# Molecular collisions

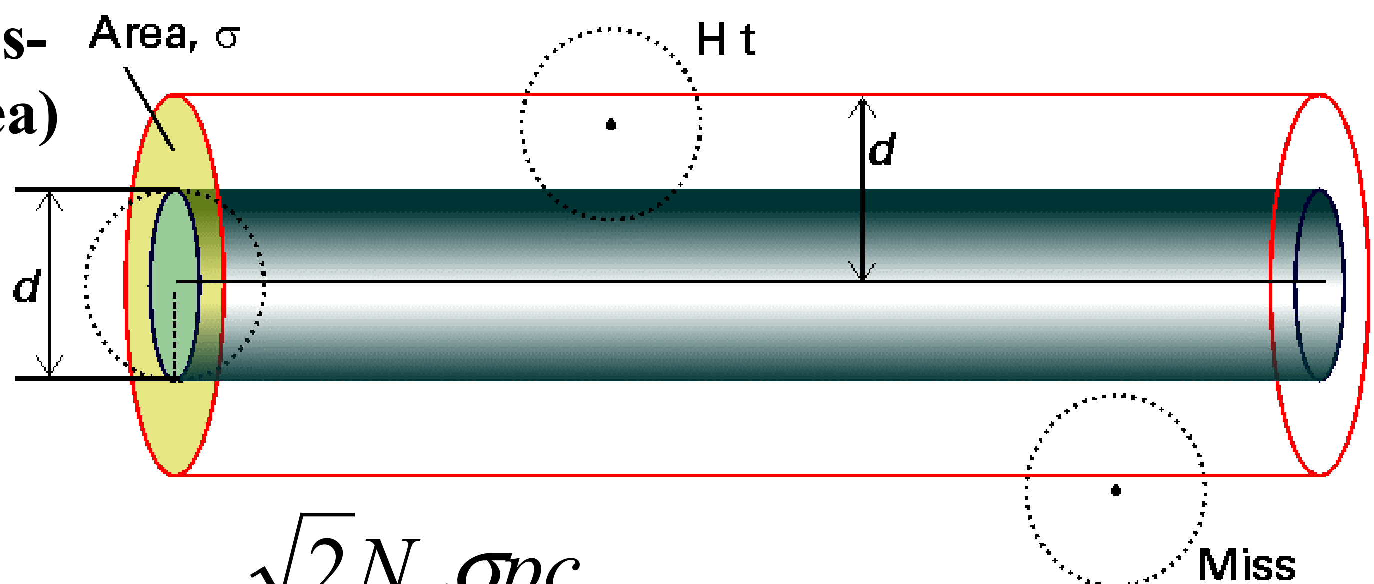
Mean free path between two collisions

r.m.s. speed $c = \dfrac{\lambda}{1/z} = \lambda z$

z = collision frequency

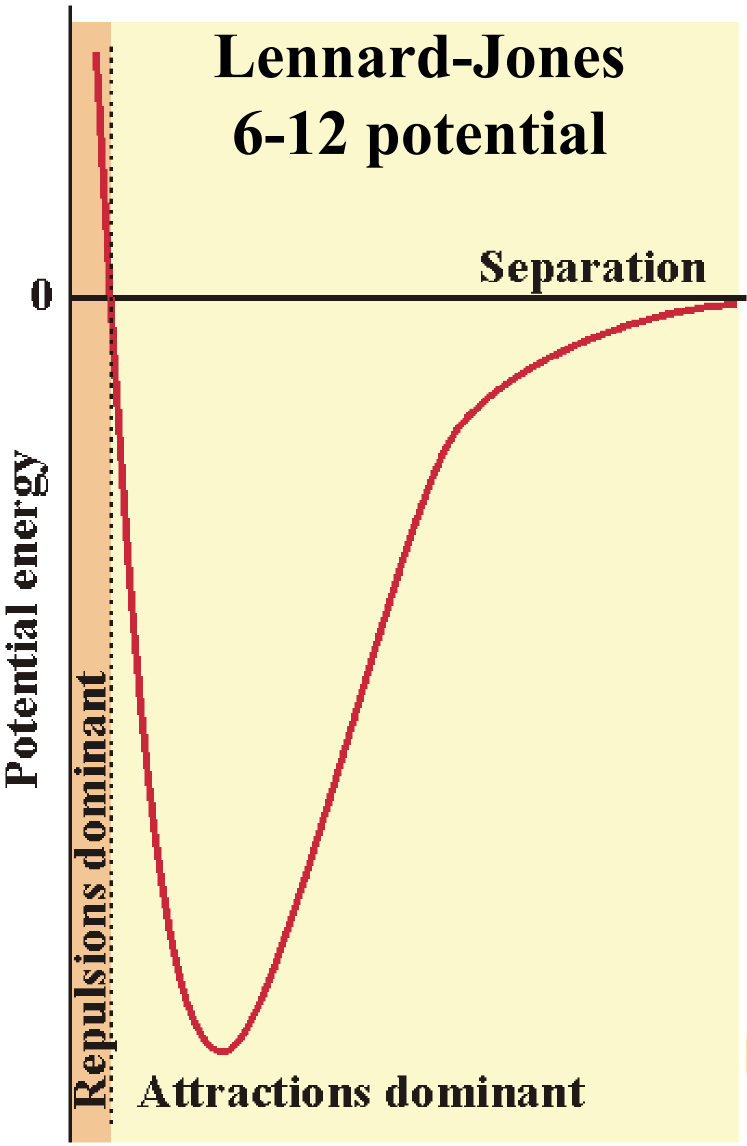
Time of flight between two collisions

σ = collision cross-section (target area) = $\pi d^2$



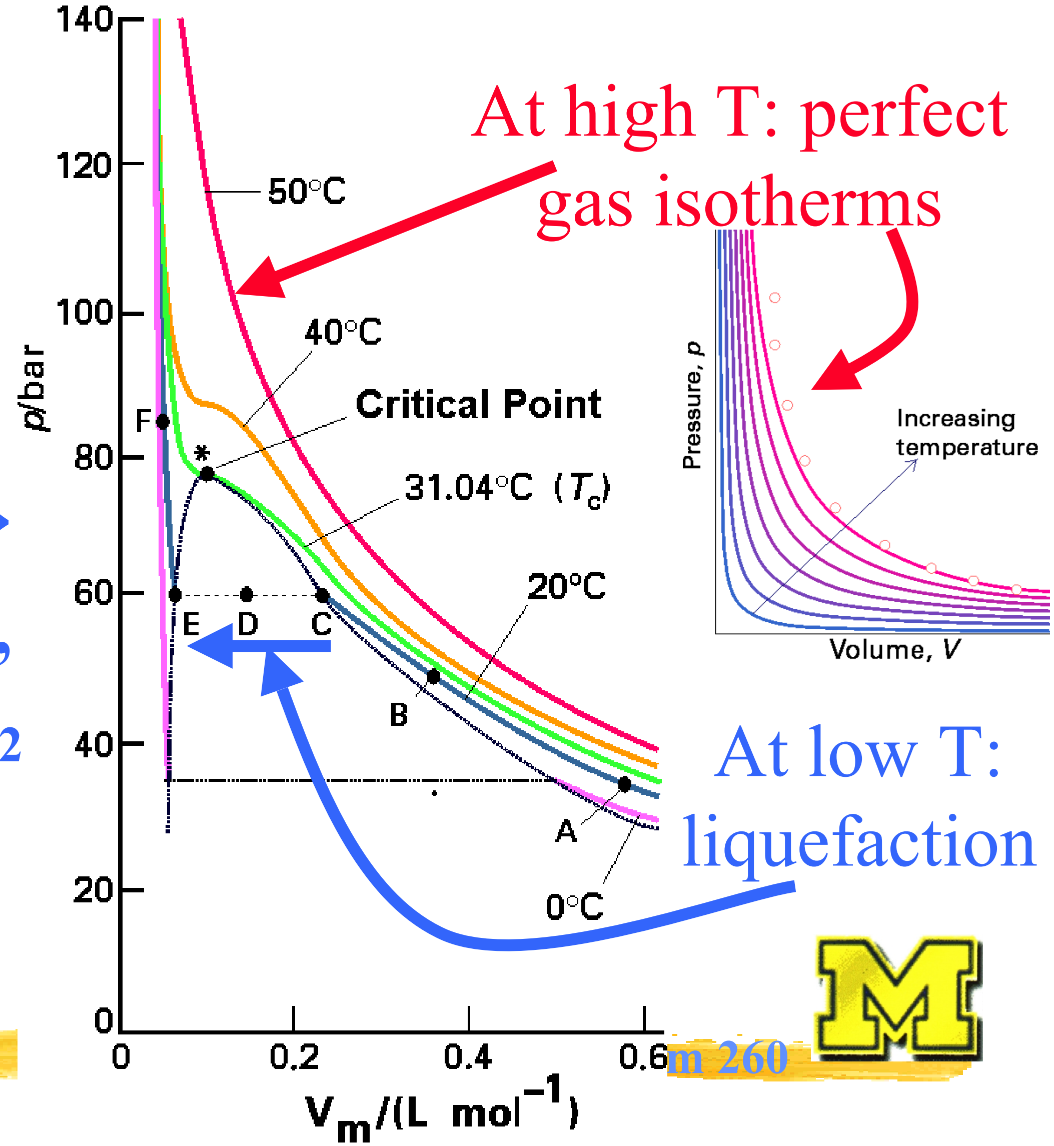

$$\Rightarrow \lambda = \frac{RT}{\sqrt{2} N_A \sigma p}; z = \frac{\sqrt{2} N_A \sigma p c}{RT}$$

# In reality: Gases have attractive and repulsive forces

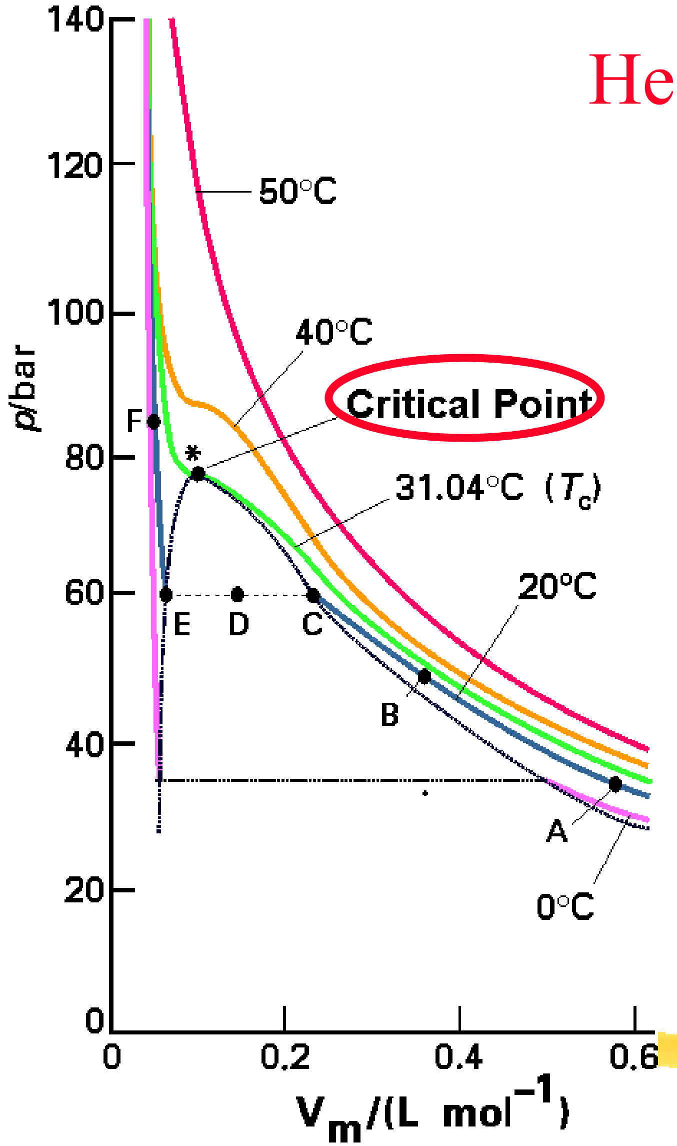



⇒

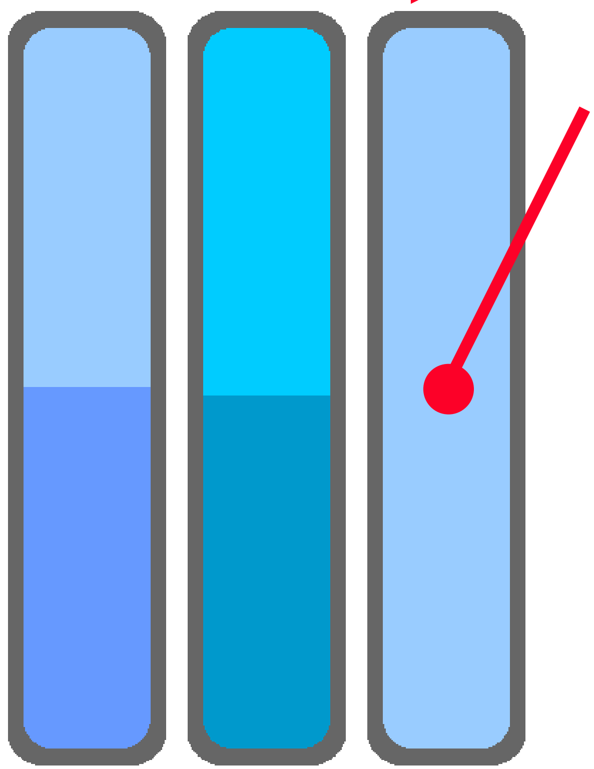
e.g., $CO_2$



# The critical point: Gas and liquid density become equal




Heating a liquid in a container

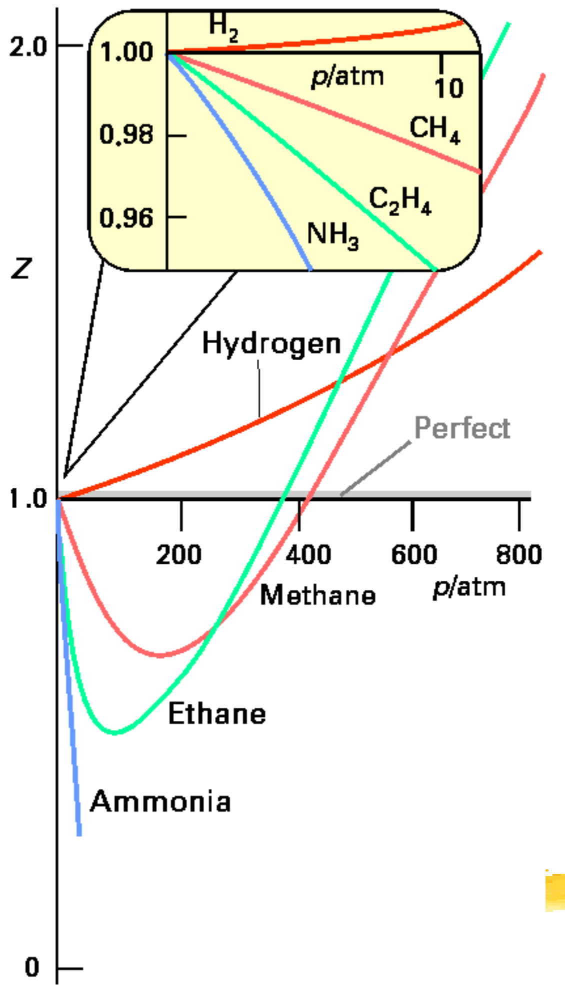


**At critical point (for water 373°C @ 218 atm!) the boundary is lost**

**⇒ Application: Extraction of caffeine from coffee with supercritical $CO_2$**

# Describing the deviation from the perfect gas

Introducing the compression factor Z: **Z= $\dfrac{\text{molar volume of real gas}}{\text{molar volume of perfect gas}}$**



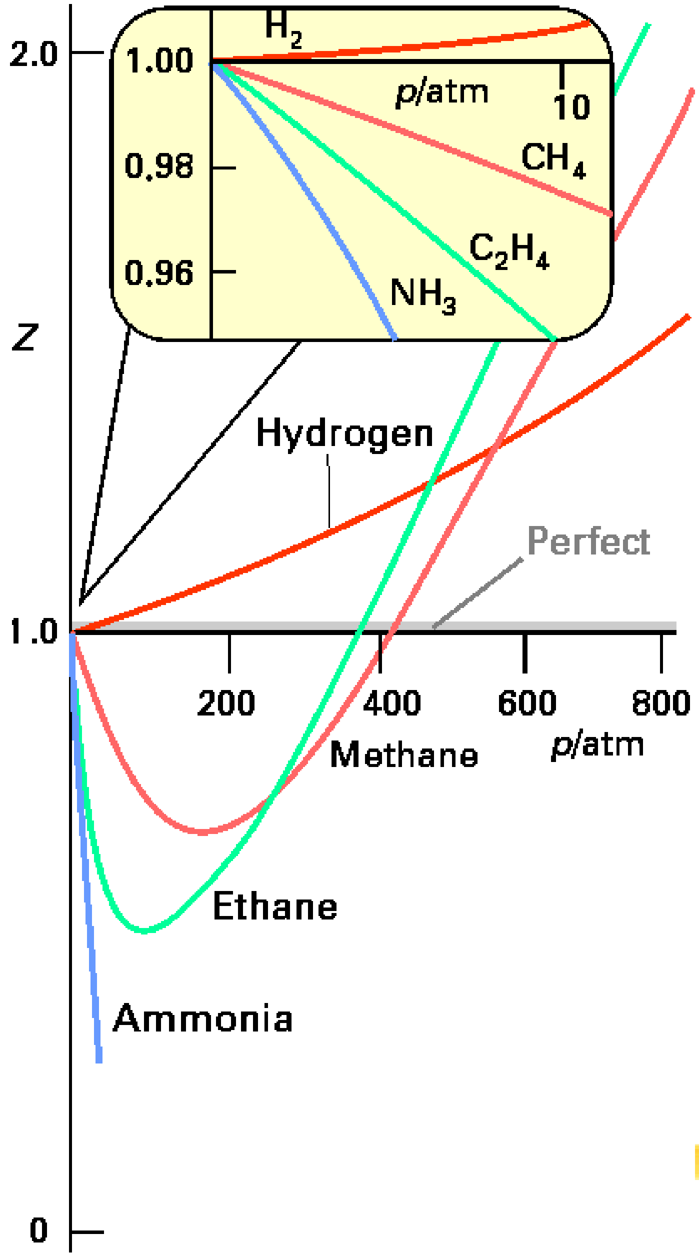

$$Z = \frac{V_m}{V_m^{\ perfect}} = \frac{V_m}{\frac{RT}{p}} = \frac{pV_m}{RT}$$

Z = 1 ⇒ perfect gas

Z < 1 ⇒ molecules cluster, attractive forces are dominant

Z > 1 ⇒ molecules repel each other, repulsive forces are dominant

# The virial equation of state




virial coefficients

Empirically: $$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^{\ 2}} + \ldots$$

$B > 0 \Rightarrow Z > 1$, e.g., $H_2$

$B < 0 \Rightarrow Z < 1$, e.g., $CH_4$, $NH_3$

$C > 0 \Rightarrow Z > 1$ at high pressure ($V_m$ small)

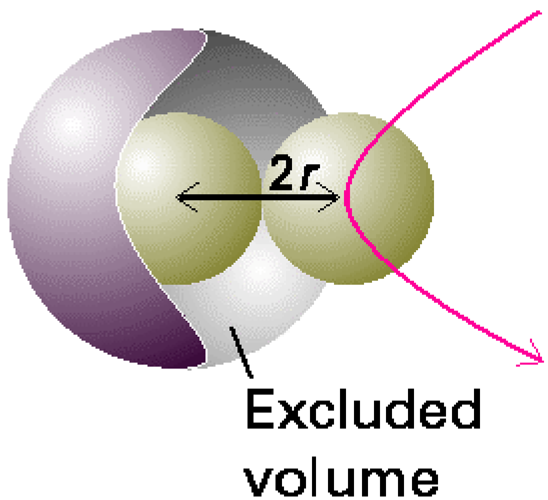
and $$Z = \frac{pV_m}{RT}$$

$$\Rightarrow \quad p = \frac{nRT}{V}\left(\overbrace{1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \ldots}^{\text{very accurate}}\right)$$

# Physically more palpable: The van der Waals equation

## [Johannes van der Waals 1873]

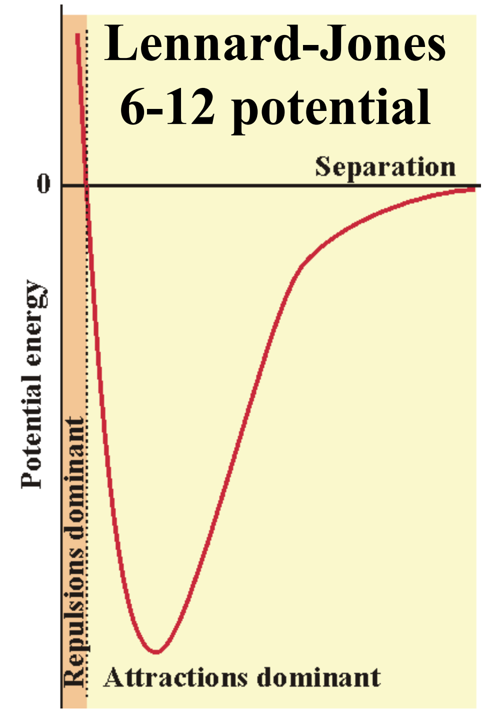
molecules have a non-zero volume




⇒ additional volume needed: **nb**

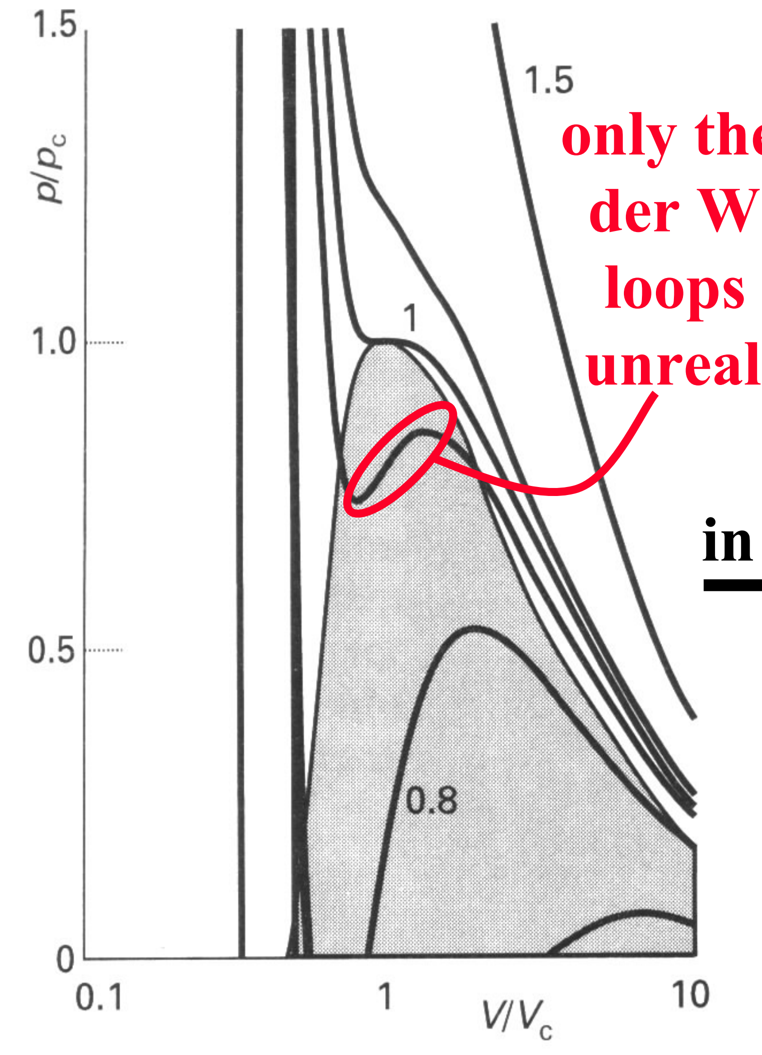
molecules have attractive forces

⇒ reduction in exerted pressure: $a(n/V)^2$ [molecules strike less frequently **and** with reduced force]




$$\Rightarrow \left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

# Plotting the van der Waals equation: In reasonable agreement with reality




in 3D

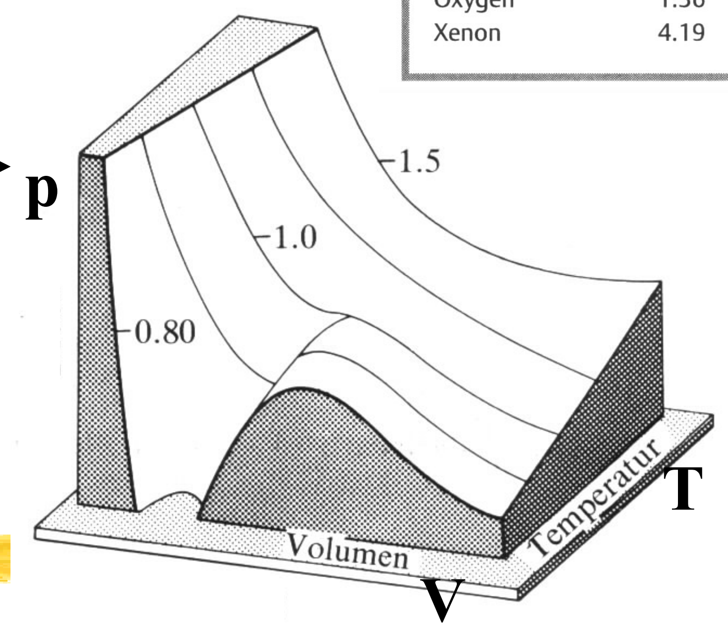



**Table 1.5** *Van der Waals parameters of gases*

| | $a$/(L$^2$ atm mol$^{-2}$) | $b$/(L mol$^{-1}$) |
|---|---|---|
| Air | 1.4 | 0.039 |
| Ammonia | 4.17 | 0.037 |
| Argon | 1.35 | 0.032 |
| Carbon dioxide | 3.59 | 0.043 |
| Ethane | 5.49 | 0.064 |
| Ethene | 4.47 | 0.057 |
| Helium | 0.034 | 0.024 |
| Hydrogen | 0.244 | 0.027 |
| Nitrogen | 1.39 | 0.039 |
| Oxygen | 1.36 | 0.032 |
| Xenon | 4.19 | 0.051 |

# Liquefaction of real gases: The Joule-Thomson effect

Real gases have attractive forces

⇒ if they are allowed to expand through a throttle without outside heat entering ("adiabatic" process) they will use their kinetic (heat) energy to escape each other's attraction

⇒ they will cool down

## Linde refrigerator