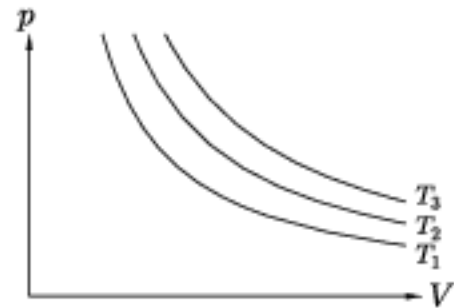


Lecture 26. *Real Gas*

- In this lecture, we will move beyond the ideal gas description!



Isotherms of ideal gas

$$pV = n_{\text{moles}}RT$$

Description fails at high p or small volume

- For instance: liquefaction
- Intermolecular interactions start to matter

van der Waals, Dieterici, virial expansion,....

The van der Waals gas

Added features:

- (1) Intermolecular attractive interactions
- (2) Non-zero size of the molecules

$$\left(p + \frac{a}{V_m^2}\right) (V_m - b) = RT$$

$V_m = V/n_{\text{moles}}$
Volume per mole

- b reduces the volume available (repulsion)
- a represents the strength of attraction
- It reduces to ideal gas law at low density

Origin of the a term $\left(p + \frac{a}{V_m^2}\right) (V_m - b) = RT$

Number of nearest neighbors is proportional to n_{moles}/V :

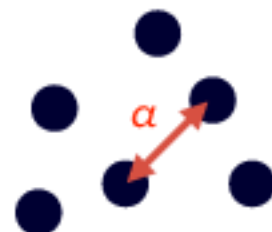
Attractive intermolecular interaction lowers the total potential energy by $\frac{an_{\text{moles}}^2}{V}$

A change in volume thus changes the energy by: $-\frac{an_{\text{moles}}^2 dV}{V^2}$

This looks like an effective pressure (due to the other molecules) with $p_{\text{eff}} = -a \frac{n_{\text{moles}}^2}{V^2} = -\frac{a}{V_m^2}$.

Actual pressure: $p_{\text{ideal}} = p - p_{\text{eff}} = p + \frac{a}{V_m^2}$

And we get (adding the b term as well): $\left(p + \frac{a}{V_m^2}\right) (V_m - b) = RT$.



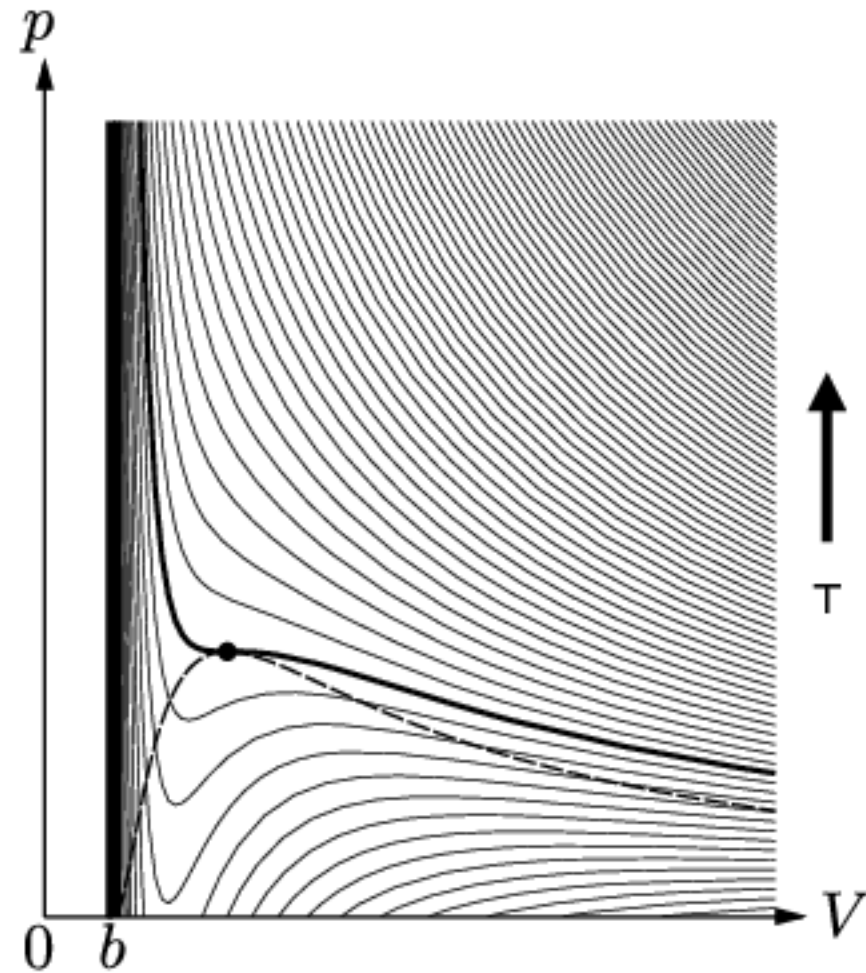
Isotherms

For one mole:

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\rightarrow pV^3 - (pb + RT)V^2 + aV - ab = 0$$

Lower T: less and less as an ideal gas; S-shape with a minimum and a maximum

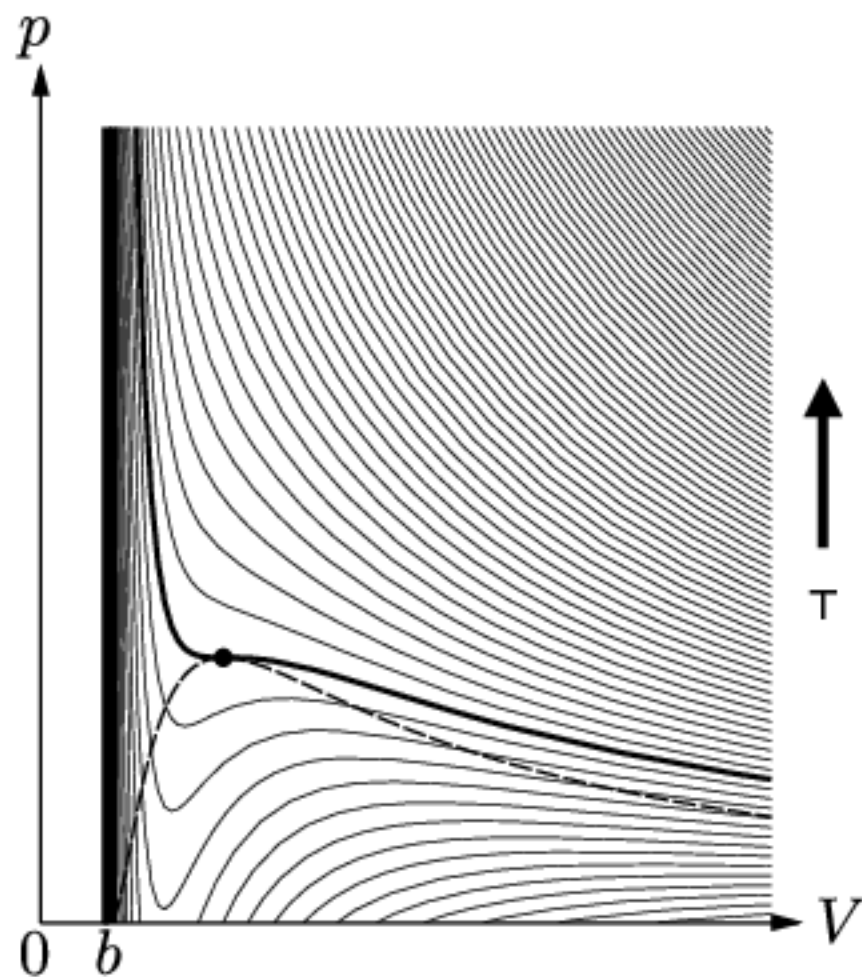


Isothermal compressibility? $\kappa_T = -\frac{1}{V}(\partial V/\partial p)_T$
($1/p$ for an ideal gas)

We could have negative compressibility!

In this case, if external p up, this leads to increase in V , corresponding to negative work, it then provides energy to amplify the pressure fluctuation; this leads to an **unstable** system!

- This happens when the system starts to have a S-shape, lower than a given *temperature*
- This is called the *critical isotherm* and the point of inflection is known as the *critical point*



Critical point

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \longrightarrow p = \frac{RT}{V - b} - \frac{a}{V^2}$$

Inflection point: first and second derivative of $p(V)$ are zero

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$
$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$
$$\left\{ \begin{array}{l} T_c = \frac{8a}{27Rb} \quad \text{Critical temperature} \\ V_c = 3b \quad \text{Critical volume} \\ p_c = \frac{a}{27b^2} \quad \text{Critical pressure} \\ \frac{p_c V_c}{RT_c} = \frac{3}{8} = 0.375, \text{ Independent of } a \text{ and } b \end{array} \right.$$

Isothermal compressibility diverges:

$$\kappa_T = -\frac{1}{V}(\partial V/\partial p)_T \rightarrow \infty$$

System is unstable for $T < T_c$

Helmholtz: $p = -(\partial F / \partial V)_T$

$$F = f(T) - RT \ln(V - b) - \frac{a}{V} \quad \text{For one mole}$$

Constant T and p (Gibbs function)

Gibbs: $G = F + pV = f(T) - RT \ln(V - b) - \frac{a}{V} + pV$

Multi-valued function!

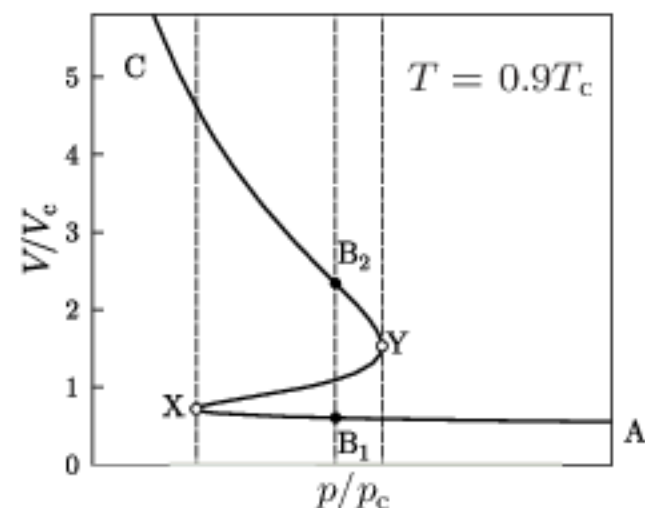
System will remain on the lower path (ABC)

B corresponds to two points B_1 and B_2 on the volume curve

We have equilibrium between the two phases!

B leads to “two-phase region”

Can exist for a limited period of time



Superheated liquid

cl

B₁ and B₂: coexistence because Gibbs is equal at these points

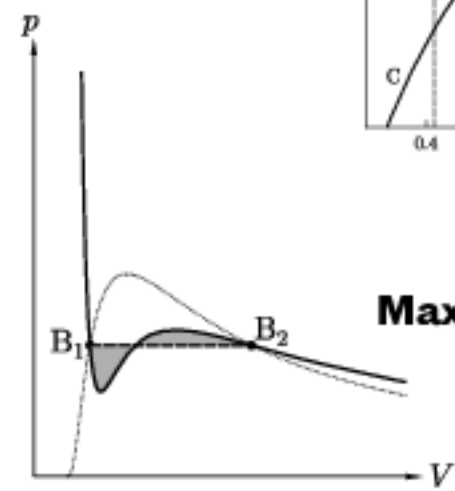
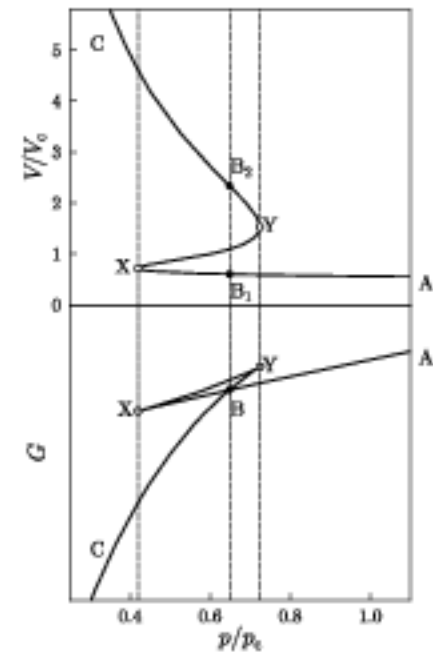
$$G(p_1, T) = G(p_0, T) + \int_{p_0}^{p_1} \left(\frac{\partial G}{\partial p} \right)_T dp. \quad \left(\frac{\partial G}{\partial p} \right)_T = V$$

$$G(p_1, T) = G(p_0, T) + \int_{p_0}^{p_1} V dp$$

Between B₁ and B₂

$$G(p_{B_2}, T) = G(p_{B_1}, T) + \int_{B_1}^{B_2} V dp$$

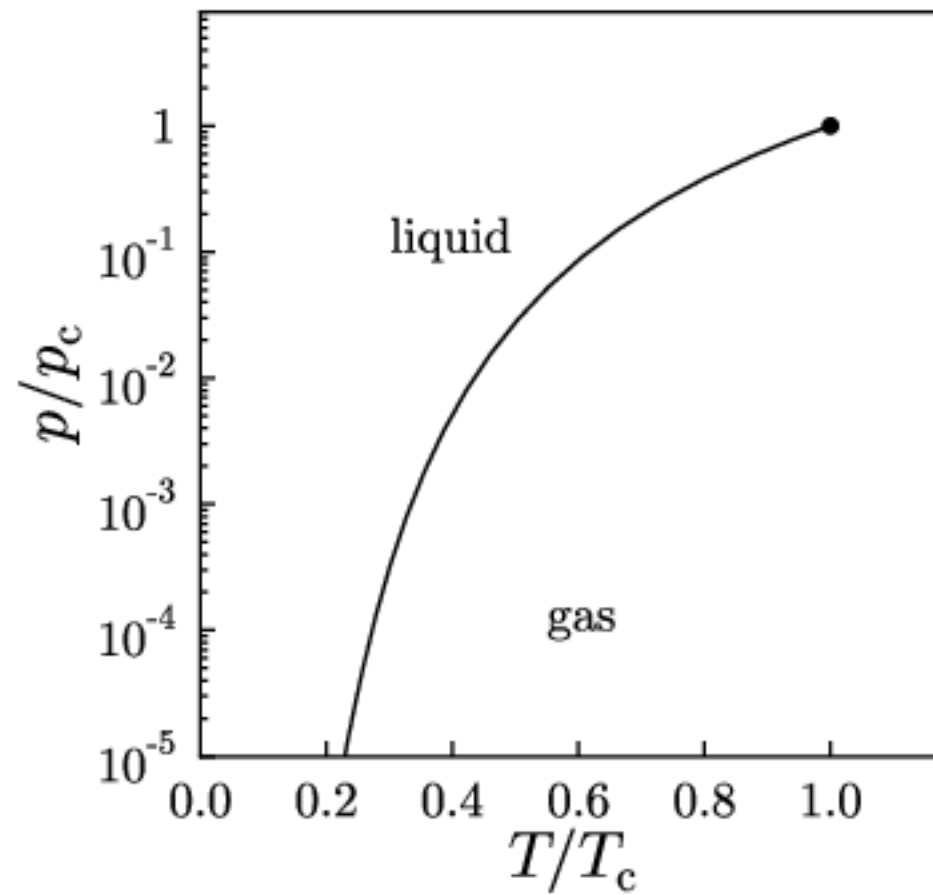
→ $\int_{B_1}^{B_2} V dp = 0$



Maxwell construction

To identify the two points!

No sharp transition above critical point



Dieterici equation

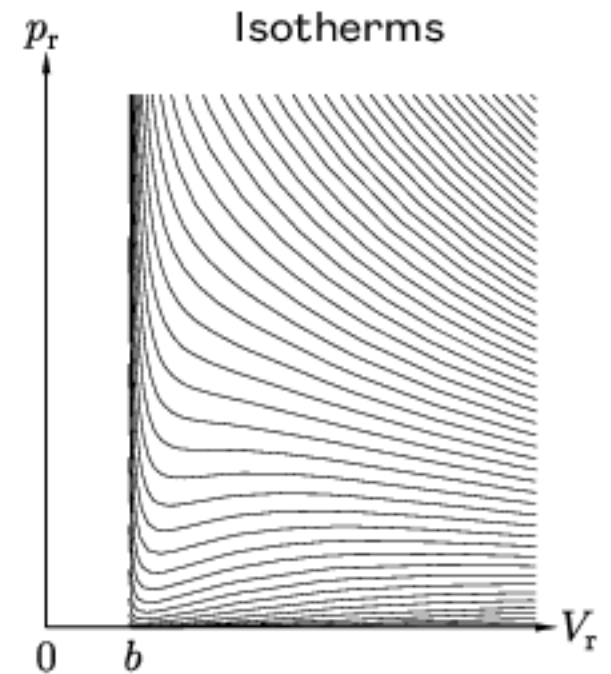
$$p = p_{\text{repulsive}} + p_{\text{attractive}}$$

- Repulsive term (hard-sphere interaction): $p_{\text{repulsive}} = \frac{RT}{V - b}$
- Attractive term: $p_{\text{attractive}} = -\frac{a}{V^2}$

Berthelot equation: $p_{\text{attractive}} = -\frac{a}{TV^2}$

Dieterici: $p = p_{\text{repulsive}} \exp\left(-\frac{a}{RTV}\right)$

$$p(V_m - b) = RT \exp\left(-\frac{a}{RTV_m}\right)$$



Critical point in the Dieterici model

Critical point: $\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \left(\frac{\partial p}{\partial V}\right)_T = 0, \quad \longrightarrow \quad T_c = \frac{a}{4Rb}, \quad p_c = \frac{a}{4e^2 b^2}, \quad V_c = 2b$

$\longrightarrow \quad \frac{p_c V_c}{RT_c} = \frac{2}{e^2} = 0.271$

	Ne	Ar	Kr	Xe
$p_c V_c / RT_c$	0.287	0.292	0.291	0.290

For van der Waals:

$$\frac{p_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

Virial expansion

We can also consider that the ideal gas law is just the zeroth order term in a Taylor series.

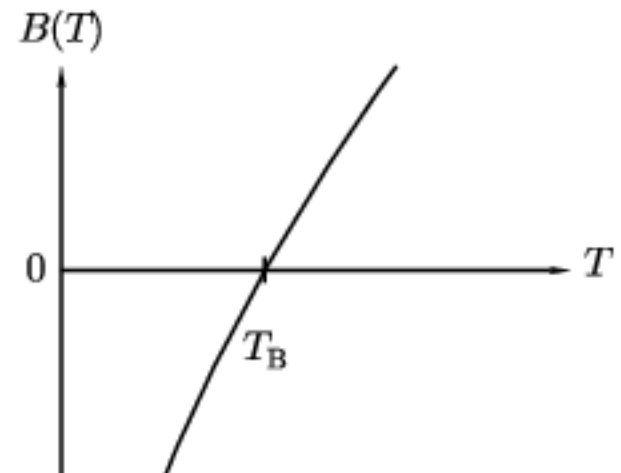
We know that if the volume is very large, the IGL is very accurate (since we can neglect interactions, both short and long ranges)

So, it would appear that expanding with respect to $1/V$ would be a good idea.

This is the motivation behind the *virial expansion*.

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

The **virial coefficients** are temperature dependent.



Boyle temperature: where $B(T)$ is zero and Boyle's law is obeyed

$$p \propto 1/V$$

Application to van der Waals equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V} \left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

$$\frac{pV}{RT} = \left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{VRT}$$

Boyle Temperature: $T_B = \frac{a}{bR}$

The law of corresponding states

For different substances, the size of the molecules (which controls b in the van der Waals model) and the strength of the intermolecular interactions (which controls a in the van der Waals model) will vary, and their phase diagrams will be different.

For example, the critical temperatures and pressures for different gases are different. However, the phase diagram of substances should be the same when plotted in reduced coordinates, which can be obtained by dividing a quantity by its value at the critical point.

We replace p , V , T , by their reduced coordinates: $\tilde{p} = \frac{p}{p_c}$, $\tilde{V} = \frac{V}{V_c}$, $\tilde{T} = \frac{T}{T_c}$

The phase diagrams become pretty much identical

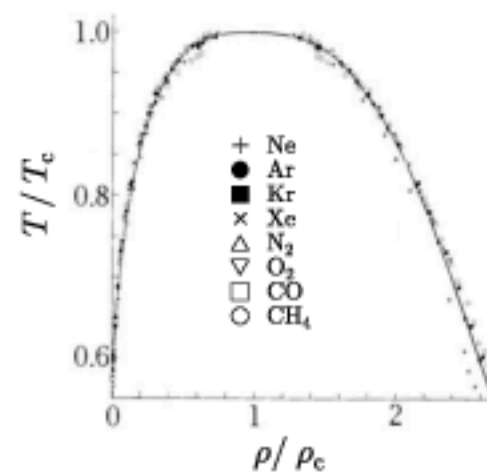
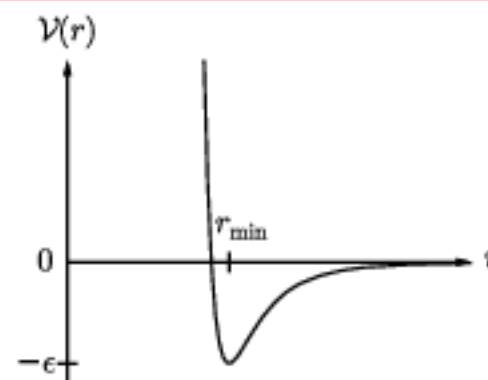
Application to van der Waals gas

$$\left\{ \begin{array}{l} T_c = \frac{8a}{27Rb} \quad \text{Critical temperature} \\ V_c = 3b \quad \text{Critical volume} \\ p_c = \frac{a}{27b^2} \quad \text{Critical pressure} \end{array} \right.$$

There is a repulsive region at small distances, a stable minimum at a separation r_{\min} corresponding to a potential well depth of $-\epsilon$ and then a long range attractive region at larger distances.

For different molecules, the length scale r_{\min} and the energy scale ϵ may be different, but these two parameters together are sufficient to give a reasonable description of the intermolecular potential energy.

The parameter r_{\min} sets the scale of the molecular size and the parameter ϵ sets the scale of the intermolecular interactions.



Summary

Attractive intermolecular interactions and the non-zero size of molecules lead to departures from ideal gas behavior.

The Dieterici equation of state is $p(V_m - b) = RTe^{-a/RTV_m}$