

9. Non-ideal gases

16th May

Last lecture

- Types of bonding, ionic, covalent, metal & Van der Waals

- For VW potential is given by,

$$U = \epsilon \left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6$$

- Atoms in a lattice vibrate, vibrations are particle like (phonons) and can carry heat. Frequency given by,

$$\omega_E = \left(\frac{144\epsilon}{mr_0^2} \right)^{1/2}$$

- Solids expand with increasing T , $\Delta L = L_0 \alpha T$
- Molar heat capacity of solid given by $C_{vm} = 3R$ at room temperatures, but phonons frozen out at low T

9.1 van der Waals Equation of State

PV diagram showing isotherms for ideal gas

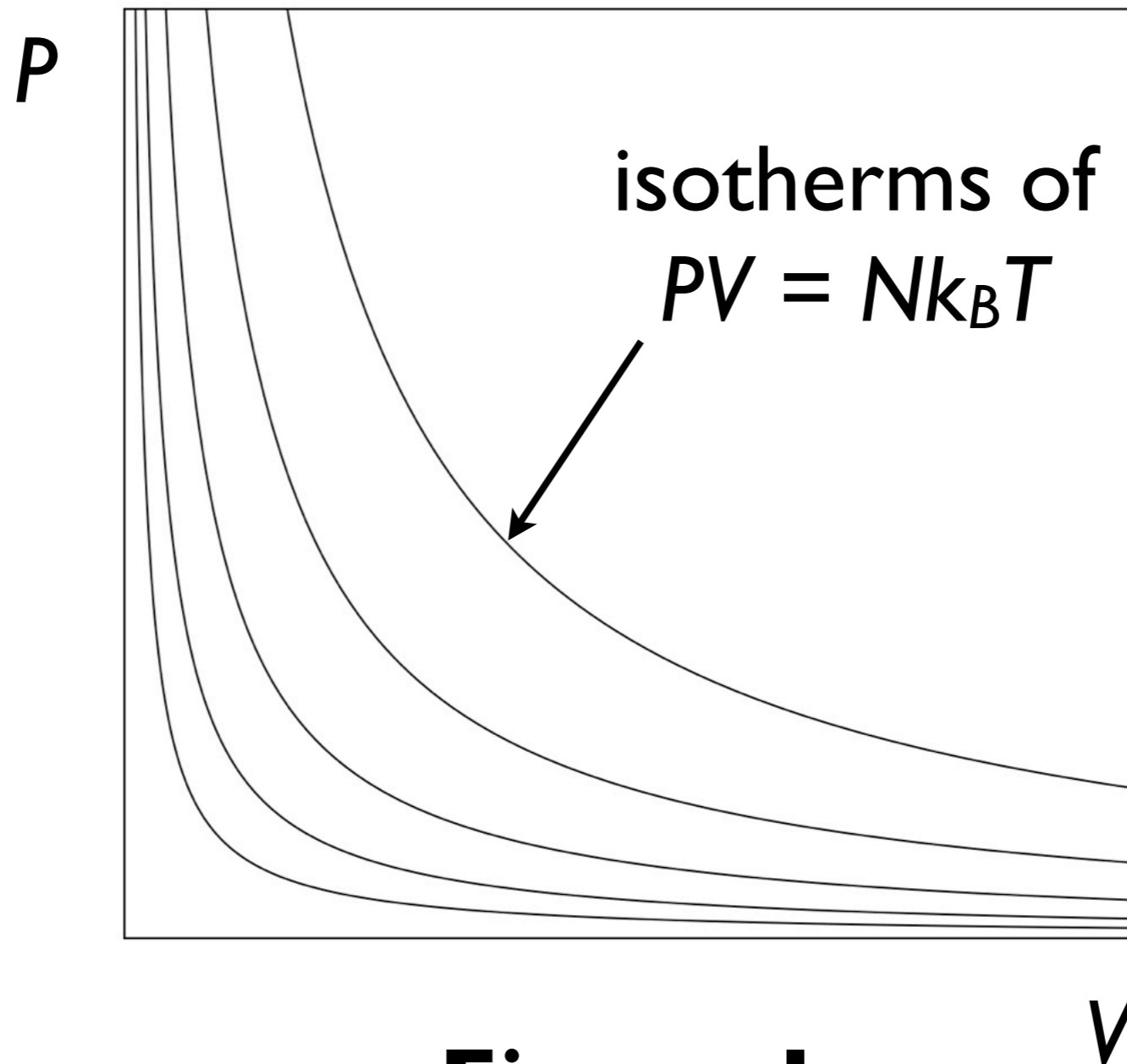


Figure 1

PV diagram showing isotherms for CO₂

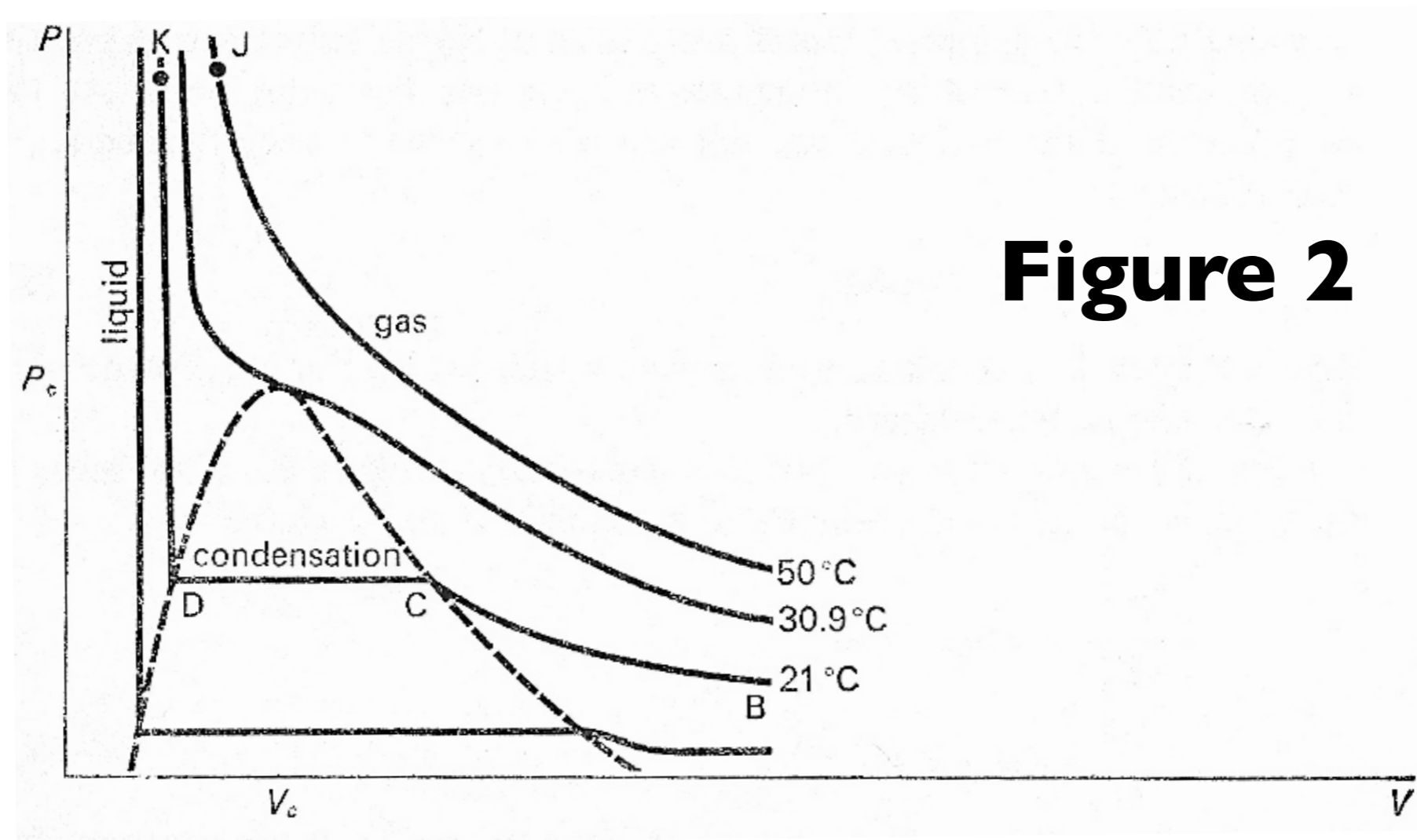


Figure 2

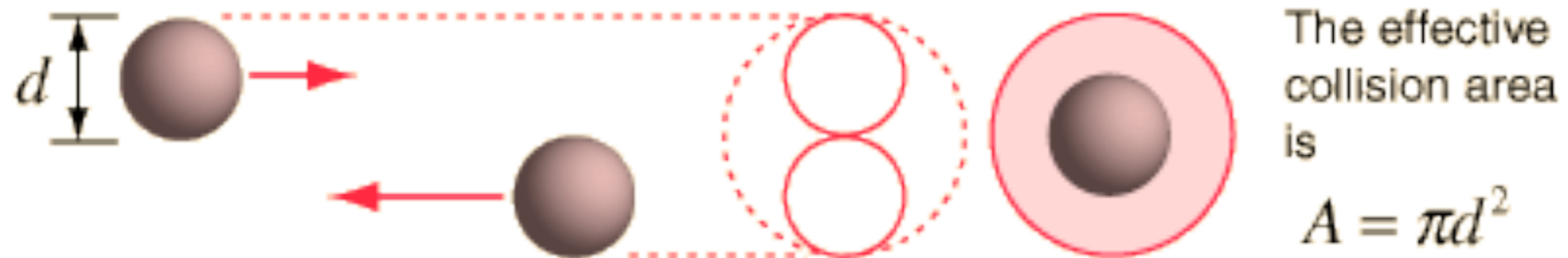
van der Waals gas:

modify ideal gas eq. of state ($PV = Nk_B T$) by assuming;

- (1) molecules are hard spheres (not points) of volume b
- (2) attractive force over finite range

(I) \rightarrow volume available for motion = $V - b N$
(N = total no. of molecules)

Equation of state $\rightarrow P (V - bN) = Nk_B T$



Effective cross-sectional area $A = \pi d^2$

Effective volume of molecule $b \approx \frac{1}{2} (4/3) \pi d^3$
($\frac{1}{2}$ is because this volume is per pair of particles)

$$b \approx \frac{1}{2} (4/3) \pi 8 r^3 = 4 V_m$$

Correcting ideal gas EOS for attractive force:

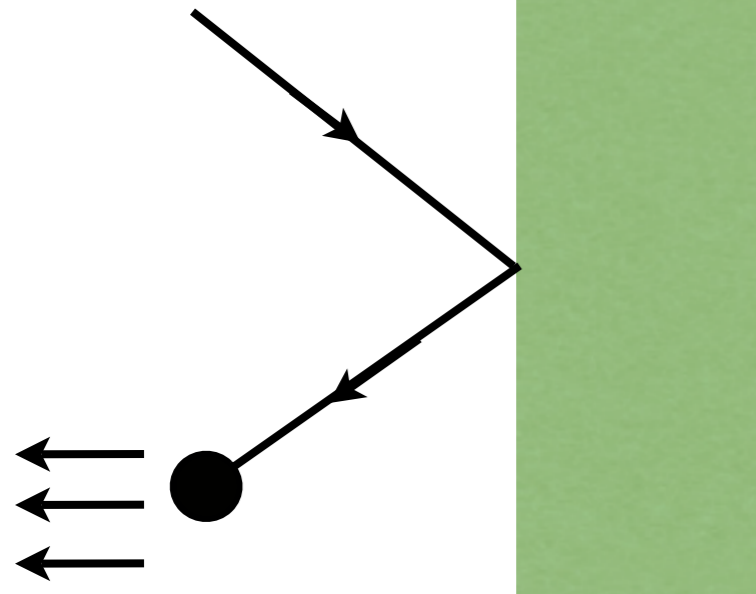
Only gas molecules near edge have unbalanced attraction from the rest of the gas

momentum reduction per impact $\propto n$

but no. of such impacts per unit area $\propto n$

$$\therefore \Delta P \propto n^2 = (N/V)^2$$

incoming
velocity
reduced



attraction
to other
molecules

van der Waal's equation

$$\therefore \text{reduction in } \Delta P \propto n^2 \quad \rightarrow \quad \Delta P = a(N/V)^2$$

Hence the ideal gas pressure is reduced by this amount,

$$P = P_{ideal} - \Delta P$$

(where P_{ideal} includes the volume correction.)

$$\rightarrow P = Nk_B T / (V - bN) - a(N/V)^2$$

a is proportionality constant

(9.1.1) van der Waals equation of state

$$(P + a(N^2/V^2))(V - Nb) = Nk_B T$$

A (low temperature) van der Waal isotherm

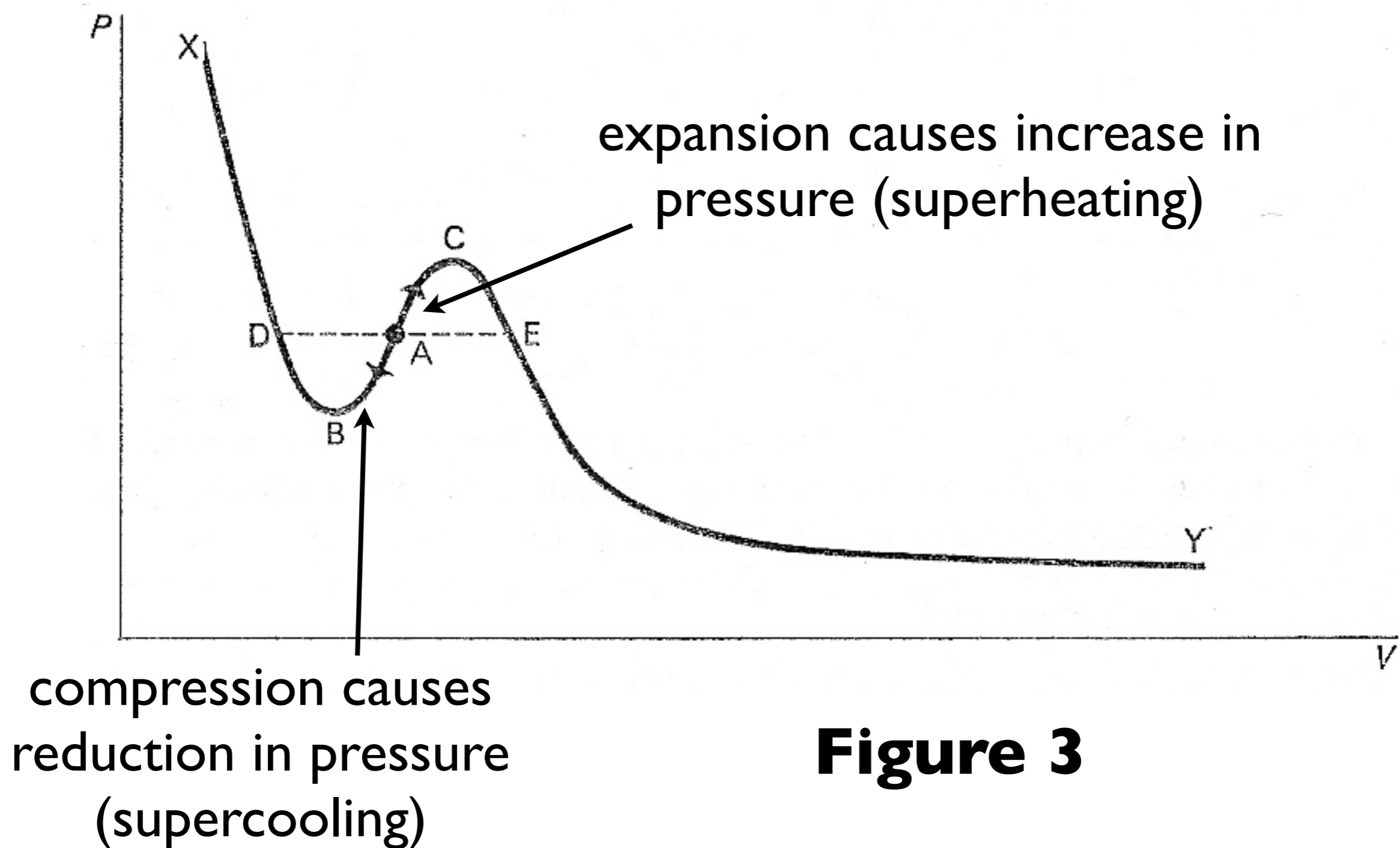


Figure 3

van der Waal isotherms

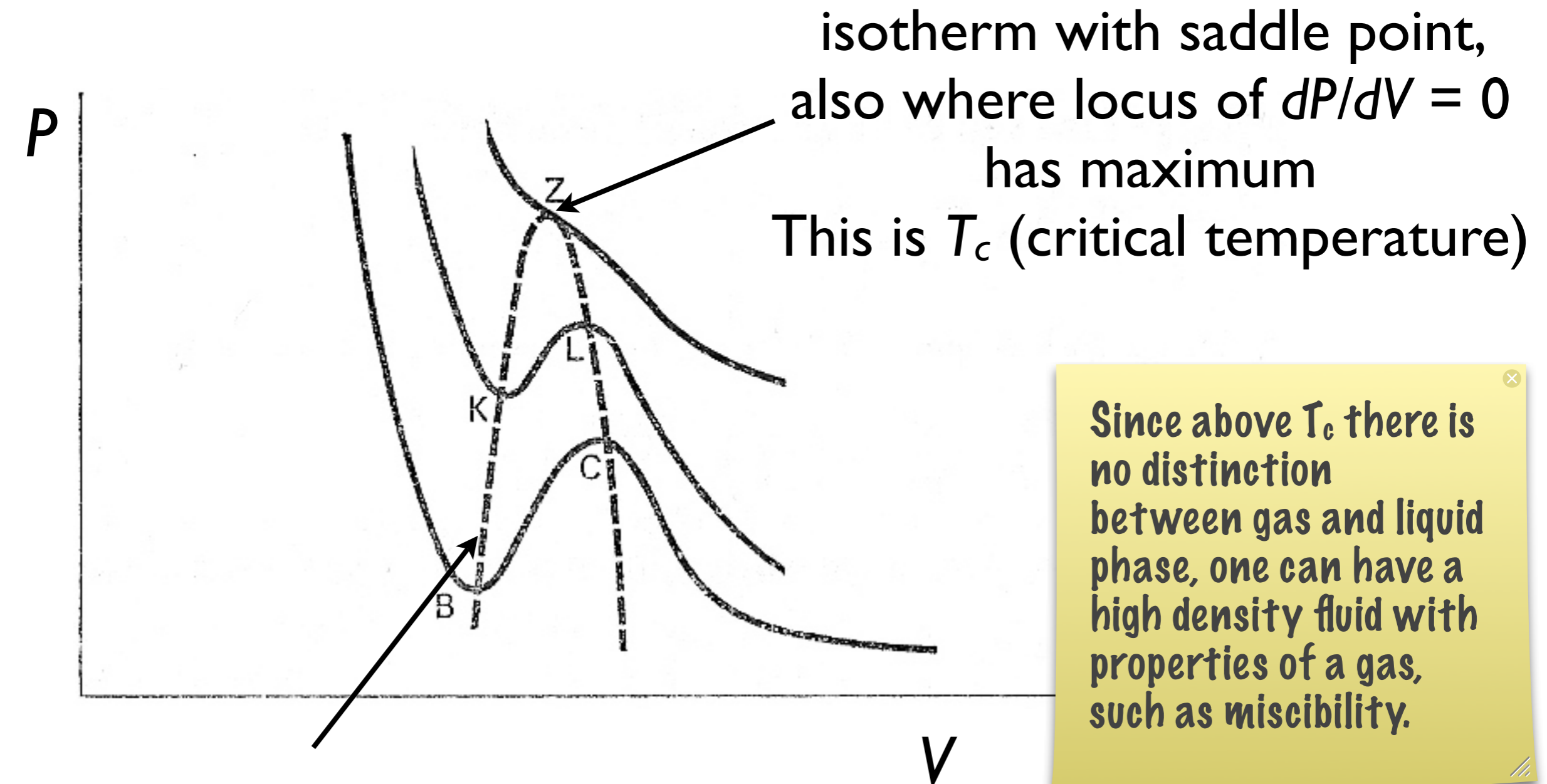


Figure 4

9.2 Internal energy of van der Waal gas

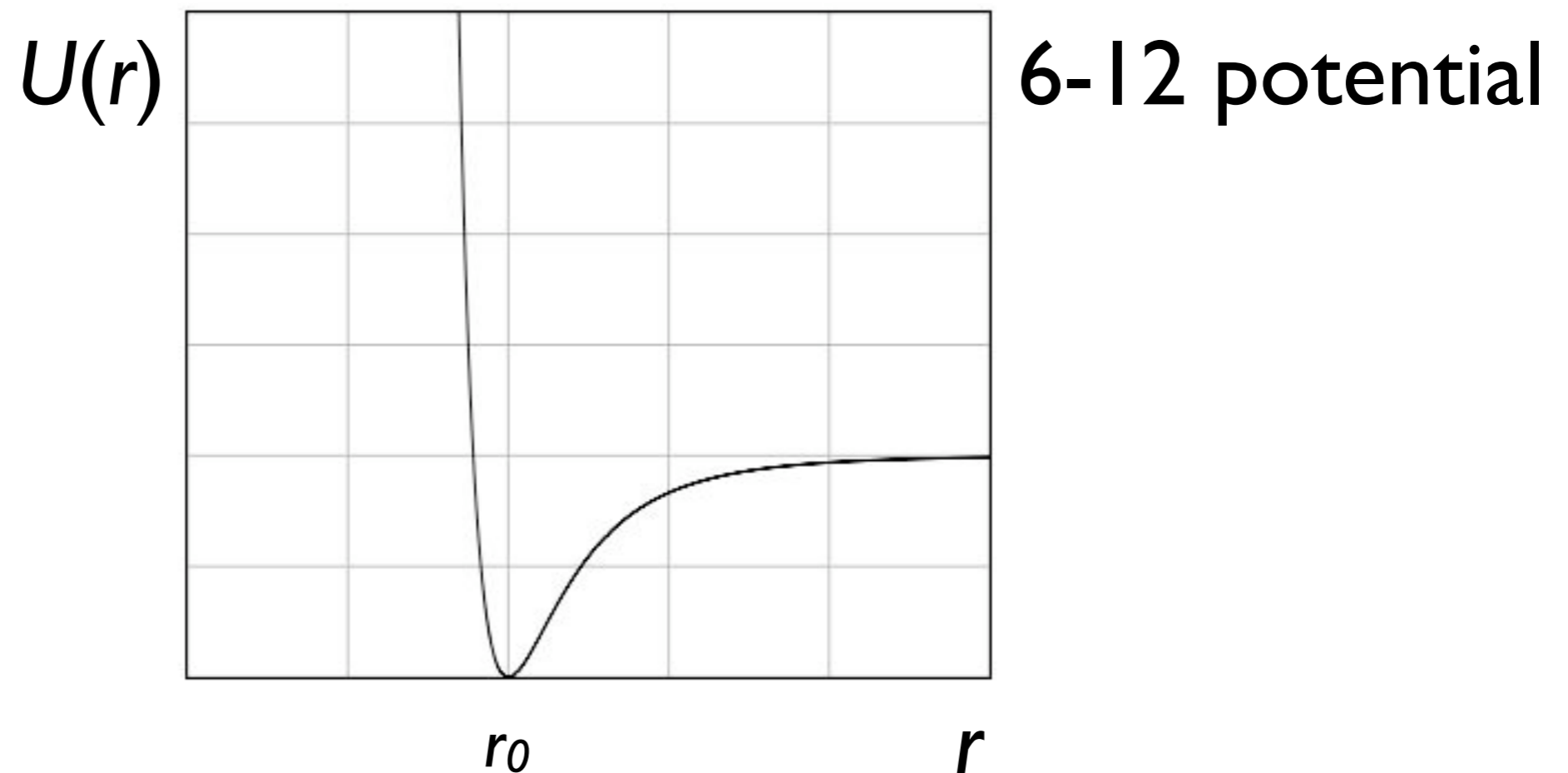


Figure 5

Simplified potential

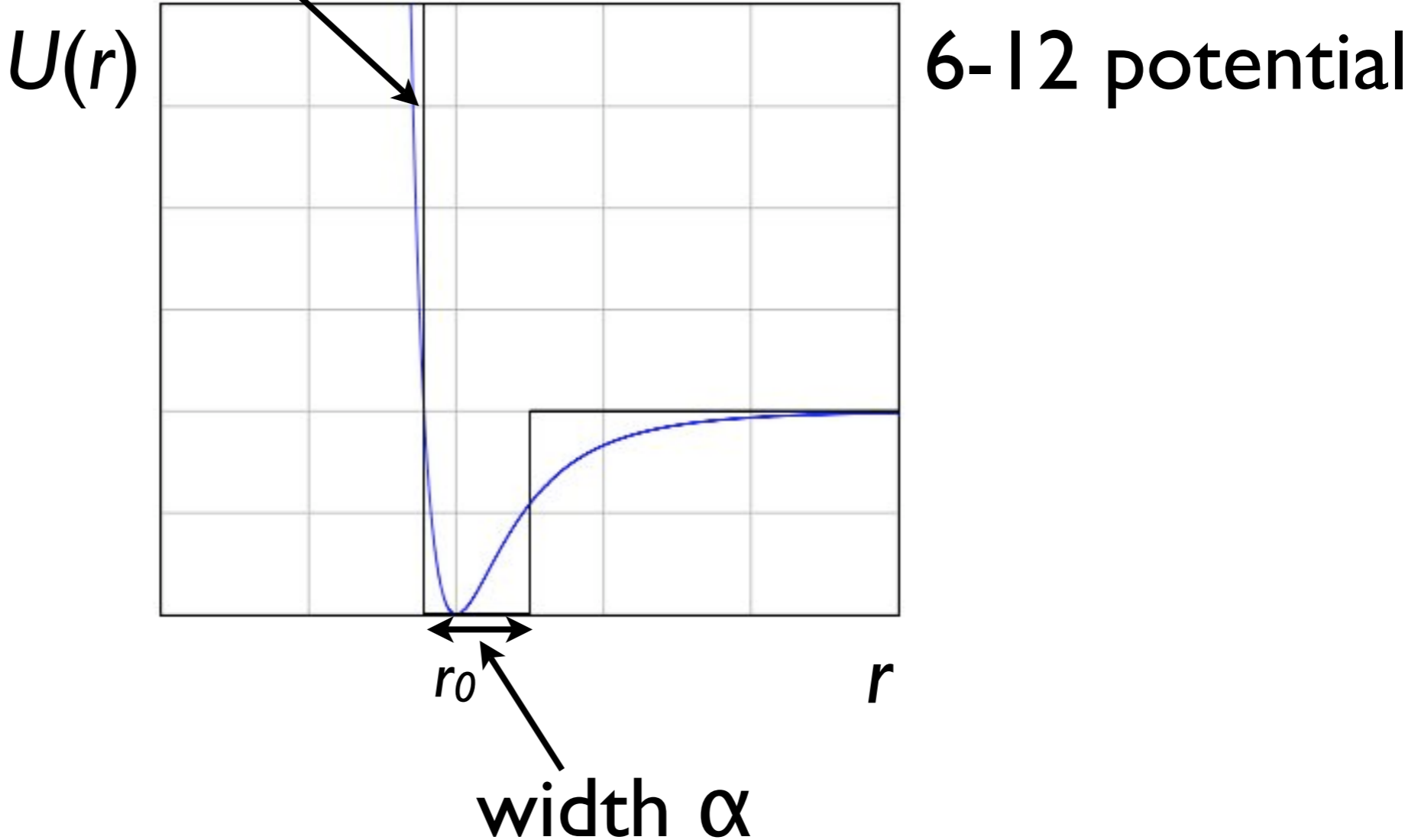
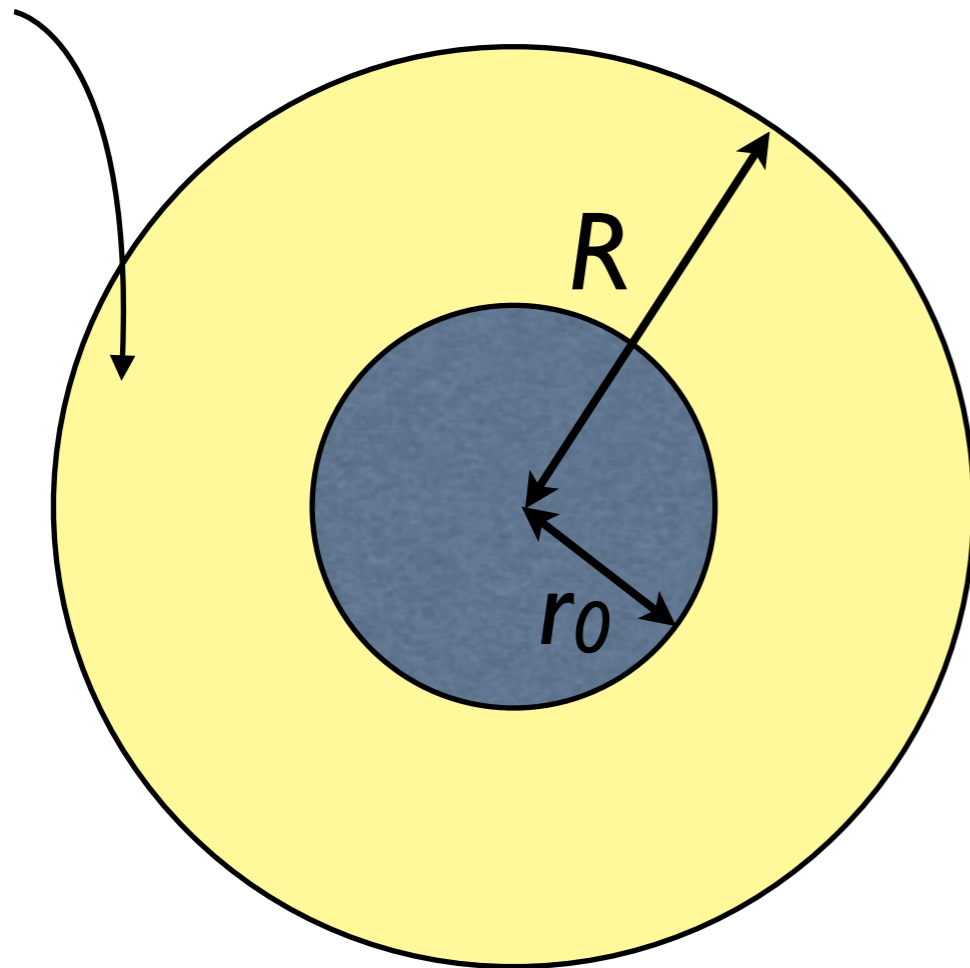


Figure 6

interaction volume V_{int}



if 2nd molecule within V_{int} , $U = -\epsilon$
if 2nd molecule outside V_{int} , $U = 0$

no. of mols in $V_{\text{int}} = n V_{\text{int}} = N V_{\text{int}}/V$

Total no. of such interactions
 $= (1/2) N (N V_{\text{int}}/V)$

(1/2) to not count same interaction
twice

Total p.e. = $- (1/2) (N^2/V) V_{\text{int}} \epsilon$

So $U = \text{internal energy} = (3/2) Nk_B T - aN^2/V$
where $a = (1/2) V_{\text{int}} \epsilon$

9.3 Joule-Kelvin free expansion

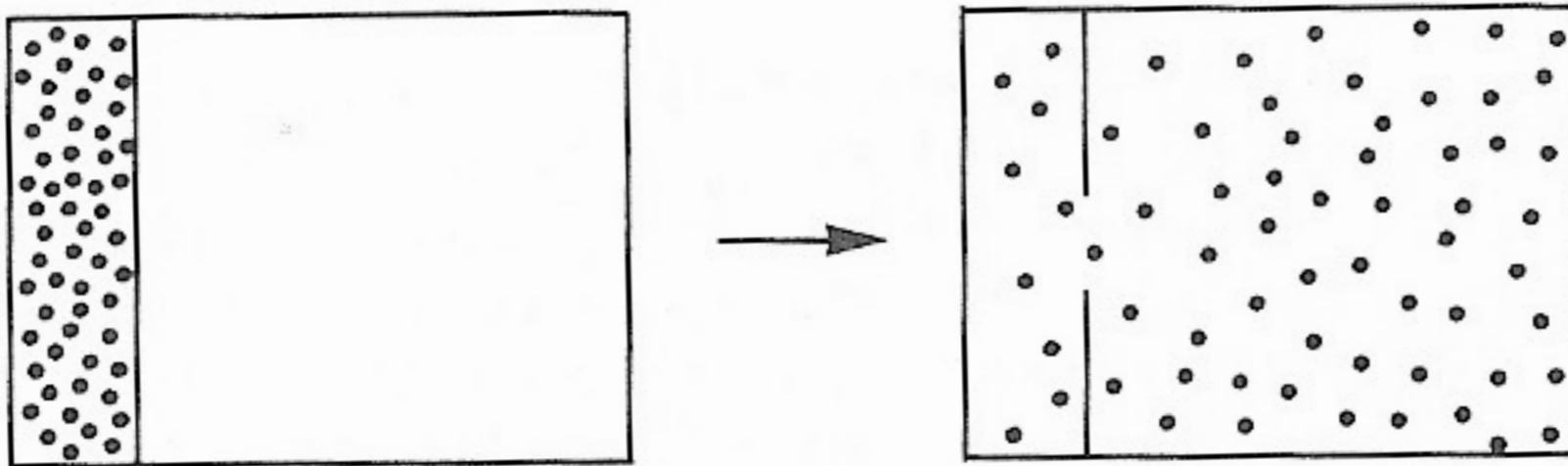


Fig. 7.14. Free expansion of a gas inside a rigid, insulated vessel.

Remove partition

→ gas expands & fills volume.

→ No work done [No piston]

→ $\Delta U = 0$ (1st Law)

ideal gas: $\frac{3}{2}Nk_B T = \text{const.} \rightarrow T = \text{const}$ [Vol increased so pressure decreased]

van der Waals gas: $\frac{3}{2}Nk_B T - aN^2/V = \text{const}$

V increases $\rightarrow aN^2/V$ decreases $\rightarrow \frac{3}{2}Nk_B T$ decreases [difference stays constant] $\rightarrow T$ decreases - i.e. gas cools

Micro picture: gas expands \rightarrow molecules further apart \rightarrow intermolecular pe increases \rightarrow ke decreases. This is the basis of the liquification of air (Joule-Thompson process).