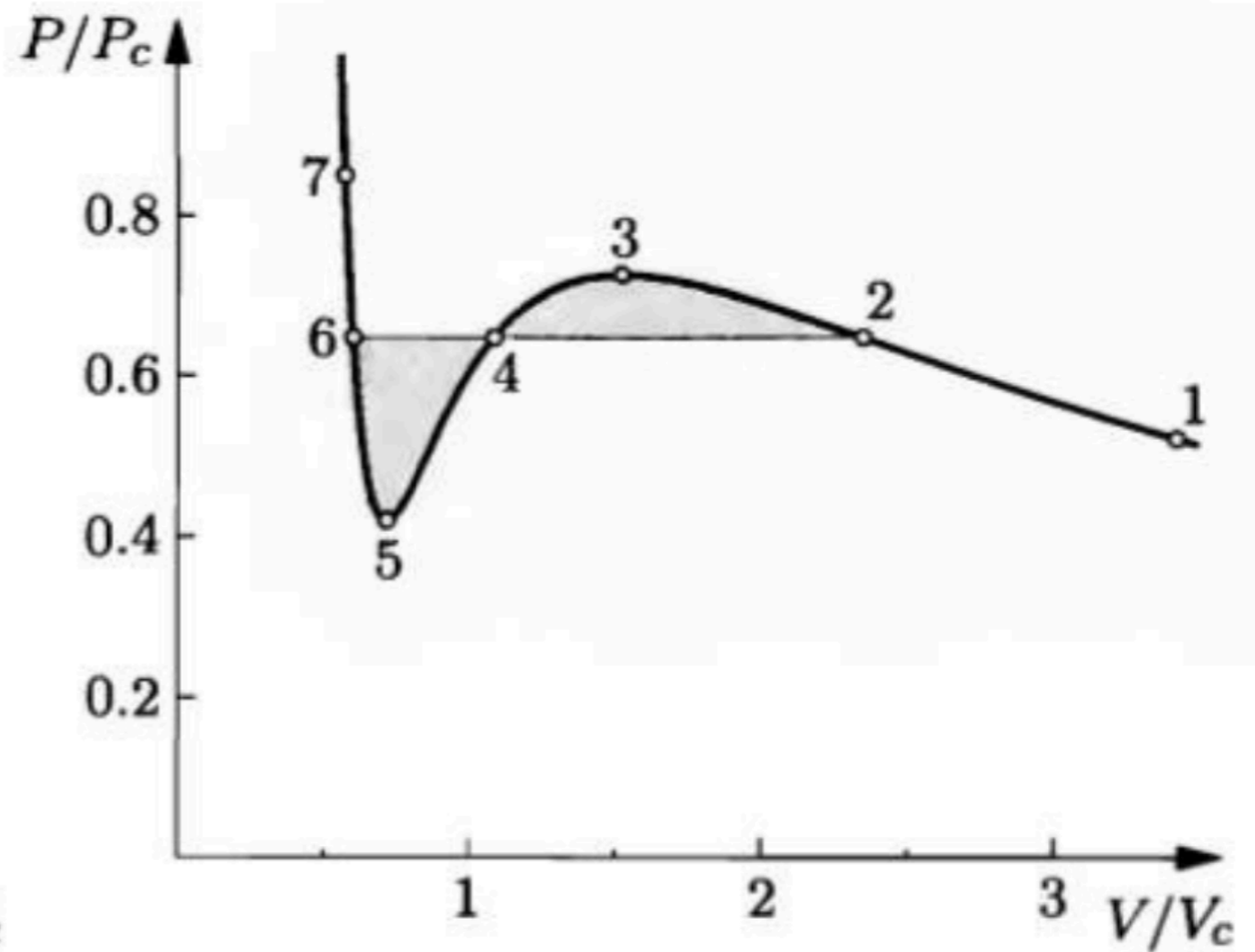
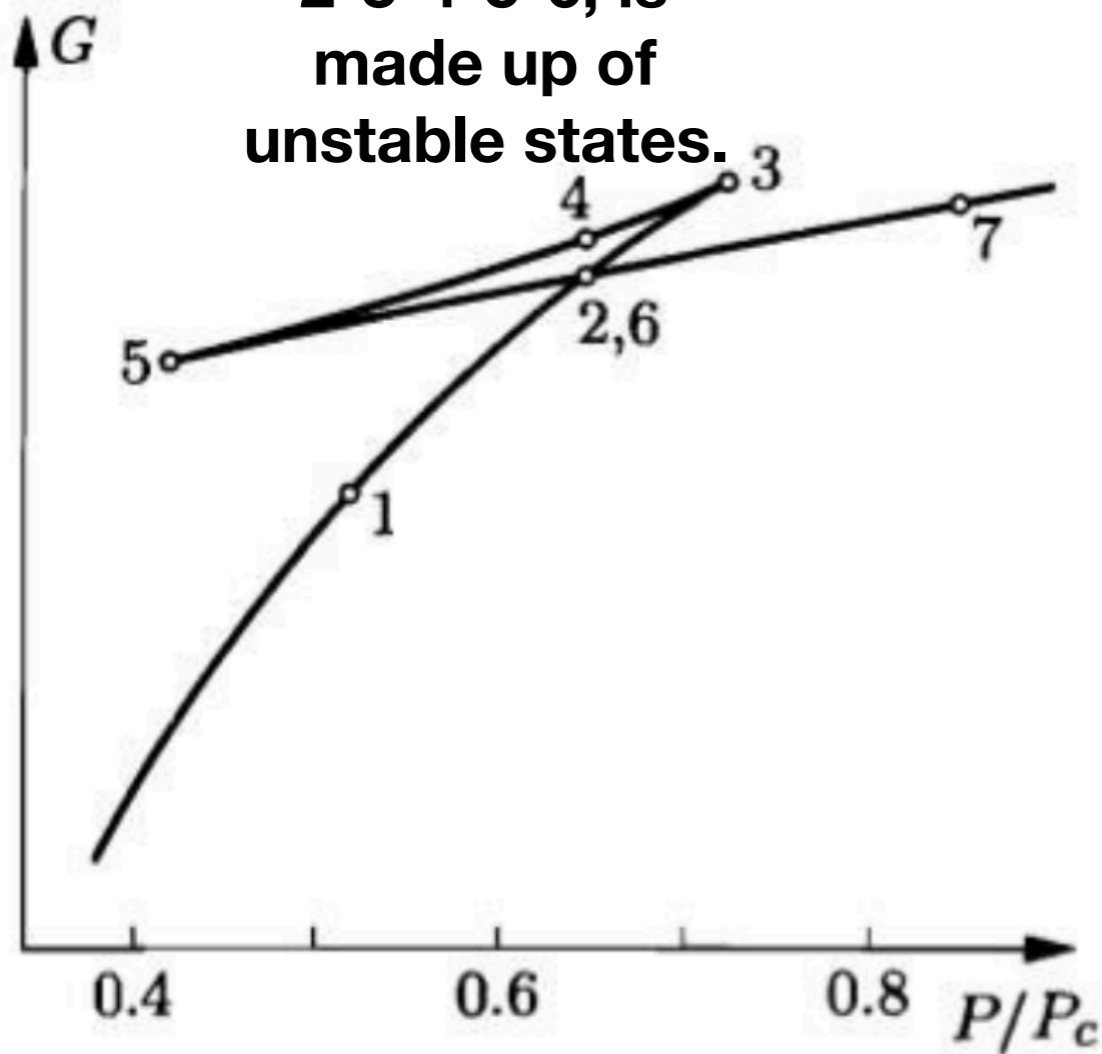


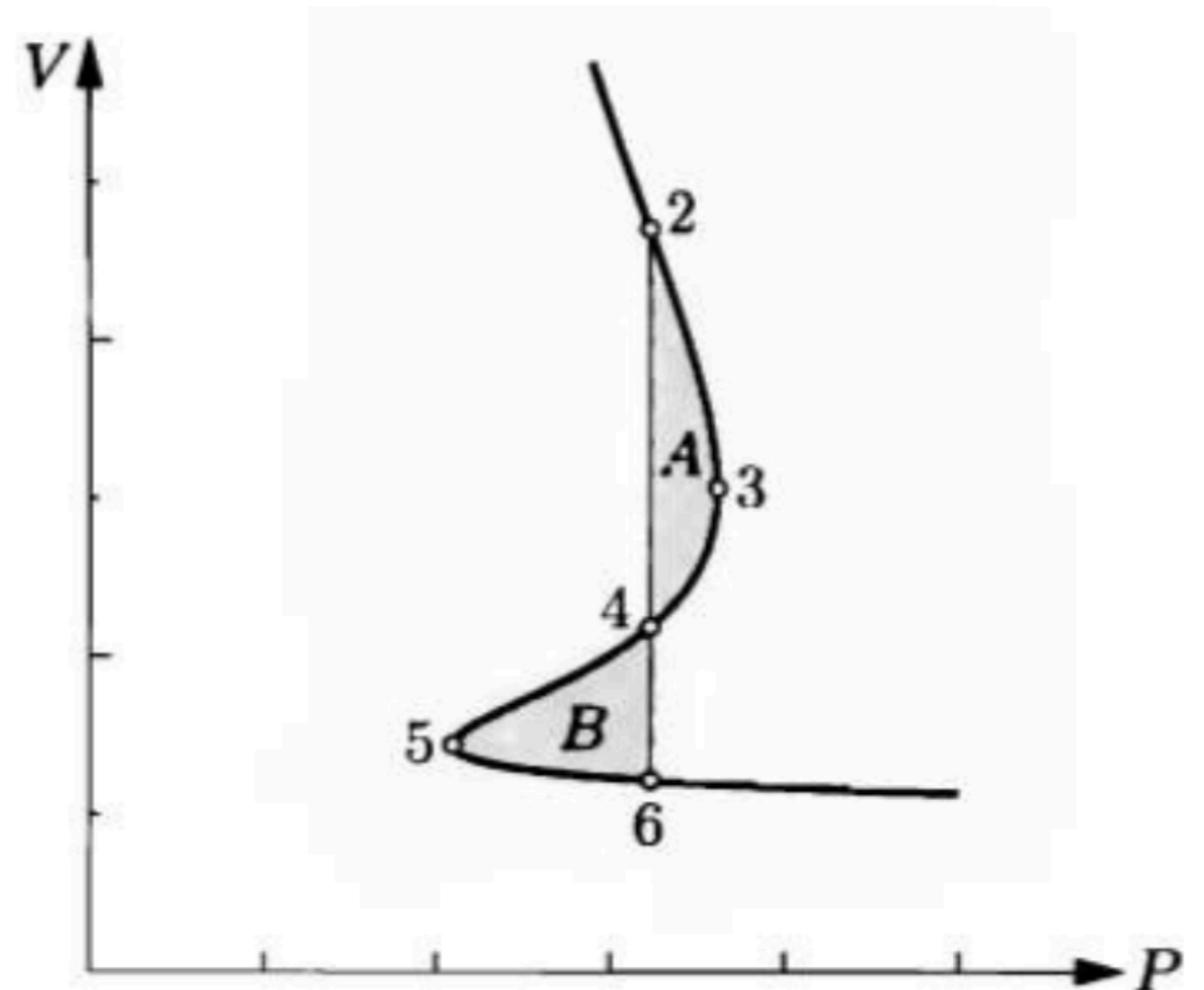
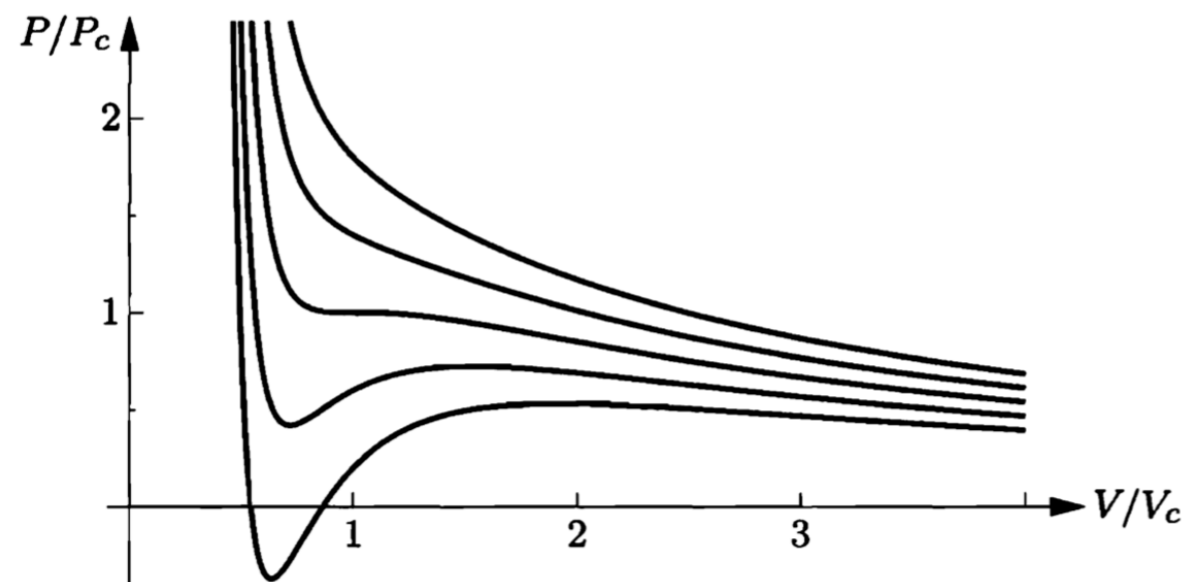
Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

Footnote: the lovely veritasium video on [supercooled water](#).

III. In traversing the triangular loop 2-3-4-5-6 we must have zero change in Gibbs free energy:

$$0 = \int_{\text{loop } 2-3-4-5-6} dG = \int_{\text{loop}} \left(\frac{\partial G}{\partial P} \right)_T dP = \int_{\text{loop}} V dP.$$

In conclusion: we see that the line connecting 2 to 6 is the line for which the areas A and B have equal magnitude.



III. Now study this phase transition also as a function of temperature:

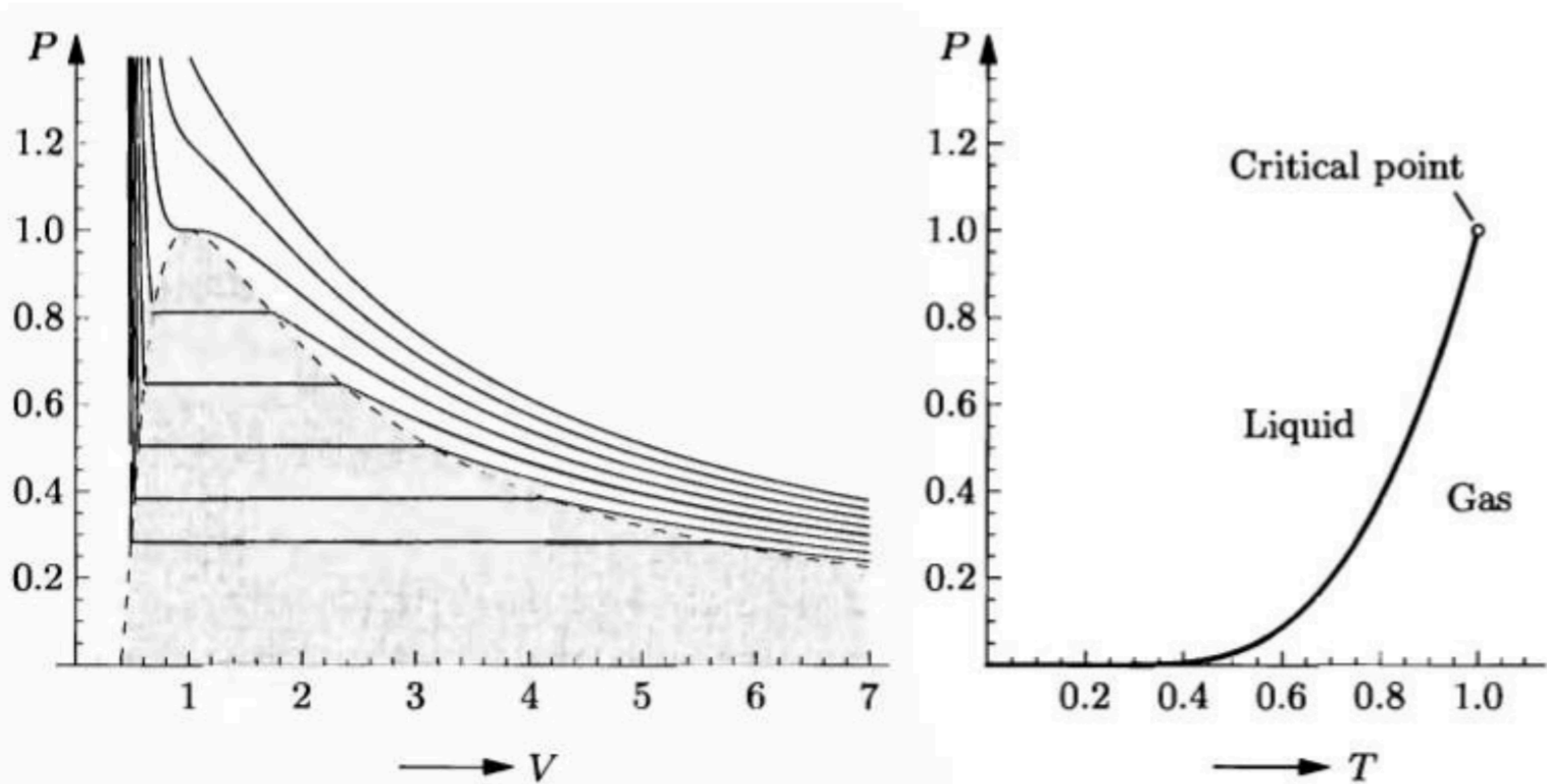


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.

III. Appendix: In the discussion after class we briefly touched on the relationship of this phase transition to the qualitative picture of a cusp catastrophe, which is pictured below.

