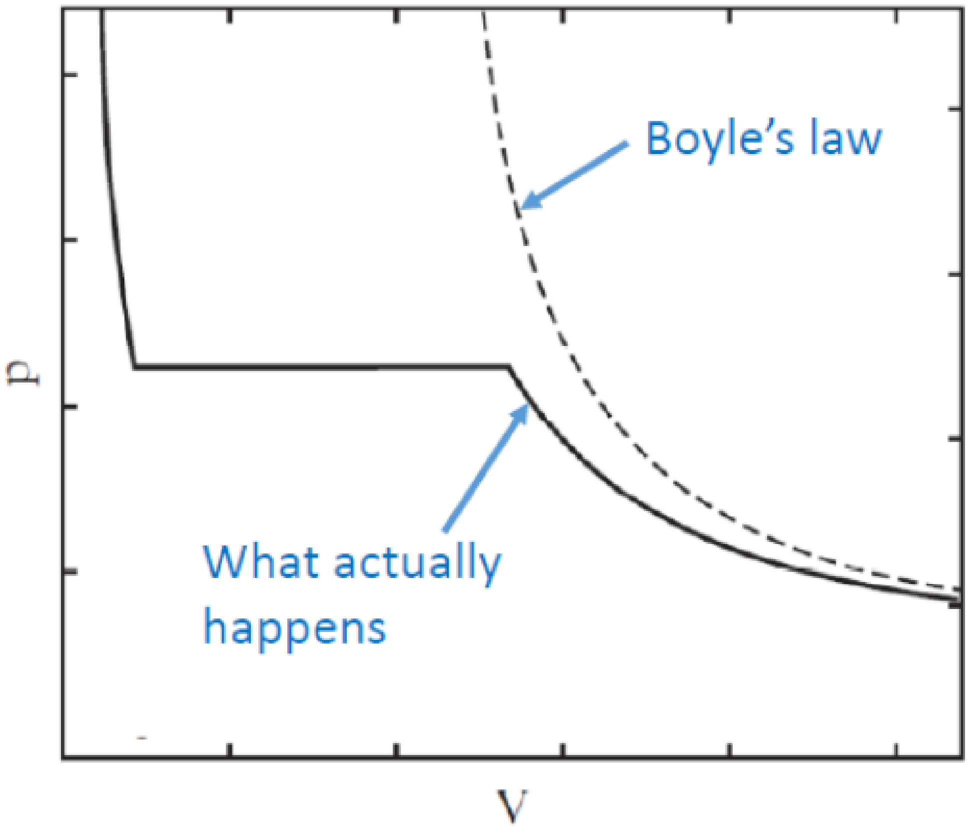
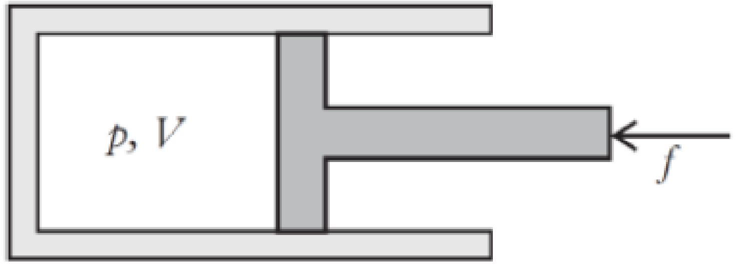
Thermodynamics lecture 12. Phase change

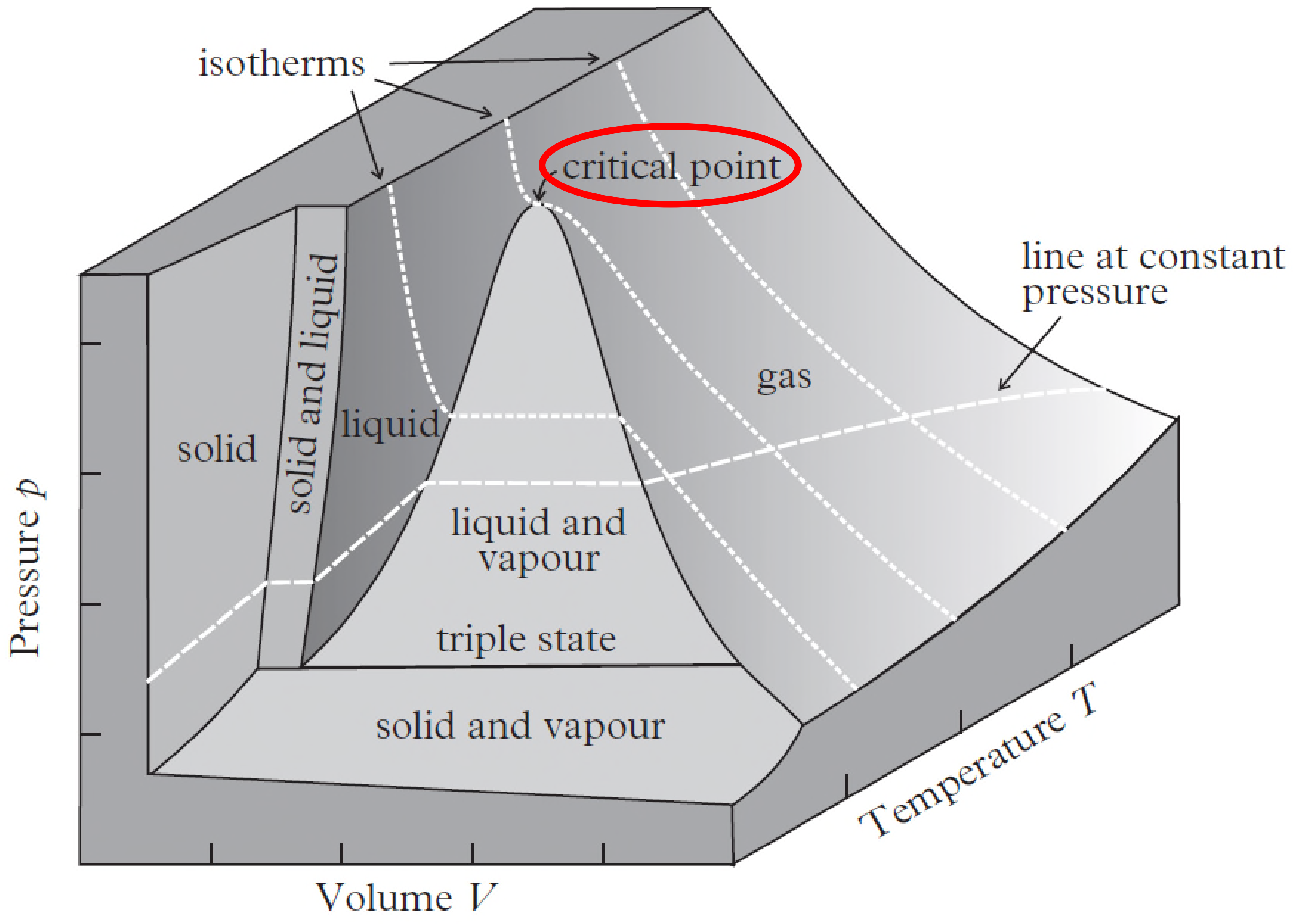
1. Main facts and terminology
2. Basic properties of first-order phase transition
3. Clausius-Clapeyron equation
4. Van der Waals treatment and Maxwell construction (off syllabus)

Compressing an ordinary substance

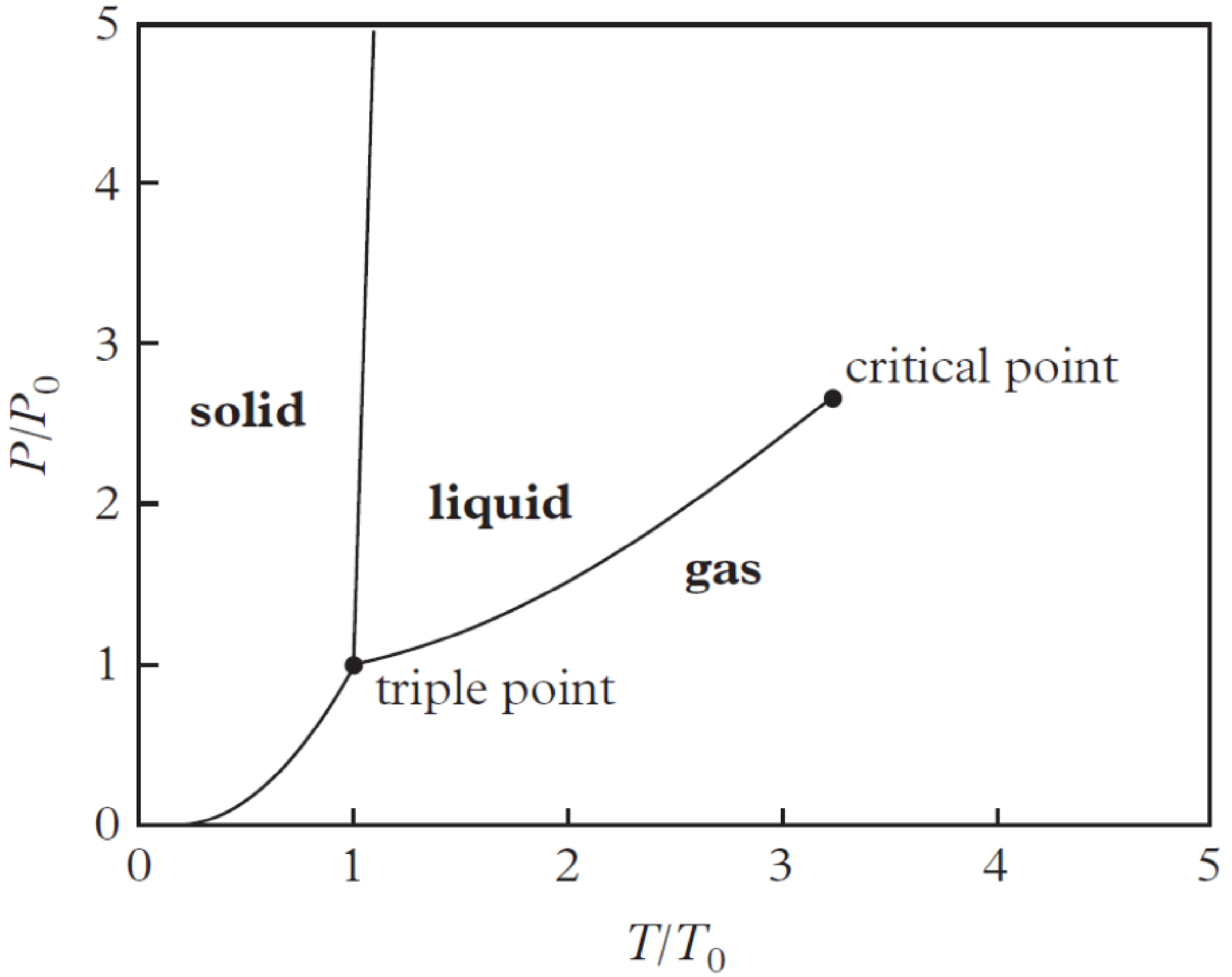




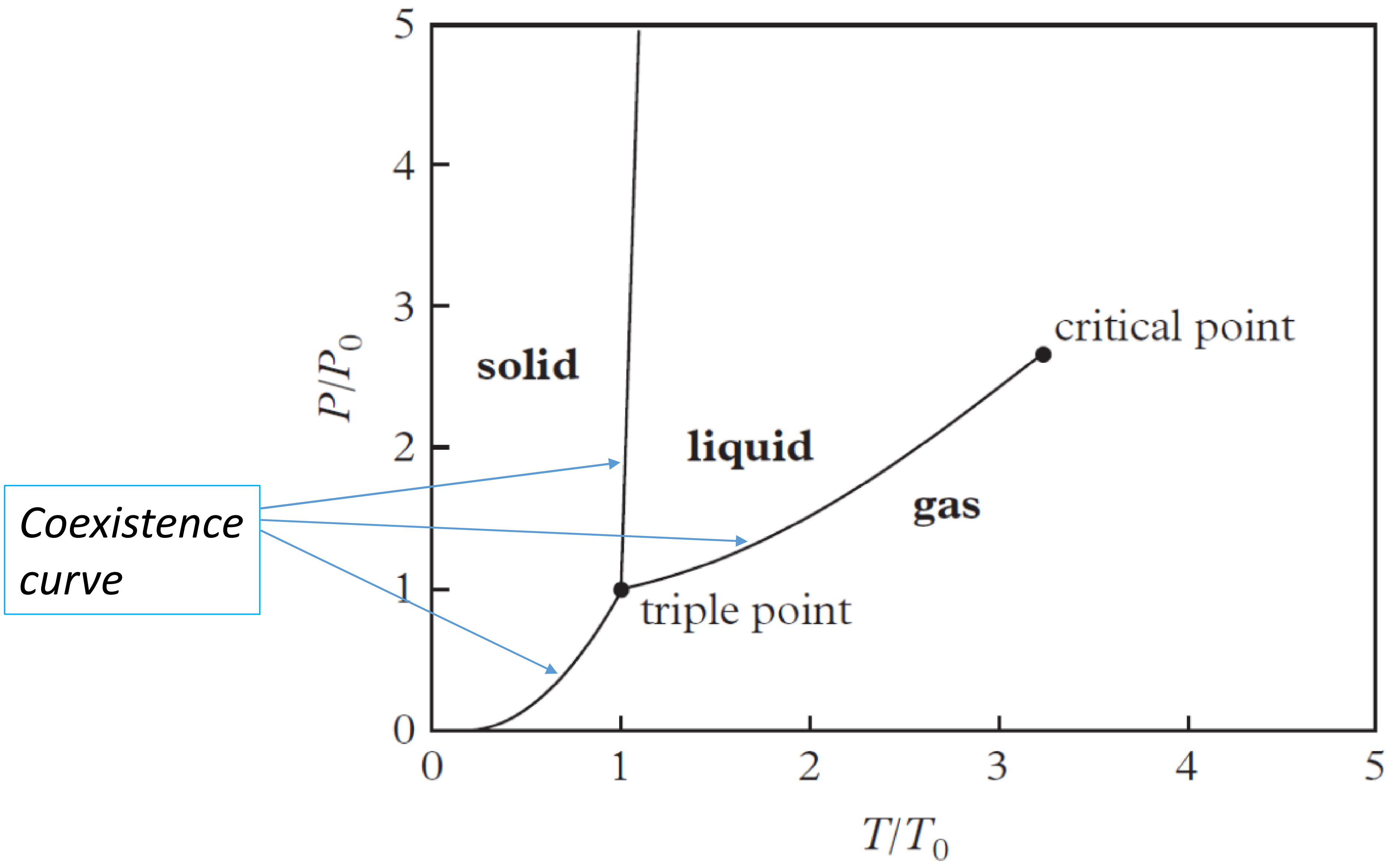
pVT surface of an ordinary substance



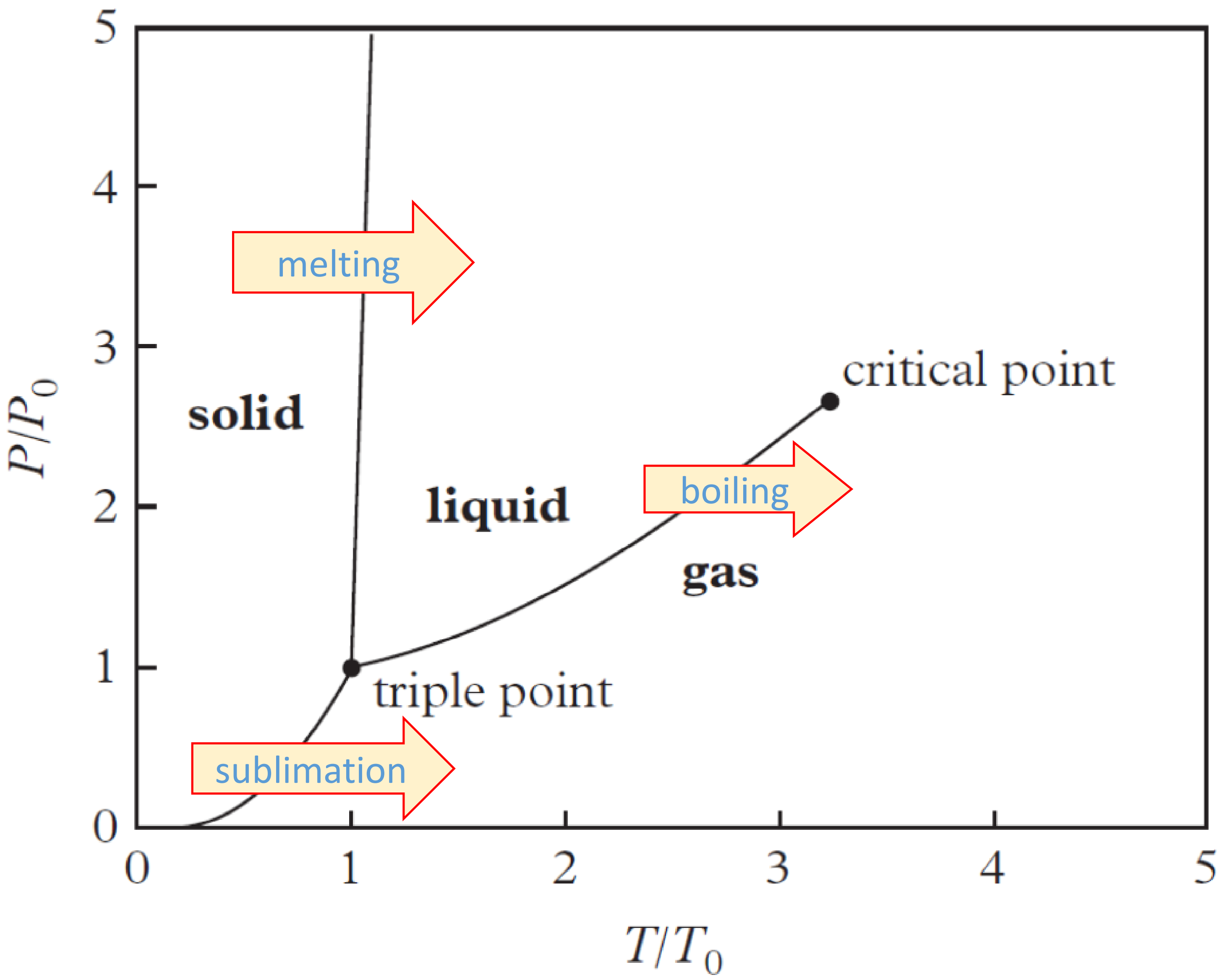
Phase diagram



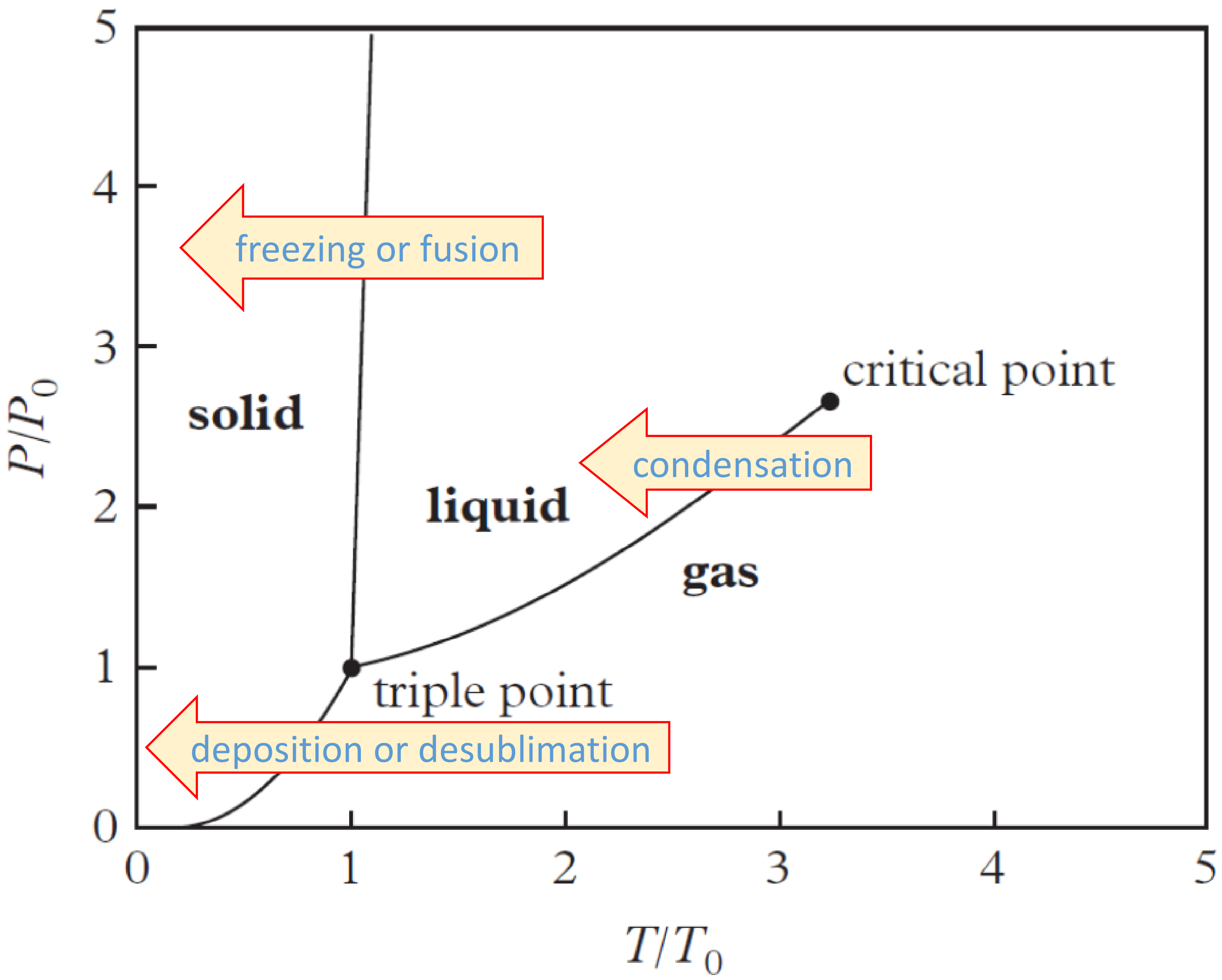
Phase diagram



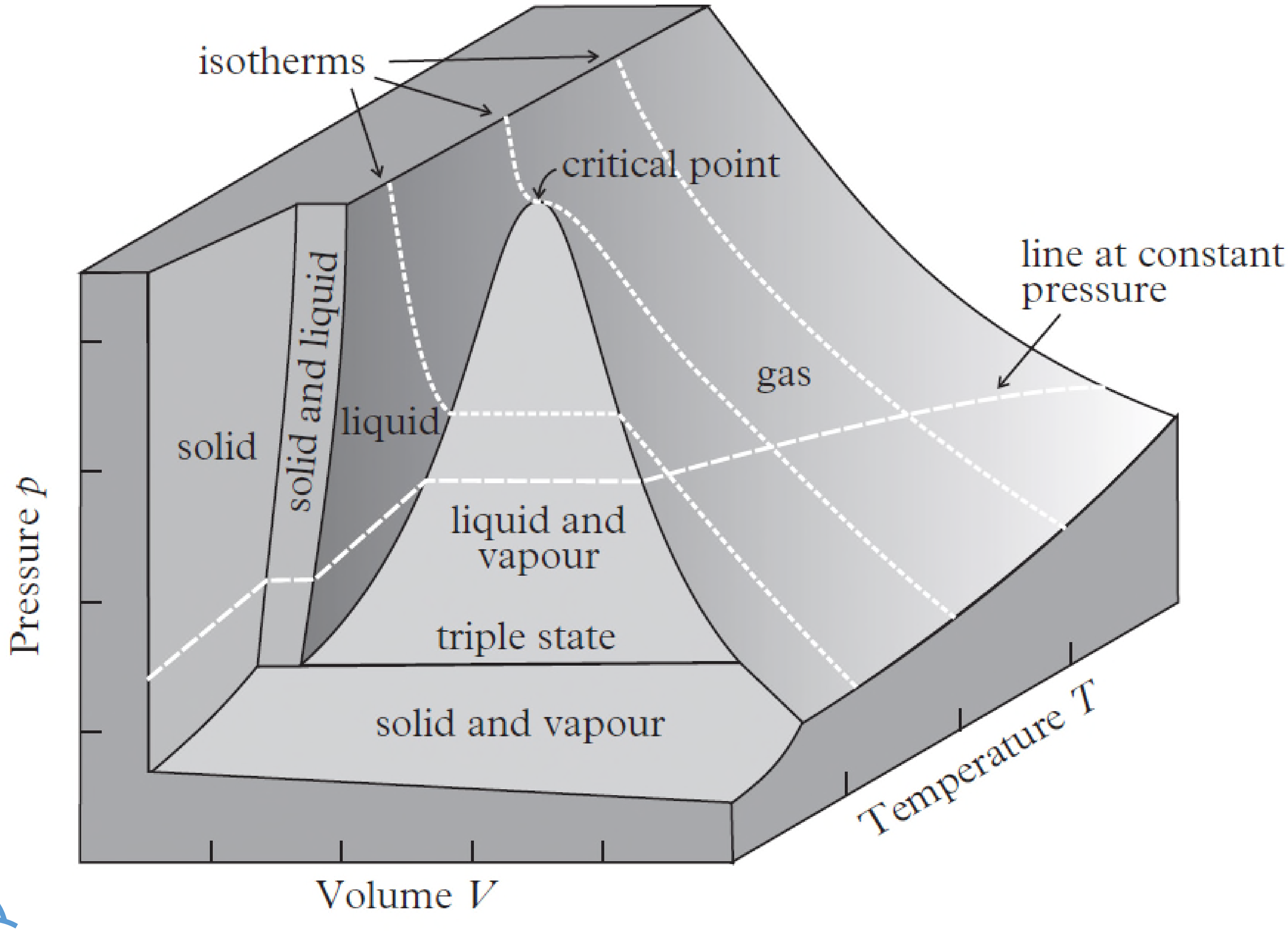
Phase diagram

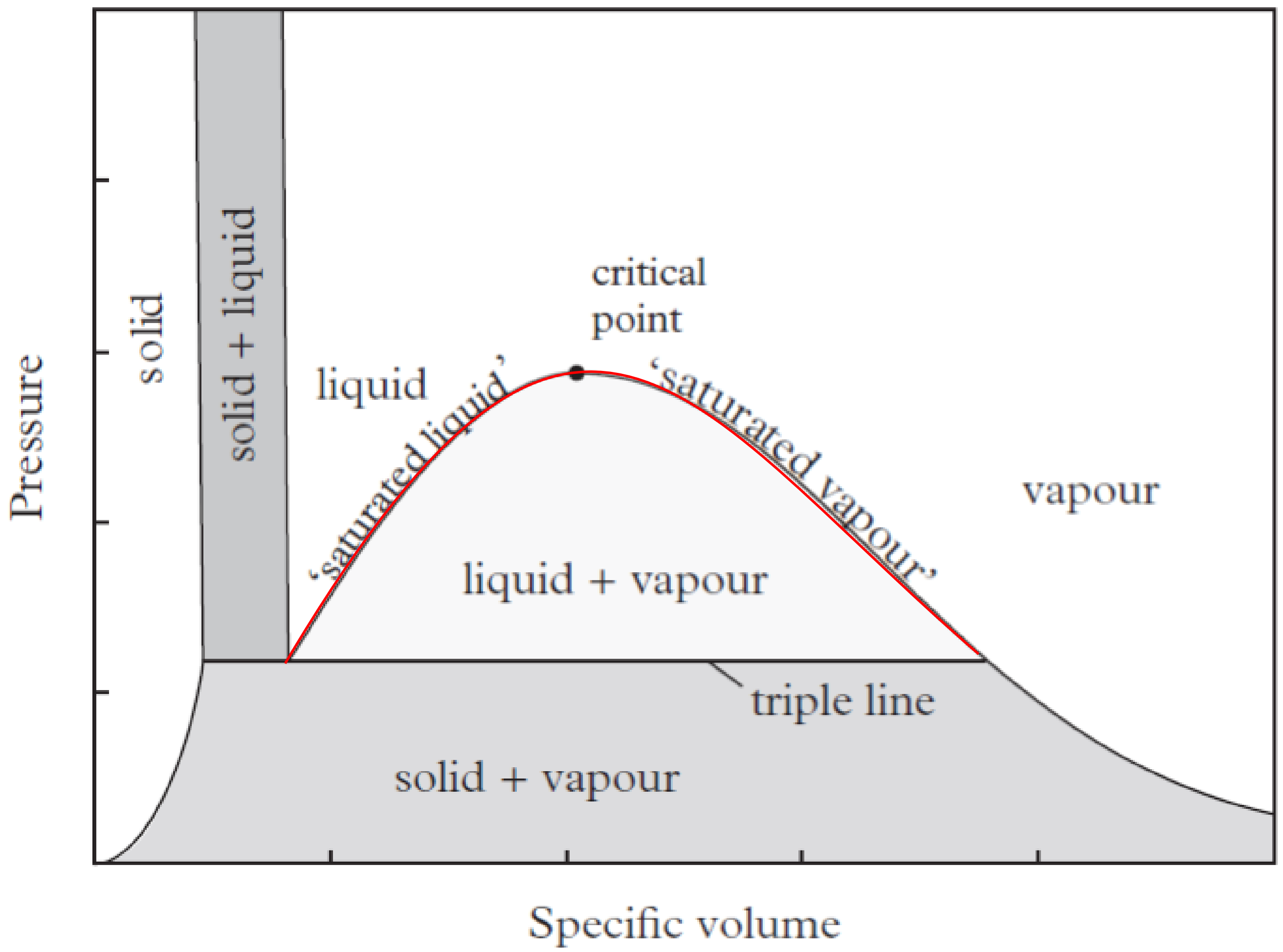


Phase diagram



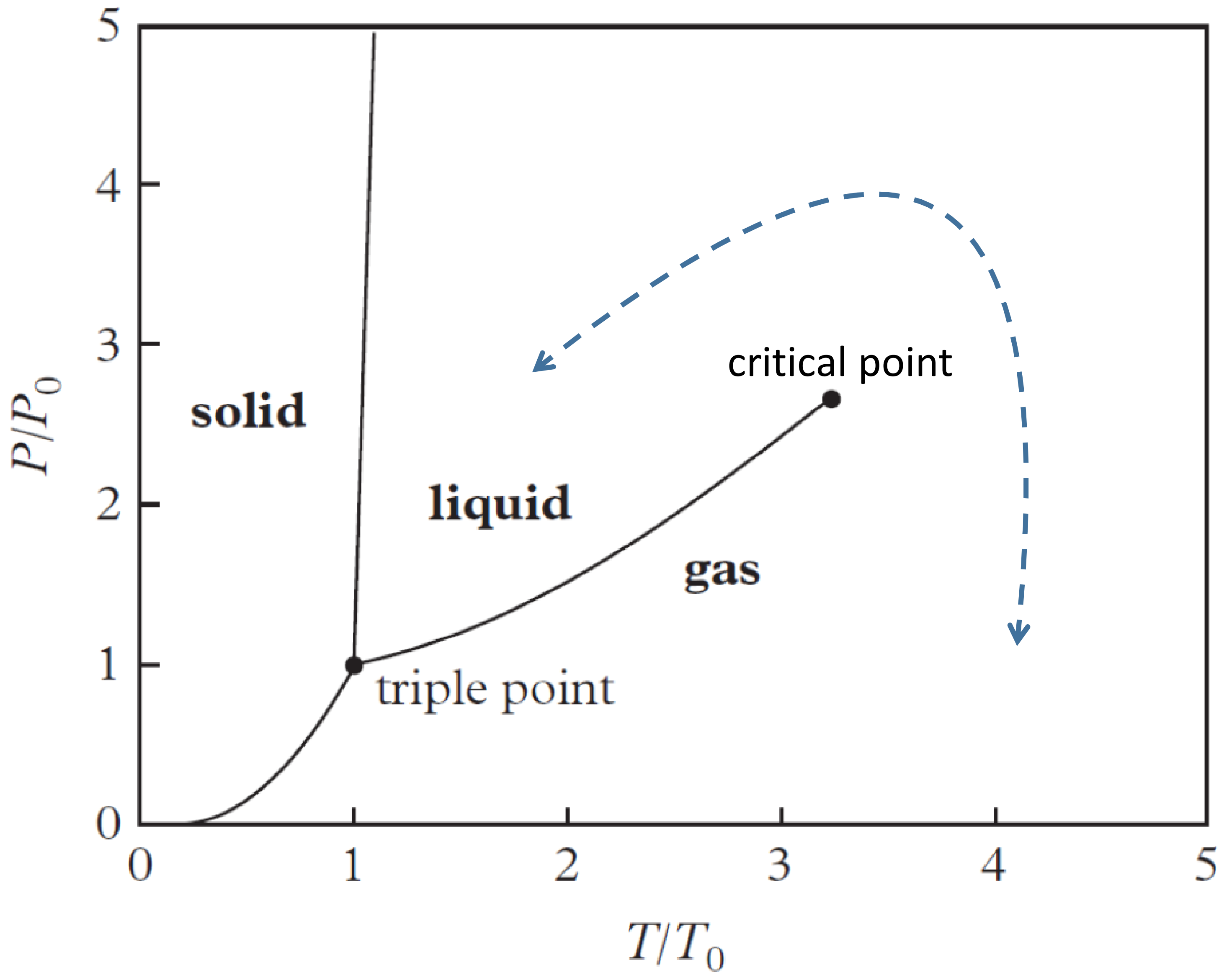
pVT surface of an ordinary substance



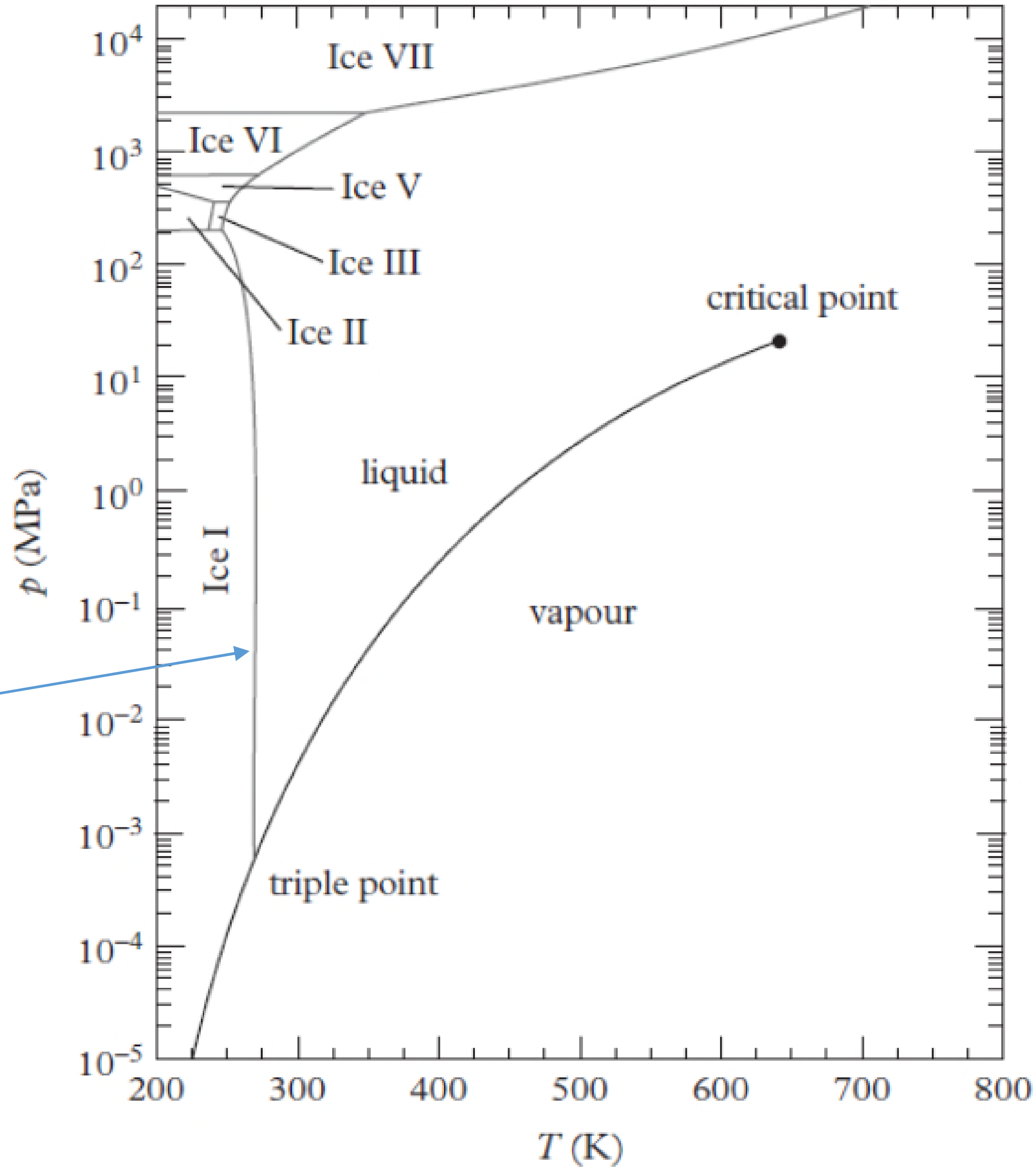


A vapour which would begin to condense if the temperature were lowered is called "**saturated**".
(similarly a pure liquid which would begin to boil if the temperature were raised may be called a "saturated liquid" but this second terminology is less widely used.)

A system can pass between **liquid and gas** without any phase transition!



Phase diagram for water (H_2O)



Unusual case: the slope of the melting line is negative (we will relate this to volume change)

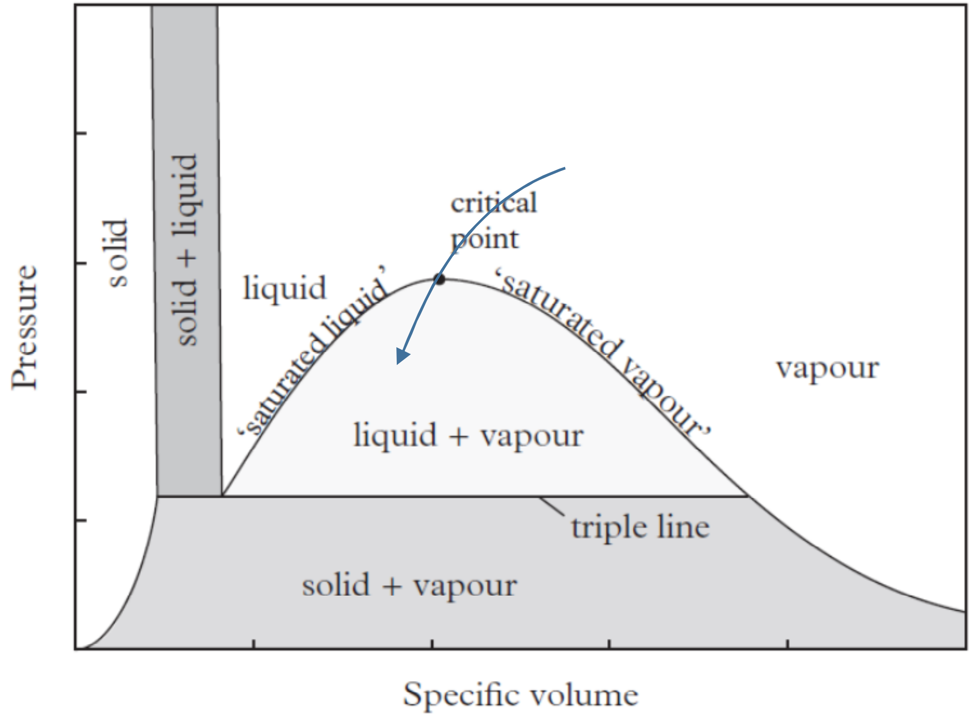
Different types of phase transition

1. ***First order*** phase transition
   - there is a discontinuity in various properties
   - there are metastable phases (superheating and supercooling)
   - in almost all cases there is a discontinuity in S(T) and therefore a latent heat

   - Examples: liquid-vapour; solid-liquid; solid-vapour; superconductivity in presence of applied B field; ferromagnetism; some solid-solid (allotrope) transitions

2. ***Continuous*** phase transition
   - S(T) is continuous but some derivative is not (e.g. continuous S but discontinuity in Cp)
   - no metastable phases and no latent heat

   - Examples: liquid-vapour via the critical point; superconductivity at B=0; many order-disorder transitions in solids; Bose-Einstein condensation



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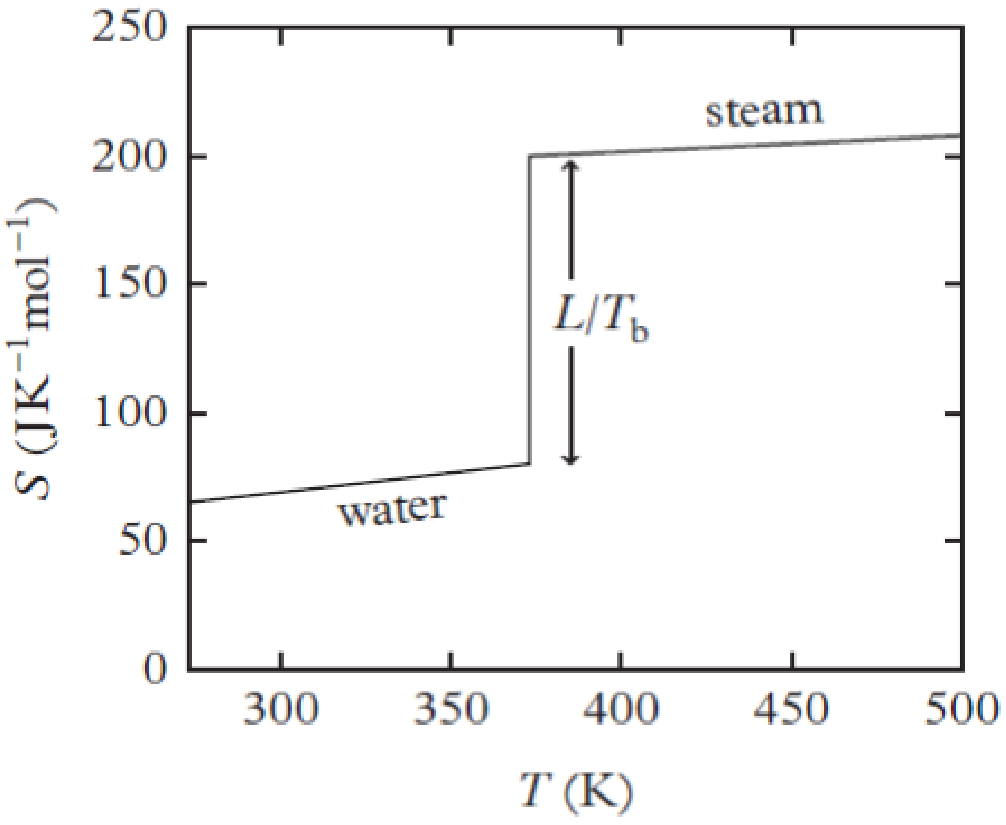
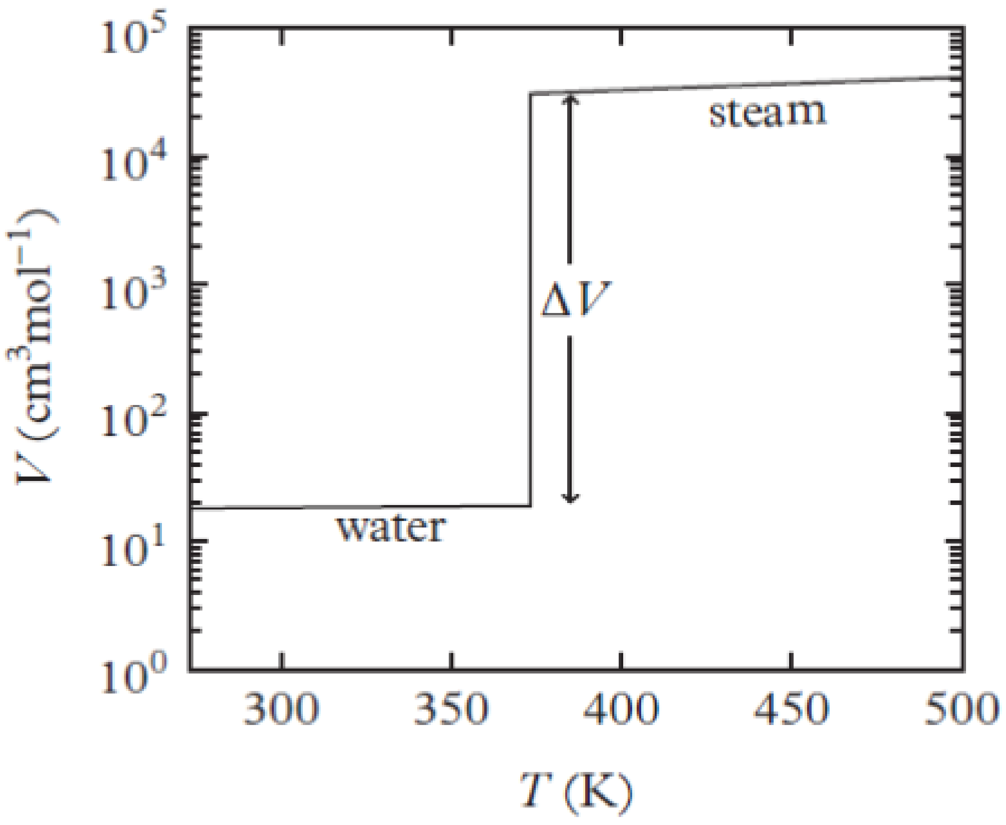
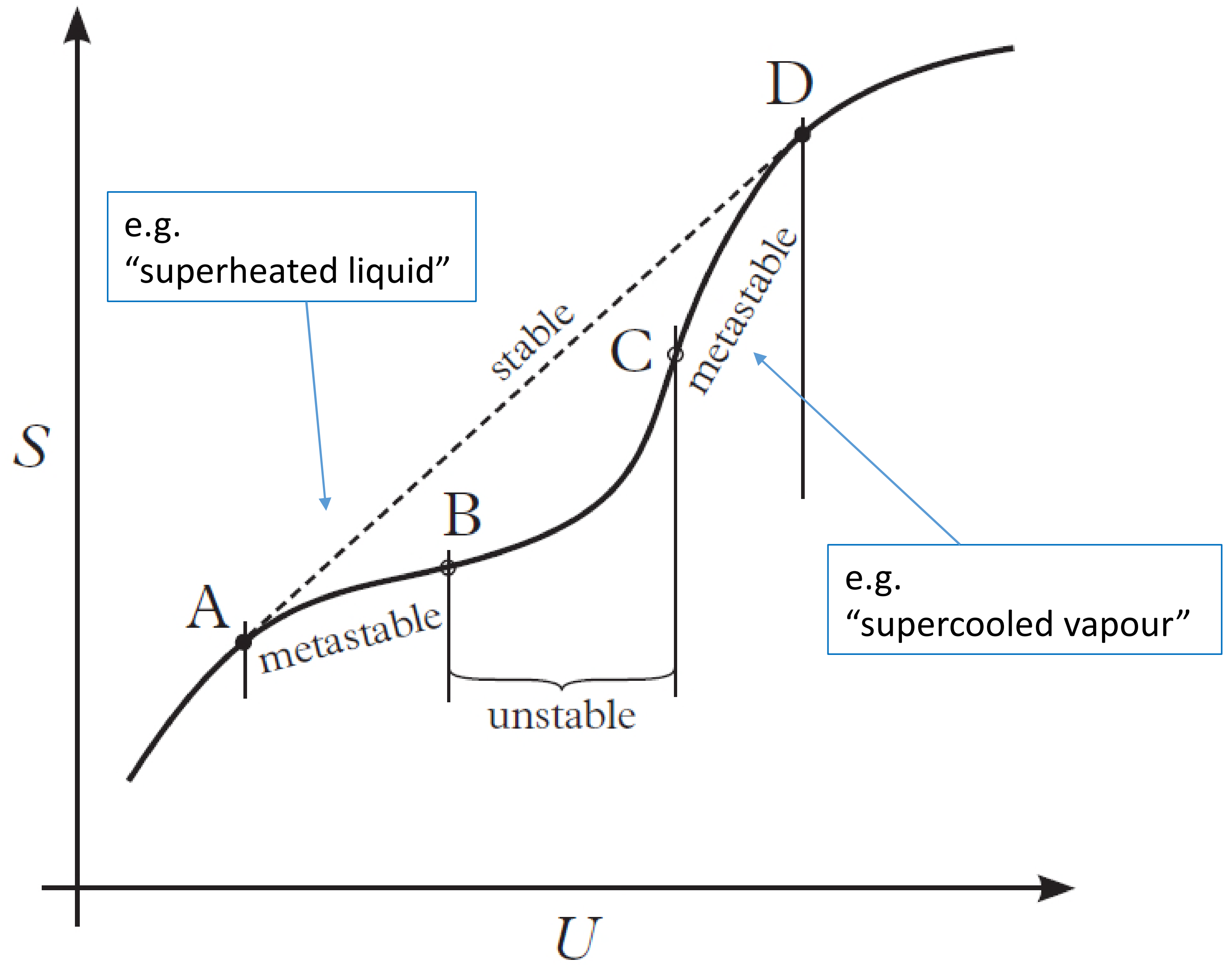
Entropy and volume changes for water (H_20)

Note large volume change (x 1000)







S
U
A
B
C
D
stable
metastable
unstable
metastable
e.g.
“superheated liquid”
e.g.
“supercooled vapour”

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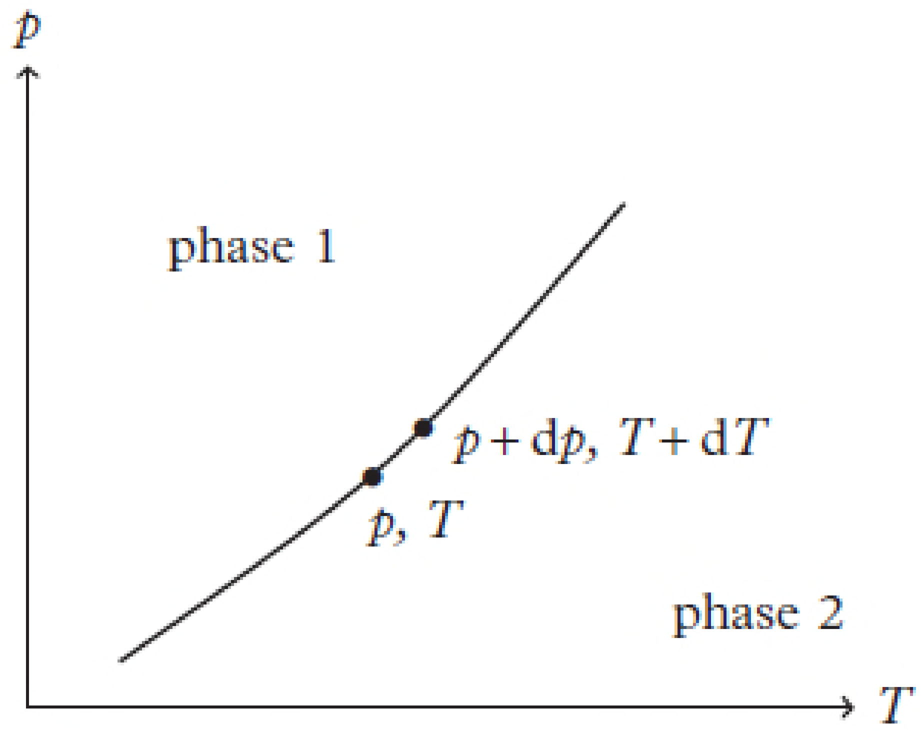
Deriving the **Clausius-Clapeyron equation** (which describes the coexistence curve for a first-order phase transition)



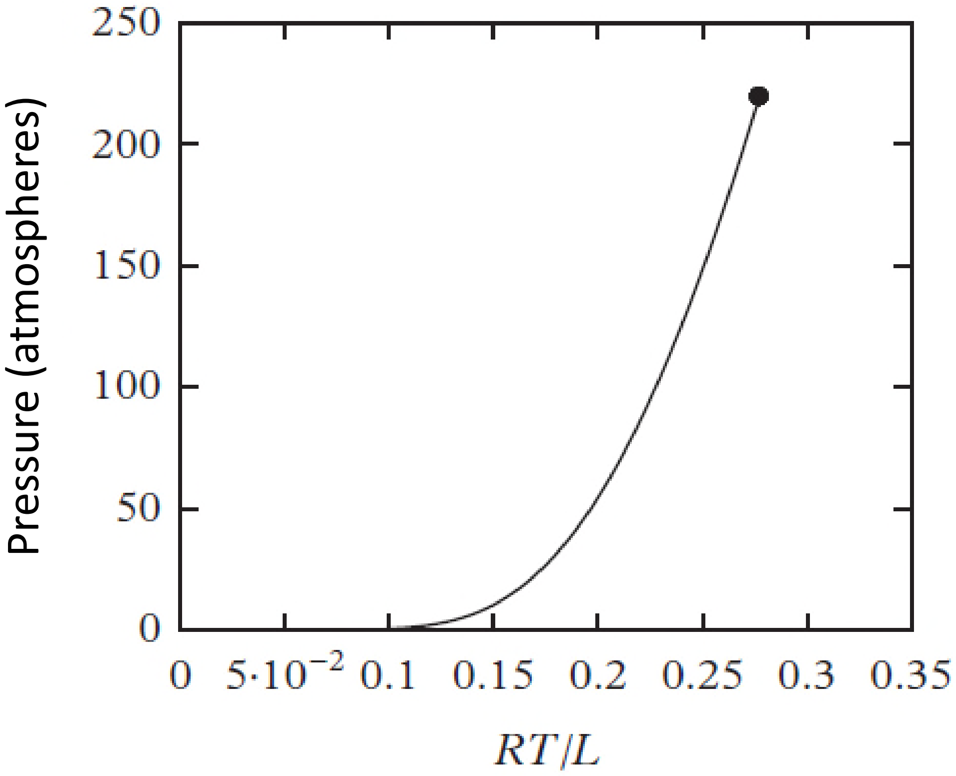
Consider neighbouring points on a co-existence line

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}$$

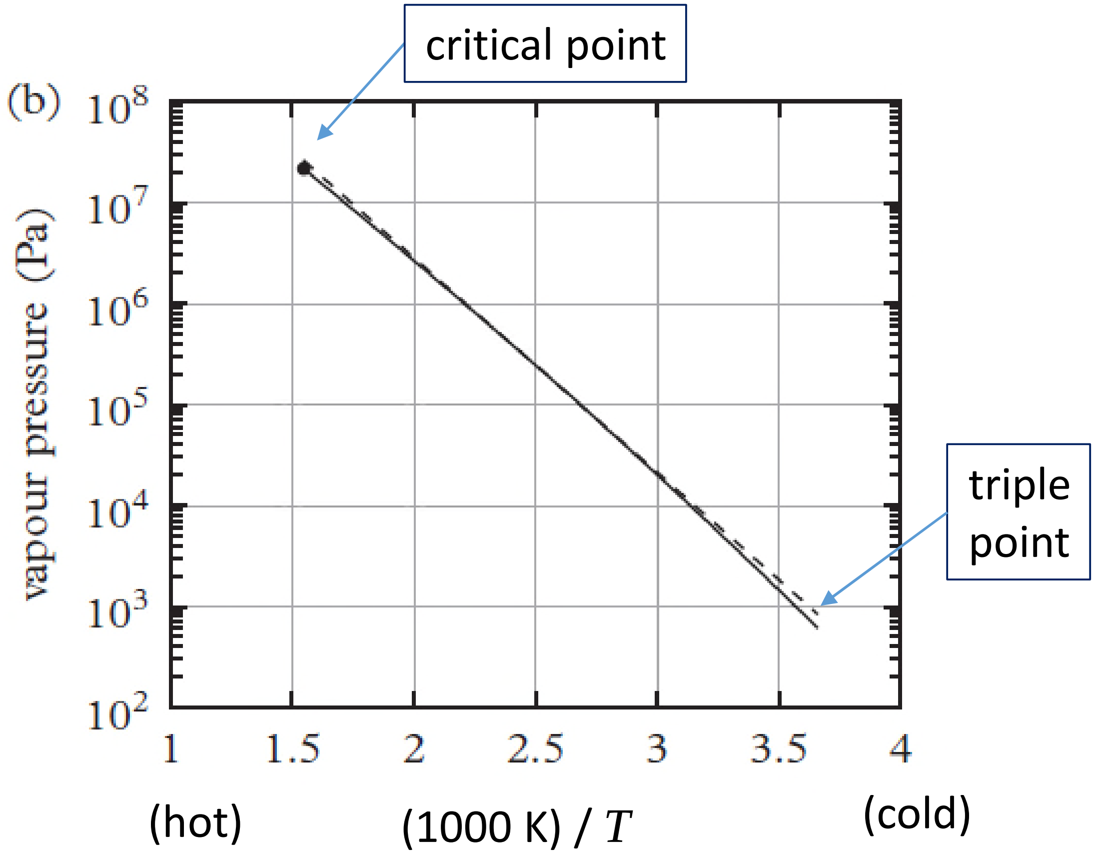
$$p = p_0\, e^{-L/RT}$$

The two plots show the SAME info, plotted vs T and 1/T, lin and log scales

Generic case with L=9 R



pressure vs. inverse-temperature for water



full curve = measured;

dashed = prediction from simple treatment

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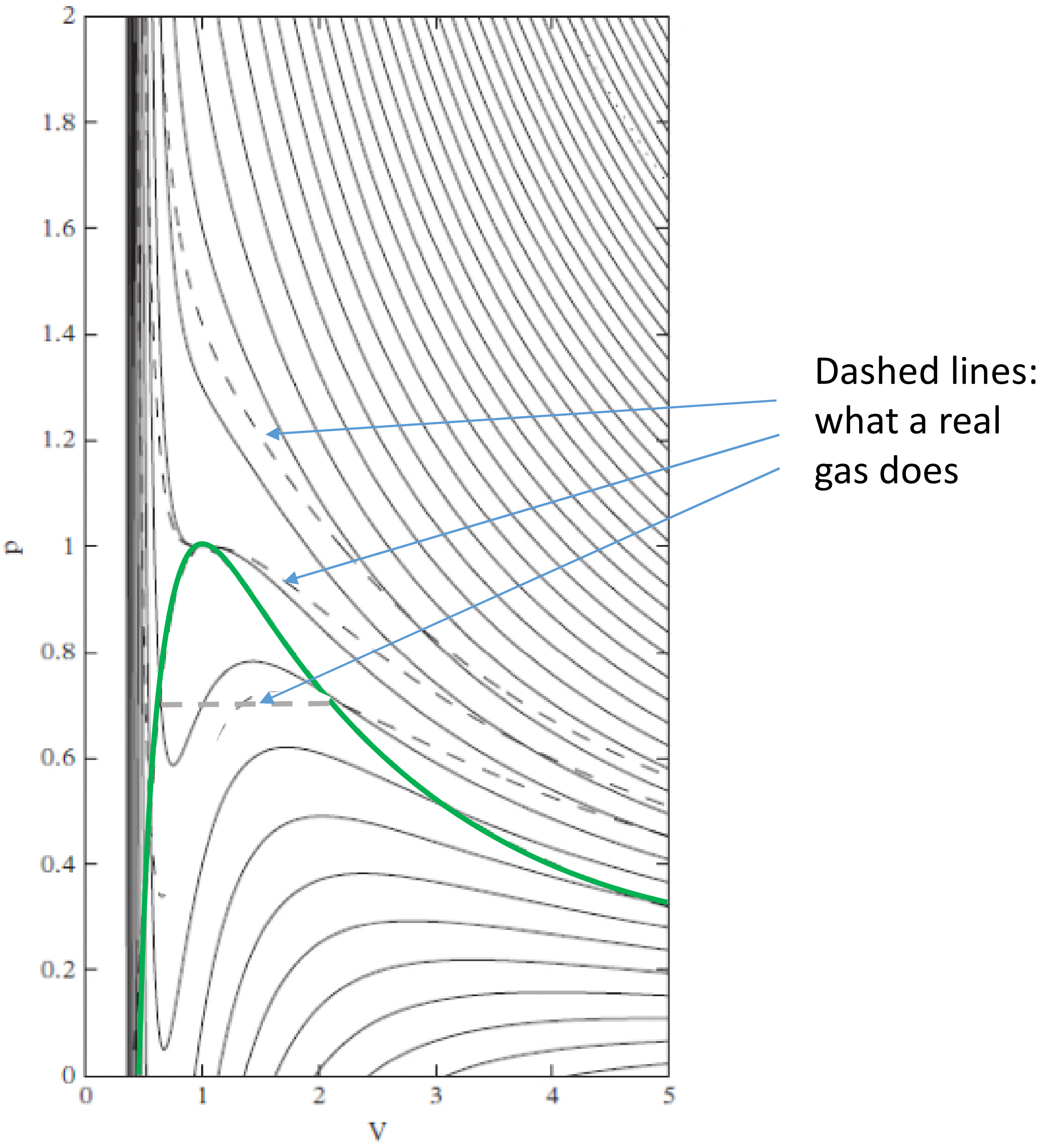
Isotherms predicted by van der Waals equation



Deriving the Maxwell construction