Non-ideal Classical gas

- Typical p-V-T diagram of a pure substance and projections into 2D diagrams
- Liquid-gas transition needs interactions
- Non-ideal classical gas within canonical ensemble theory
- Deviation from ideal gas behavior
- Critical point: No distinction between gas and liquid beyond critical point

This serves as a part on Introduction to Phase Transitions.

I. Behavior of Real (Simple) Substances

- Different phases (e.g. solid, liquid, vapour) for different conditions
- If everything were of ideal classical gas behavior

  $$pV = NkT$$

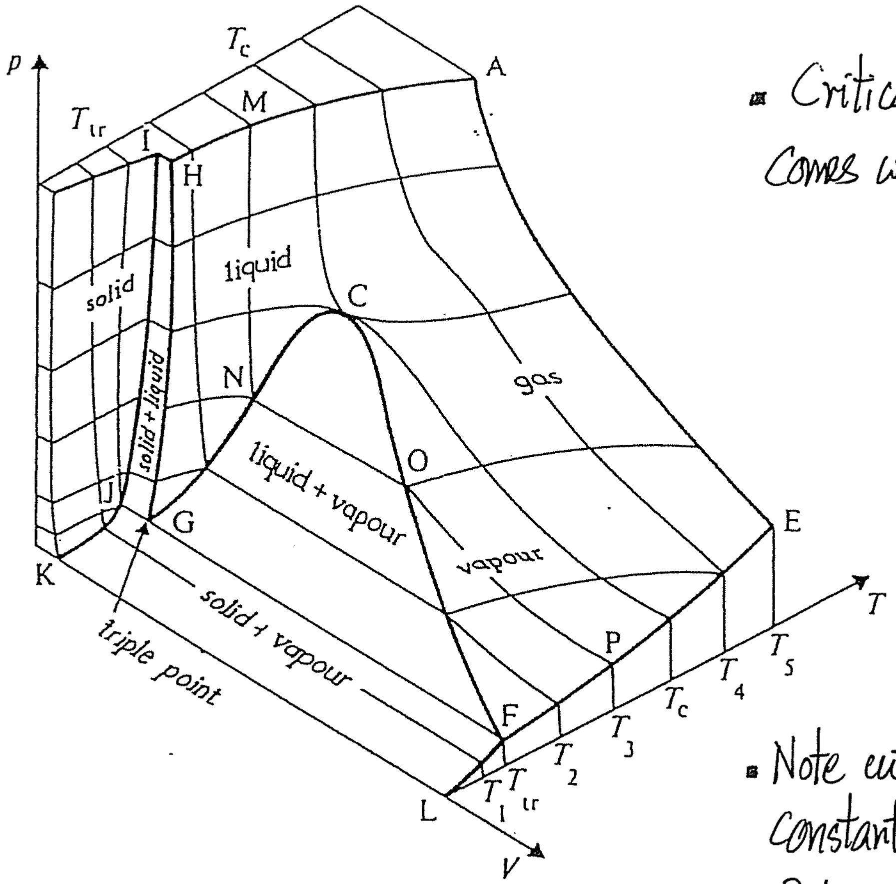
  No fun! No phases!

  Note: Ideal gas means no interaction between particles (atoms/molecules)

  $\Rightarrow$ No two-body interaction terms in potential energy term $V(\{\vec{r}_1, \ldots, \vec{r}_N\})$ in Hamiltonian
- Thus, particle-particle interaction is needed for gas to become liquid/solid.

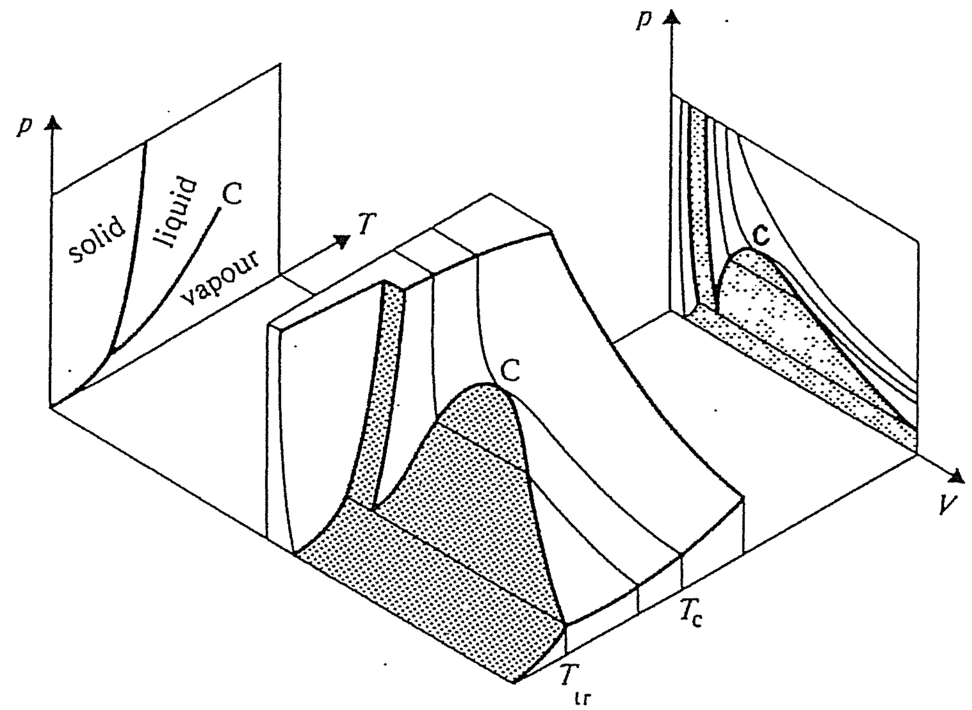
Typical Behavior

The p–V–T relation of a pure substance.



- Critical point C comes with (T_c, p_c, V_c)
- Note cuts at constant T (isotherms)
- Below T_c (critical temp.), vapour undergoes phase transition(s) on compression.

The two most useful projections of the p–V–T surface. Mixed phase regions are shown shaded.

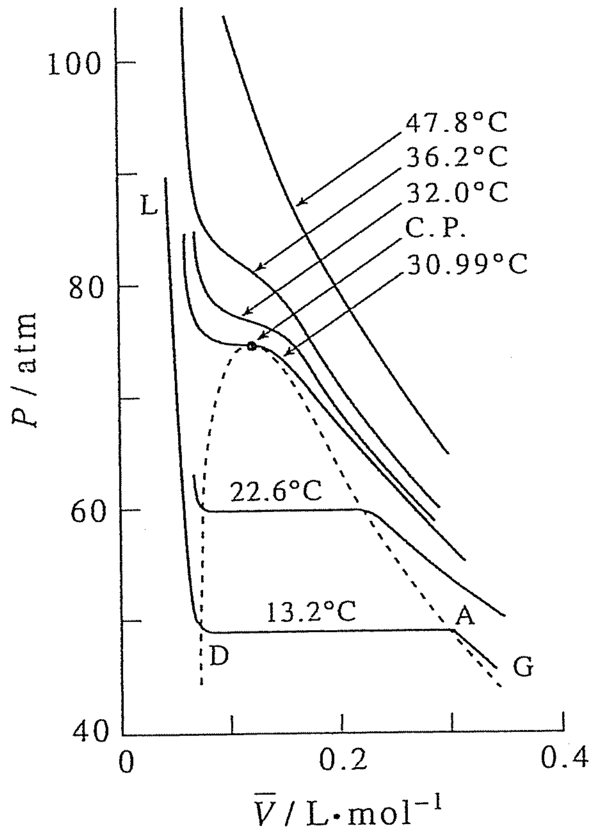


[Figures taken from C.J. Adkins "Equilibrium Thermodynamics"]

Look at Real Data

CO_2

p-V projection



Experimental pressure-volume isotherms

Q: Classical ideal gas

$$pV = NkT \quad \text{or} \quad p\overset{\nwarrow \text{ molar volume (volume per mole) (also called } \bar{V})}{v} = RT$$

equation of state <u>cannot</u> describe the feature.

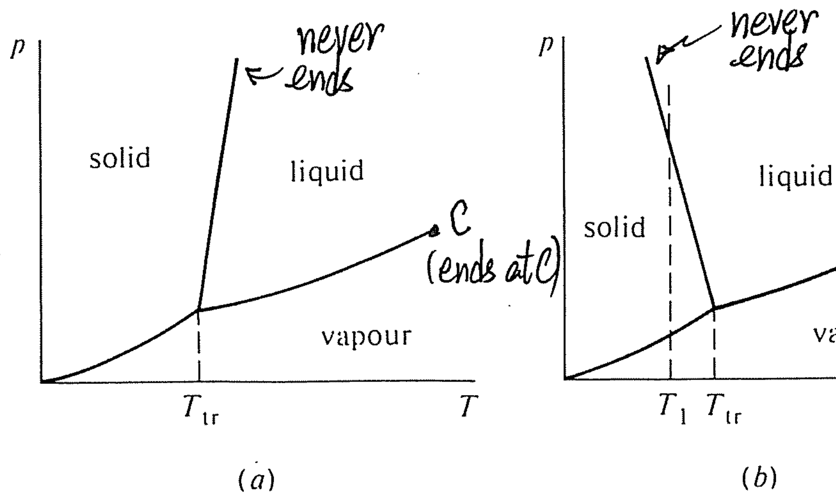
[Any other equation that works?]

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

Van der Waals equation [1910 Nobel Prize in Physics]

$\boxed{\text{Can Stat. Mech. be used to derive } (*)\text{?}}$

Phase diagrams. (*a*) is typical of most simple substances, while (*b*) shows the behaviour of water which expands on freezing.



(ends at C)

- Note the description often involves p and T, which are the natural variables of the <u>Gibbs free energy</u>[†] $G(T,p,N)$. Spontaneous processes: $\Delta G < 0$

Reminder: $E(S,V,N)$ $(dE = TdS - pdV + \mu dN)$
and carry out Legendre Transforms $\begin{cases} S \to T \\ V \to p \end{cases}$

$$\boxed{G = E + \underbrace{pV}_{} - TS}$$

OR

$$\boxed{G = H - TS}$$

$$\boxed{dG = -SdT + Vdp + \mu dN}$$

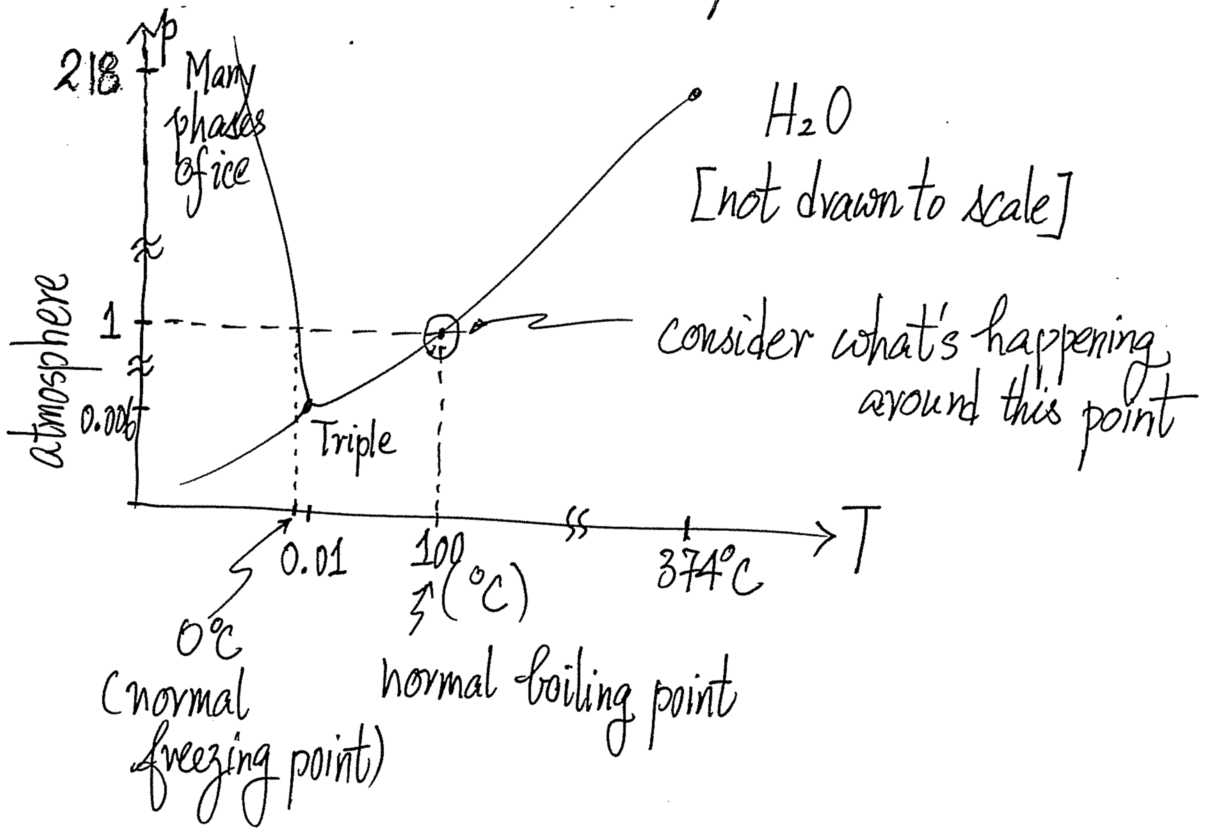
where H = enthalpy = $H(S,p)$

and $G = G(T,p,N)$

G is important in describing phase changes.

[†] To develop an ensemble theory for (T,p,N), we need to allowed system and bath to exchange energy and volume. This is the T-p ensemble.

Boiling Water tells us much physics



- Consider <u>vaporization</u> of <u>water at 100°C and 1 atm.</u>

$(\Delta H)_{vap}$ for one mole $= Q_p$[†] (Heat required to vaporize 1 mole at constant pressure at 100°C)
$= 40.65$ kJ/mole

A phase transition is a good example of a <u>reversible process</u>, as the process can be reversed by a tiny change in temperature. This gives (by definition)

$$(\Delta S)_{vap} = \frac{Q \leftarrow 40.65\,\text{kJ/mol}}{T_{vap} \leftarrow 373.15\,\text{K (transition temperature)}} = 108.9\ \text{JK}^{-1}\text{mol}^{-1}$$

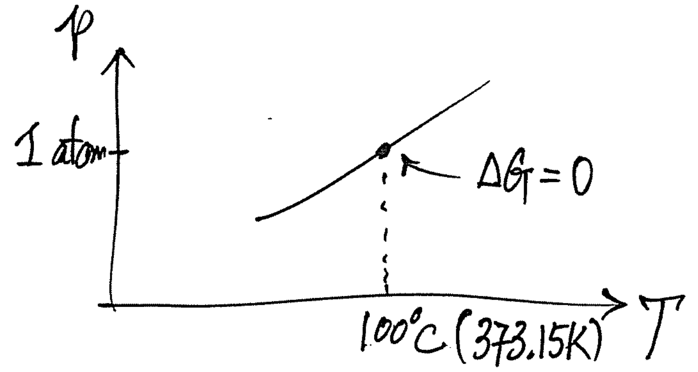
[†] This is the "latent heat of vaporization", usually in kJ Kg^{-1}. Here it is given in kJ mol^{-1}. Its value is ≈ 2265 <u>kJ Kg^{-1}</u> for H_2O.

$(\Delta S)_{vap} = 108.9\,JK^{-1}mol^{-1} > 0 \xrightarrow{\text{Meaning}} S_{vap}^{1\,mole} > S_{liq}^{1\,mole}$

⇒ Vapor phase is less ordered than liquid phase

The Gibbs free energy (by construction/definition) is changed by

$(\Delta G)_{vap} = (\Delta H)_{vap} - \overset{\text{OR boiling point}}{T_{vap}}(\Delta S)_{vap} = 0$ at the boiling point (per mole)



Meaning: At that point, liquid and vapor are at equilibrium, and $\underbrace{G_{liq}^{(1\,mole)} = G_{vap}^{(1\,mole)}}_{\text{equilibrium condition}}$.

coexist

What if temperature is a bit lower or a bit higher?

$$(\Delta G)_{vap} = (\Delta H)_{vap} - T(\Delta S)_{vap}$$

$$= 40.65\,kJ\cdot mol^{-1} - T(108.9\,J\cdot K^{-1}\cdot mol^{-1})$$

e.g. $T = 363.15K < \overset{\text{normal boiling point}}{373.15K}$ (in liquid phase)

$(\Delta G)_{vap} = +1.1\,kJ\cdot mol^{-1} > 0$

⇒ vaporization is not a spontaneous process at 363.15K and 1 atm. (thus H_2O is in liquid phase)

$T = 383.15K > 373.15K$ (in vapor phase)

$(\Delta G)_{vap} = -1.08\,kJ\cdot mol^{-1} < 0$

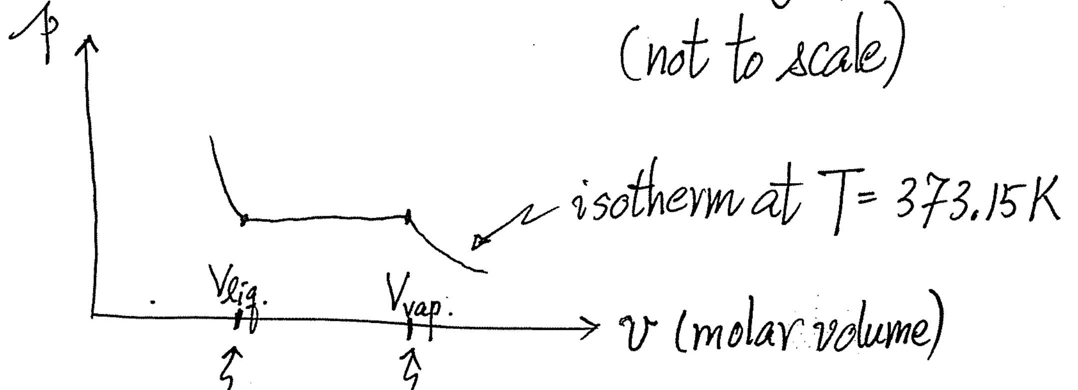
⇒ formation of 1 mole of vapor from 1 mole of liquid is a spontaneous process at 383.15K and 1 atm. (thus H_2O is in vapor phase)

One would reverse this vaporization-condensation process by a tiny-tiny change of temperature about the normal boiling point!

Key message: $G_A^{1\,mole} = G_B^{1\,mole}$ for a pure substance
[phase A and phase B in equilibrium]
[Same as saying chemical potentials are equal as $G = \mu N$]

Follow the isotherm at normal boiling point

(not to scale)



Volume of 1 mole of liquid

($V_{liq} = 0.018$ liter/mole)

Volume of 1 mole of vapor

($V_{vap} = 30.6$ liter/mole)

$(\Delta V)_{vap} = (30.6 - 0.018) \approx 30.6$ liter/mole

= change in volume in vaporizing 1 mole of water

$(\Delta H)_{vap} = 40.65\ kJ\cdot mol^{-1}$ "latent heat of vaporization"

Recall: $\underbrace{(\Delta H)_{vap.}}_{40.65\ kJ\cdot mol^{-1}} = \underbrace{(\Delta E)_{vap}}_{} + \underbrace{p(\Delta V)_{vap.}}_{}$

energy to overcome intermolecular forces holding molecules in liquid phase

energy as work done against p (expansion) in vaporization

$= (1\cdot atm)\cdot(30.6\ liter\cdot mol^{-1})$

$= \left(30.6\ \frac{liter\cdot atm}{mol}\right)\cdot\underbrace{\left(\frac{8.314 J}{0.08206\ liter\cdot atm}\right)\left(\frac{1 kJ}{10^3 J}\right)}_{\text{unit conversion}}$

$\cong 3.1\ kJ\cdot mol^{-1}$

$(\Delta E)_{vap} \approx (40.65 - 3.1)\ kJ\cdot mol^{-1}$

$\approx \underbrace{37.55\ kJ\cdot mol^{-1}}_{}$

Need this amount of energy to free 1 mole of molecules from each other

⇒ $\boxed{\text{Interaction between particles is needed for phase transitions!}}$

No interaction ⇒ $H = \sum_{i=1}^{N} \frac{p_i^2}{2m}$ (k.e. only)

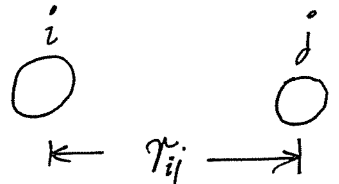
⇒ Ideal gas behavior

Interaction is important for behavior deviated from ideal gas!

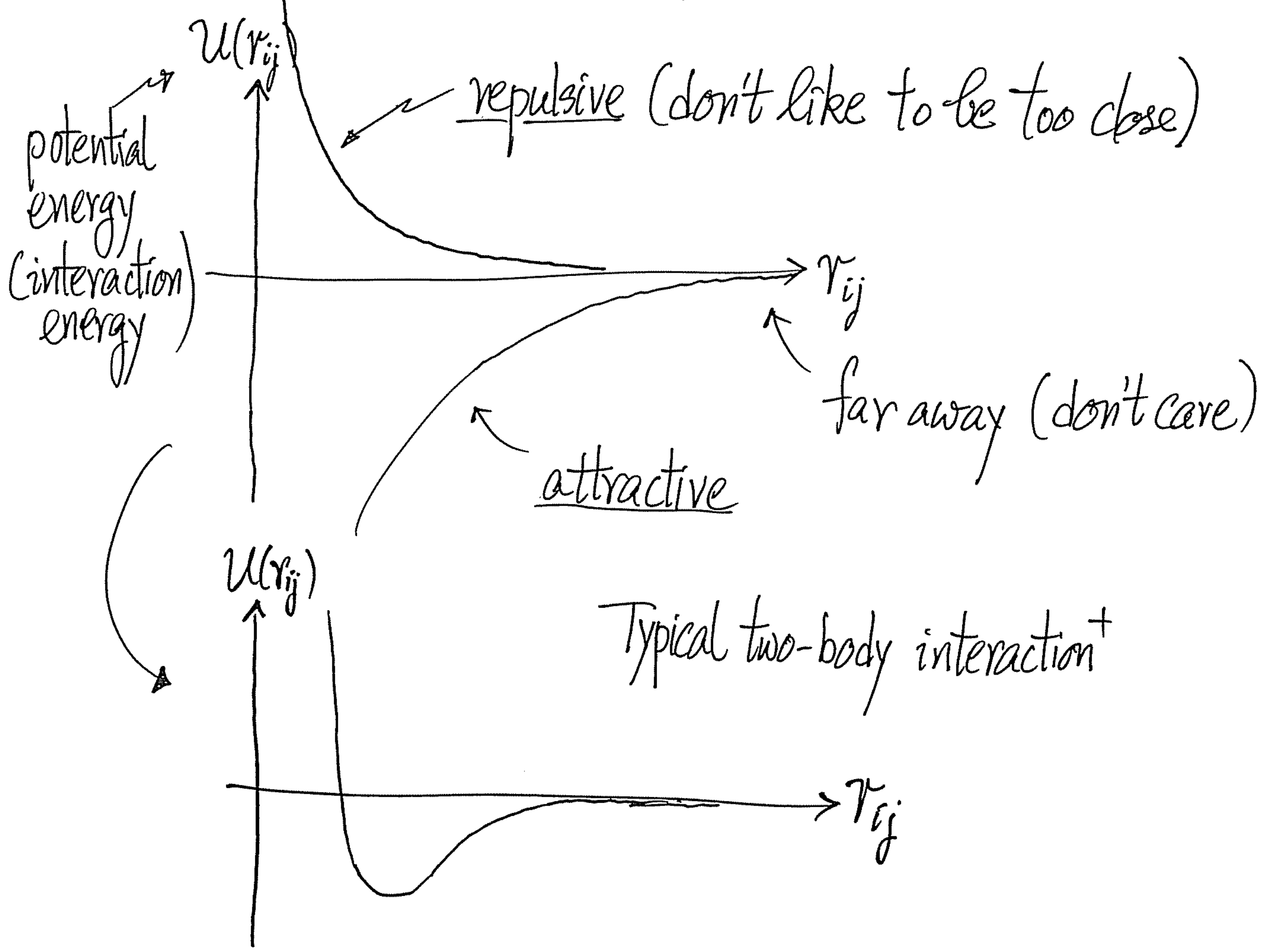
→ Interaction! What interaction?

Interaction between particles

Typically, (Think like a physicist)



- particles far apart don't feel each other's presence
- particles can't get too close to each other
- the fact that vapor condenses implies some attractive interaction



Typical two-body interaction†

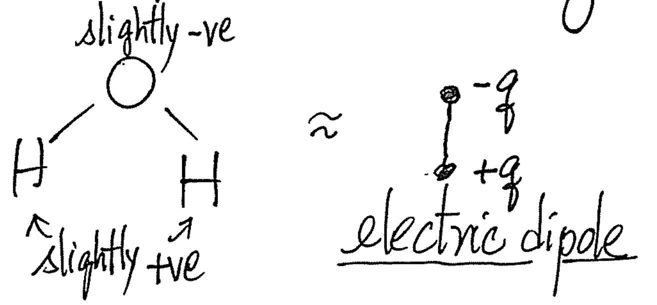
---

† The discussion here works for atoms, molecules, solids, and protons & neutrons in nuclei.

We are interested in vapor (gases) at ordinary temperature that condenses as temperature is lowered.

∴ Interaction is not strong (c.f. $kT \sim \frac{1}{40}$ eV)

Atoms/Molecules in a gas are neutral†



electric dipole - electric dipole interaction

For atoms/molecules with no permanent electric dipole, still could have some instantaneously induced electric dipole due to fluctuations.

∴ It is electric dipole - electric dipole type of interaction that's matter, for the attractive part.

[Detailed consideration of the interaction is rather involved, e.g. dipoles rotate, etc. It is beyond the scope of our course].

---

† Ionic interaction (due to electron transfer) and covalent bonding lead to ~ a few eV in the interaction energy. They, therefore, are solids at room temperature. Thus, the subject of Solid State Physics.

Model $U(r)$:

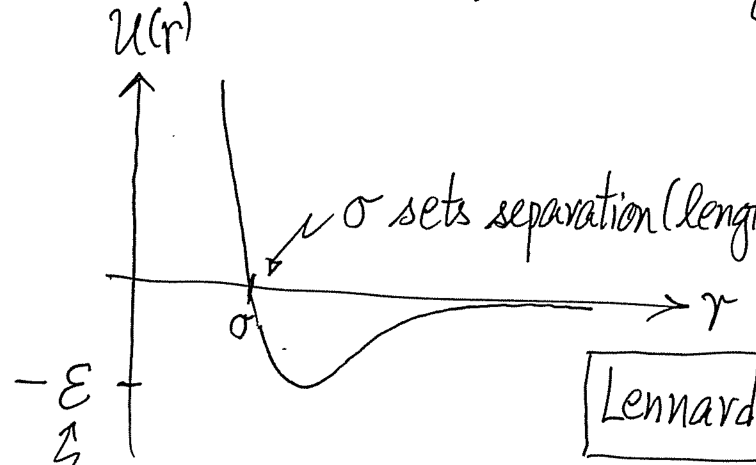
2 parameters

2 parameters

$$U(r) = \underbrace{\frac{C_{12}}{r^{12}}}_{\text{repulsive}} - \underbrace{\frac{C_6}{r^6}}_{\text{attractive}} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

[phenomendogical]

← can be traced back to dipole-dipole interaction



σ sets separation (length scale/range) of interaction

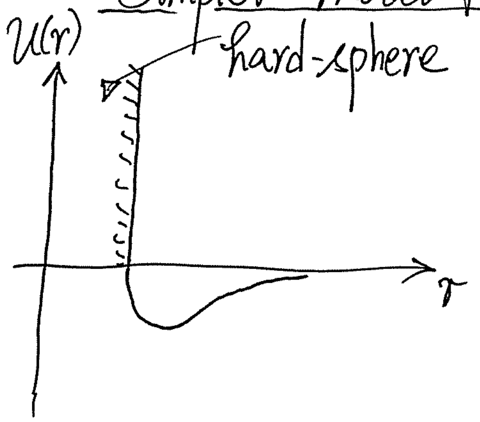
ε sets energy scale (strength) of interaction

Lennard-Jones potential OR "6-12" potential

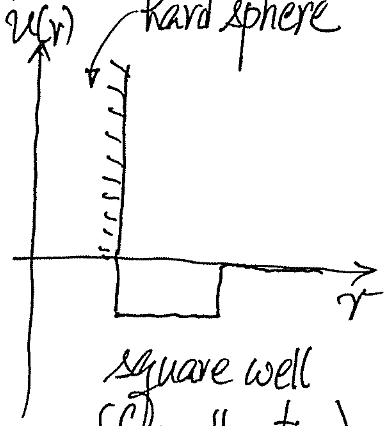
Typical values: $\sigma \sim 3\text{-}5\,\text{Å}$, $\underbrace{\varepsilon \sim 0.01\,\text{eV}}$

OR $\frac{\varepsilon}{k} \sim 100\text{-}200\,\text{K}$

Simpler Model Potentials

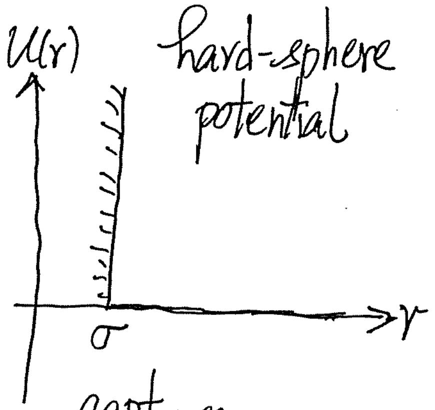


hard-sphere



hard sphere

square well (for attractive part)



hard-sphere potential

captures repulsive part