Recall $\frac{\partial G}{\partial \tau} = -\sigma$ $\frac{\partial G}{\partial p} = V$

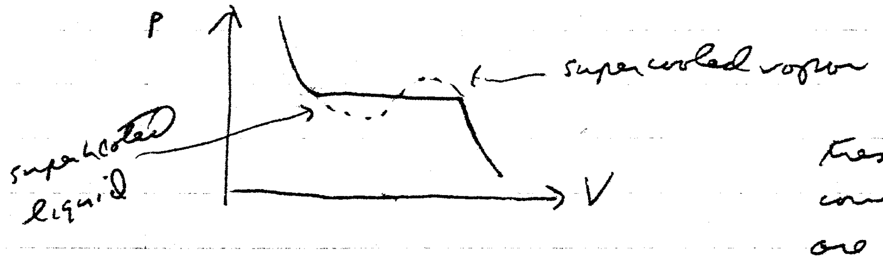
In 1st order transition $\sigma_1 \neq \sigma_2$ $V_1 \neq V_2$ discontinuity of derivatives

And there is latent heat: recall $\frac{dp}{d\tau} = \frac{L}{\tau \Delta v}$
• (coexistent phases)

$$L = \tau \frac{\Delta \sigma}{N}$$

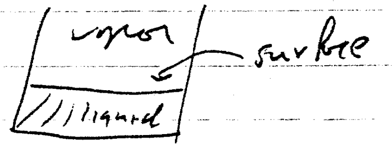
Note: Maxwell construction is much more general than van der Waals.
Homogeneous phase unstable ⇒ coexistence (1st-order transition)

Supercooling and Superheating



these have positive compressibility, and are metastable

Metastability is a consequence of surface effects i.e. interface between vapor and liquid, which we have ignored so far



Superheated liquid will boil — bubbles of gas form
Supercooled vapor will form droplets

10.15

There is ~~competition~~ between formation of thermodynamically favored phase and need to form a surface

E.g., in vapor,

a tiny droplet is dominated by surface tension, and will shrink

For a sufficiently big droplet, surface tension is less important, and it can grow

We need to wait until a sufficiently large droplet can arise as a fluctuation. How long does this take

Probability of fluctuation ~ $e^{\Delta\sigma}$

$\Delta\sigma < 0$, since this is a fluctuation away from (metastable) most probable configuration

For system in contact with a reservoir

$$\sim e^{-\Delta F/\tau}$$

(takes into account change in entropy of reservoir)

Probability of Droplet ~ $e^{-\Delta F/\tau}$

Rate of Droplet formation ~ $(\text{timescale})^{-1} e^{-\Delta F/\tau}$

Now, when we include surface effects

$$dW = -p\,dV + \underbrace{\gamma}_{\uparrow\ \text{surface tension}} \underbrace{dA}_{\text{area}}, \quad dU = dQ + dW$$

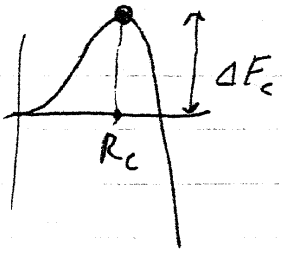
Note sign: when surface area increases, system stores more energy in its surface

If $f = \frac{F_{gas} - F_{liquid}}{V}$

then $(\Delta F)_{droplet} = -f \cdot V + \gamma \cdot A$

Small droplet has large A/V, and tension dominates. ΔF is smallest for given V if droplet is spherical, so consider that case

$$(\Delta F)_{droplet} = -\frac{4\pi}{3} R^3 f + 4\pi R^2 \gamma$$



There is critical size for which droplet can grow

$$0 = -4\pi R_c^2 f + 8\pi R_c \gamma$$

$$\Rightarrow R_c = 2\gamma/f$$

$$\Delta F_c = \frac{16\pi}{3} \gamma^3/f^2$$

And time ~ $e^{\Delta F_c/\tau}$

For some systems, may be a long time –

As droplets form, vapor pressure is reduced, so that equilibrium is eventually attained.

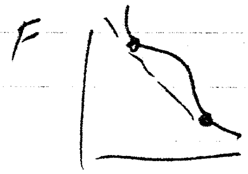
10.17

this theory has limited applicability:

- Wetting: liquid may prefer to condense on walls of container
- Impurities: droplet may form around dust, etc.

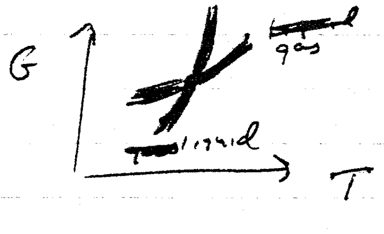
"Second-Order Phase-Transition"

characteristic feature of 1st order phase transition



Helmholtz free energy of homogeneous phase is not concave upward (in some region) ⇒ instability

Hence (neglecting surface effects) can lower F with inhomogeneous phase



Gibbs free energy has discontinuous derivatives (two phases cross)

1st derivatives of G are discontinuous

$$\Delta s = \frac{1}{N}\left[\left(\frac{\partial G}{\partial \tau}\right)_1 - \left(\frac{\partial G}{\partial \tau}\right)_2\right]$$

"1st order"

$$\Delta v = \frac{1}{N}\left[\left(\frac{\partial G}{\partial p}\right)_1 - \left(\frac{\partial G}{\partial p}\right)_2\right]$$

Latent heat

change of Density ($\rho_\ell \neq \rho_g$)

Logic dictates that "2nd order" means 2nd derivs of G are discontinuous.

10.18

Actually, no such transitions are known.
Instead, use "2nd order" to mean that

- 1st derivs are continuous:
  - No latent heat
  - No density discontinuity

- 2nd derivs *diverge*:

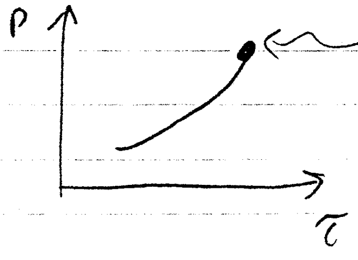
e.g. specific heat $C_p = \tau\left(\frac{\partial\sigma}{\partial\tau}\right)_p = -\tau\left(\frac{\partial^2 G}{\partial\tau^2}\right)_p$

compressibility $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T$

$$C_p \sim (\tau - \underset{\uparrow\ \text{critical temp}}{\tau_c})^{-(\text{power})}$$

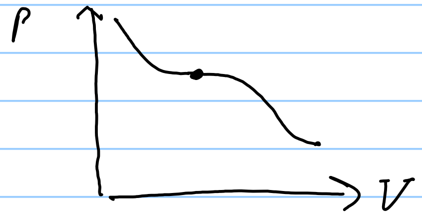
Note: Hard to *tell* experimentally that transition is *really* 2nd order (Latent heat = 0) as opposed to "weakly" 1st order (Latent heat = small)

Example: Gas-Liquid



line of 1st order transitions ends on a second order transition

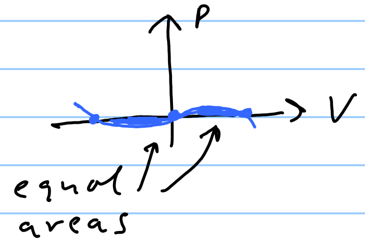
10.19



What happens, in the van der Waals model, as we approach the critical isotherm? This is where

$$\frac{dp}{dV} \to 0 \quad \text{or} \quad \frac{dV}{dp} \to \infty;$$ the compressibility diverges.

For τ just below the critical temperature τ_c, the isotherm is a cubic function such that there are three values of V with the same value of p. The discontinuity in volume at the weakly first order phase transition is determined by the equal area construction.



we define rescaled values of the volume, pressure, and temperature by dividing by the critical values:

$$\hat{V} = V/V_c, \qquad \hat{p} = p/p_c, \qquad \hat{\tau} = \tau/\tau_c.$$

And we define the dimensionless deviation of these variables from their critical values:

$$\delta\hat{V} = \hat{V} - 1 = \frac{V - V_c}{V_c}, \qquad \delta\hat{p} = \hat{p} - 1 = \frac{p - p_c}{p_c}, \qquad \delta\hat{\tau} = \hat{\tau} - 1 = \frac{\tau - \tau_c}{\tau_c}$$

In terms of the rescaled variables, the law of corresponding states is

$$\left(\hat{V} - \tfrac{1}{3}\right)\left(\hat{p} + 3/\hat{V}^2\right) = \tfrac{8}{3}\hat{\tau},$$

or $$\left(\hat{V} - \tfrac{1}{3}\right)\left(\hat{p}\hat{V}^2 + 3\right) = \tfrac{8}{3}\hat{\tau}\hat{V}^2;$$

expanding we have

$$0 = \hat{p}\hat{V}^3 - \left(\tfrac{1}{3}\hat{p} + \tfrac{8}{3}\hat{\tau}\right)\hat{V}^2 + 3\hat{V} - 1,$$

which in terms of the deviations from the critical points

10.20

becomes $0 = (1+\delta\hat{p})\hat{V}^3 - \left(3+\frac{1}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right)\hat{V}^2 + 3\hat{V} - 1$

$$= (\hat{V}-1)^3 + \delta\hat{p}\,(1+\delta\hat{V})^3 - \left(\frac{1}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right)(1+\delta\hat{V})^2,$$

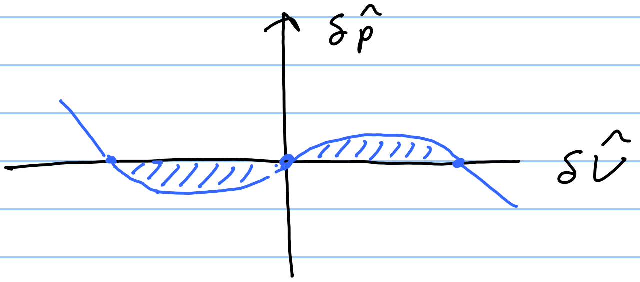
which implies

$$(\delta\hat{V})^3 = \left(-\frac{2}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right) + \left(-3\delta\hat{p}+\frac{2}{3}\delta\hat{p}+\frac{16}{3}\delta\hat{\tau}\right)\delta\hat{V}$$
$$+ \left(-3\delta\hat{p}+\frac{1}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right)\delta\hat{V}^2 - \delta\hat{p}\,\delta\hat{V}^3$$
$$= \left(-\frac{2}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right) + \left(-\frac{7}{3}\delta\hat{p}+\frac{16}{3}\delta\hat{\tau}\right)\delta\hat{V}$$
$$+ \left(-\frac{8}{3}\delta\hat{p}+\frac{8}{3}\delta\hat{\tau}\right)\delta\hat{V}^2 - \delta\hat{p}\,\delta\hat{V}^3$$

So far we have made no approximations; we have merely rewritten the van der Waals equation of state in terms of different variables. But now suppose V, p, and τ are close to their critical values, so that

$$\delta\hat{V},\ \delta\hat{p},\ \delta\hat{\tau} \ll 1.$$

In that case, we can neglect the terms of order $\delta\hat{V}^2$ and $\delta\hat{V}^3$ on the right-hand side of this equation, because they are higher order in small quantities than terms we have kept. Furthermore, the Maxwell equal area construction requires the constant term to vanish. Thus



$$-\frac{2}{3}\delta\hat{p} + \frac{8}{3}\delta\hat{\tau} = 0 \Rightarrow \delta\hat{p} = 4\delta\hat{\tau},$$

and the linear term becomes $\left(-\frac{7}{3}\delta\hat{p}+\frac{16}{3}\delta\hat{\tau}\right)\delta\hat{V} = (-4\delta\hat{\tau})\delta\hat{V}$.

We have found that close to the critical point the equation of state is

$$\delta\hat{V}^3 = (-4\delta\hat{\tau})\delta\hat{V} + \text{higher order}$$

10.21

For $\tau < \tau_c$ where have $\delta\hat{\tau} < 0$, and the stable solutions for volume as a function of temperature are
$$\delta\hat{V} = \pm\left(-4\,\delta\hat{\tau}\right)^{1/2} = \pm 2\left(\frac{\tau_c-\tau}{\tau_c}\right)^{1/2}$$

Thus the discontinuity in the volume is
$$\frac{V_{gas} - V_{liquid}}{V_c} = 4\left(\frac{\tau_c-\tau}{\tau_c}\right)^{1/2}.$$

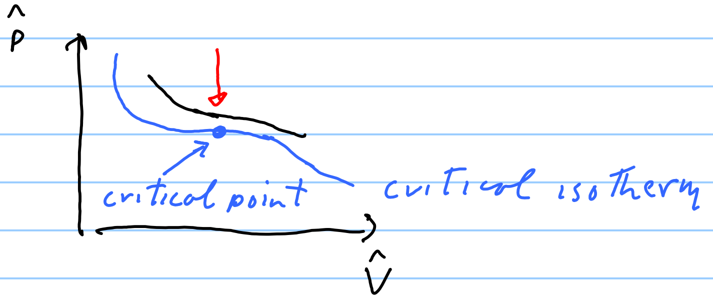
A similar result applies to the discontinuity in the density ρ:
$$\rho \propto 1/V \Rightarrow \frac{\Delta\rho}{\rho} = -\frac{\Delta V}{V} \Rightarrow \frac{\rho_{liquid} - \rho_{gas}}{\rho_c} = 4\left(\frac{\tau_c-\tau}{\tau}\right)^{\frac{1}{2}}$$

To derive the factor of 4 we used the details of the van der Waals model. But the observation that the volume discontinuity scales like $(-\delta\hat{\tau})^{1/2}$ is more general. To derive the scaling, we only needed to know that the critical point is a cubic inflection point in the p-V plane on the critical isotherm.

In experiments with liquid-gas phase transitions, one finds that the density discontinuity follows a "universal" scaling law applying to many different fluids:
$$\frac{\rho_{liquid} - \rho_{gas}}{\rho_c} \sim \left(\frac{\tau_c-\tau}{\tau_c}\right)^{\beta}$$
but the scaling exponent β is $\beta \simeq .32$ rather than $\beta = .5$ as we predicted.

We can also use the van der Waals model to predict how the isothermal compressibility behaves near the critical point. As we'll see, we get a somewhat different formula for the compressibility depending on whether we approach the critical temperature T_c from above or below.

First consider $\tau > \tau_c$. Our goal is to find the minimal slope $\left(\frac{\partial p}{\partial V}\right)_\tau$ along the isotherm.



Recall again the equation of state near the critical point:

$$\delta\hat{V}^3 = \left(-\tfrac{2}{3}\delta\hat{p} + \tfrac{8}{3}\delta\hat{\tau}\right) + \left(-\tfrac{7}{3}\delta\hat{p} + \tfrac{16}{3}\delta\hat{\tau}\right)\delta\hat{V} + \text{higher order}$$

(where we neglect the higher-order terms when $\delta\hat{V}$, $\delta\hat{p}$, $\delta\hat{\tau}$ are all <u>small</u>). Now vary the volume and pressure with the temperature held fixed:

$$3\,\delta\hat{V}^2(d\,\delta\hat{V}) = -\tfrac{2}{3}(d\,\delta\hat{p}) - \tfrac{7}{3}(d\,\delta\hat{p})\,\delta\hat{V} + \left(-\tfrac{7}{3}\delta\hat{p} + \tfrac{16}{3}\delta\hat{\tau}\right)(d\,\delta\hat{V}) + \cdots$$

But as we approach the critical isotherm from above, the minimum slope occurs at $\delta\hat{V} = 0$, where this equation becomes

$$0 = -\tfrac{2}{3}(d\,\delta\hat{p}) + \left(-\tfrac{7}{3}\delta\hat{p} + \tfrac{16}{3}\delta\hat{\tau}\right)(d\,\delta\hat{V}).$$

Furthermore, for $\delta\hat{V} = 0$, the constant term on the right-hand side of the equation of state is zero, so

$$-\tfrac{2}{3}\delta\hat{p} + \tfrac{8}{3}\delta\hat{\tau} = 0 \Rightarrow \delta\hat{p} = 4\,\delta\hat{\tau} \Rightarrow$$

$$0 = -\tfrac{2}{3}(d\,\delta\hat{p}) + (-4\,\delta\hat{\tau})(d\,\delta\hat{V}) \Rightarrow$$

$$\left(\frac{\partial\,\delta\hat{p}}{\partial\,\delta\hat{V}}\right)_{\delta\hat{\tau}} = (-6)\,\delta\hat{\tau}.$$

10.22A

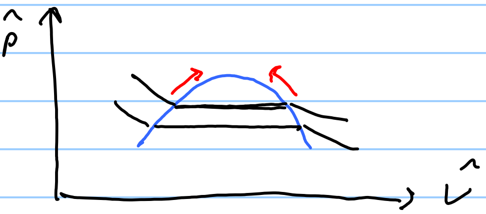
Recalling $\delta\hat{p} = \frac{p-p_c}{p_c}$ and $\delta\hat{V} = \frac{V-V_c}{V_c}$, we have:

$$\left(\frac{\partial p}{\partial V}\right)_\tau = \frac{p_c}{V_c}\left(\frac{\partial \hat{p}}{\partial \hat{V}}\right)_\tau = \frac{p_c}{V_c}(-6)\,\delta\hat{\tau}$$

The isothermal compressibility is defined as

$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\tau$, and our conclusion becomes

$$\boxed{K_T^{-1} = -V\left(\frac{\partial p}{\partial V}\right)_\tau \cong 6\,p_c\left(\frac{\tau-\tau_c}{\tau_c}\right)} \quad \text{for } \tau > \tau_c$$



Now consider approaching the critical isotherm from $\tau < \tau_c$. The computation is similar to before, except now we approach from either the gas or liquid phase, with the value of $\delta\hat{V}$ fixed by the Maxwell equal area construction, so that

$$\delta\hat{V} = \pm 2\,(-\delta\hat{\tau})^{1/2} \quad \text{and} \quad \delta\hat{p} = 4\,\delta\hat{\tau}.$$

The above equation relating $d\,\delta\hat{p}$ and $d\,\delta\hat{V}$ becomes

$$3(\delta\hat{V})^2(d\,\delta\hat{V}) = -\tfrac{2}{3}(d\,\delta\hat{p}) - (4\,\delta\hat{\tau})(d\,\delta\hat{V})$$

where the left-hand side is $12(-\delta\hat{\tau})(d\,\delta\hat{V})$ so that

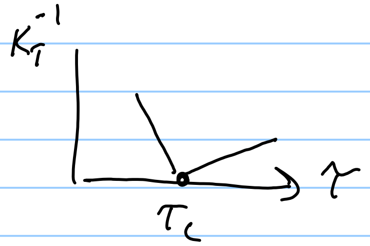
$$\tfrac{2}{3}(d\,\delta\hat{p}) = 8\,\delta\hat{\tau}\,(d\,\delta\hat{V}) \Rightarrow \left(\frac{\partial\,\delta\hat{p}}{\partial\,\delta\hat{V}}\right) = 12\,\delta\hat{\tau}$$

and

$$\boxed{K_T^{-1} = -V\left(\frac{\partial p}{\partial V}\right)_\tau \cong 12\,p_c\left(\frac{\tau_c-\tau}{\tau_c}\right)} \quad \text{for } \tau < \tau_c$$

The factors 6 and 12 were derived using details of the van der Waals model, but two of our predictions are more general, following only from the property that the critical isotherm has a cubic inflection point:

1) For both $\tau > \tau_c$ and $\tau < \tau_c$, the isothermal compressibility diverges like $\kappa_T \sim |\tau - \tau_c|^{-\gamma}$ where $\gamma = 1$

2) 

The (absolute value of) the slope of κ_T^{-1} as a function of τ is twice as large for $\tau < \tau_c$ as for $\tau > \tau_c$.

In experiments with actual liquid-gas transitions, the divergence of κ_T does follow a universal scaling law obeyed by various different fluids, but with an exponent $\gamma \simeq 1.3$ rather than our predicted value $\gamma = 1$.