

# Physical Chemistry for Energy Engineering (Homework-01 answers, #8, 10/08)

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\*The class follows the text book: D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

# Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Equation of state of gas
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	Around 10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	No lecture

# Contents of today

<Today's class>

**1.X.2. Gas equations**

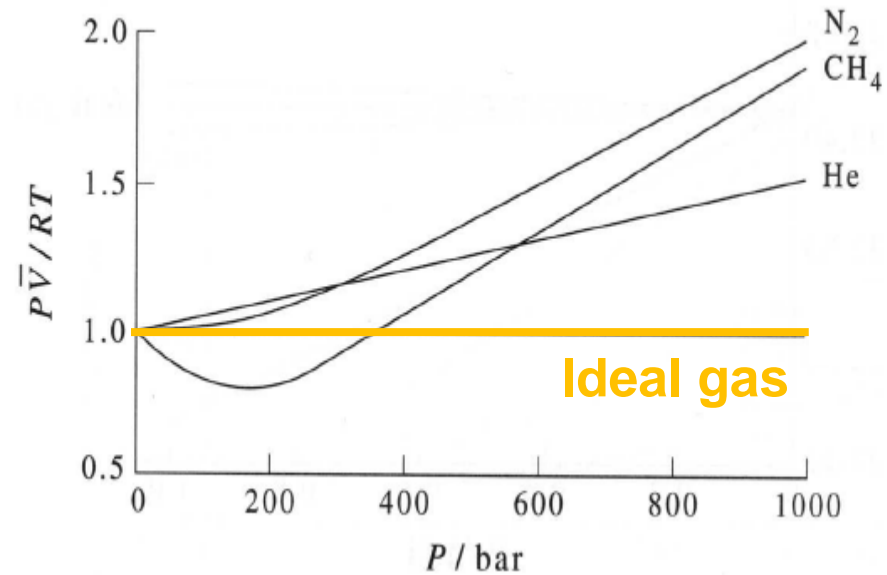
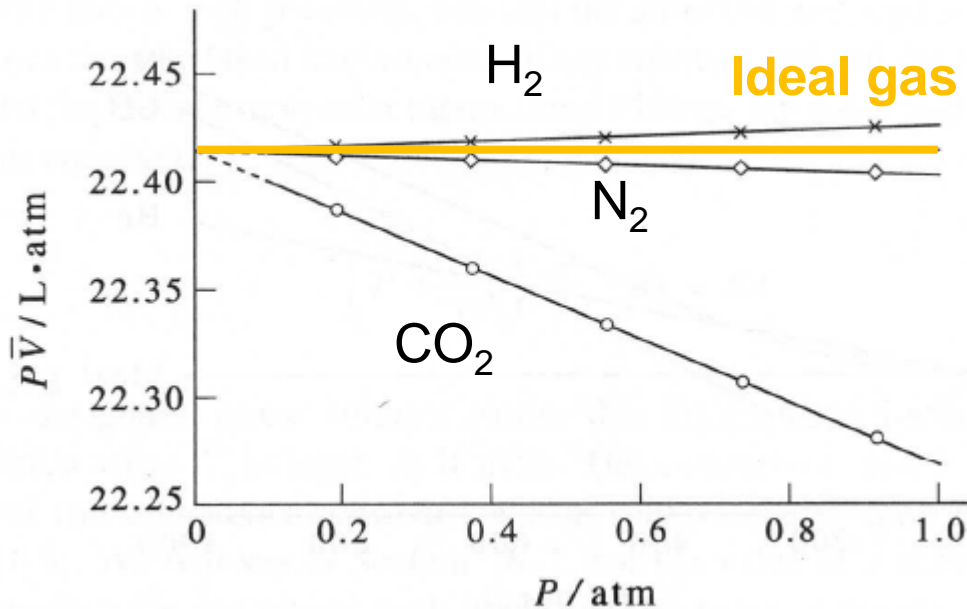
# 1.X.2. Gas equation

## - \$16: ideal gas and real gas -

- ✓ An ideal gas is a theoretical gas composed of a set of randomly moving, non-interacting point particles. (\*wikipedia)
  - ✓ Thus, molecules move independently of each other and do not experience any intermolecular interactions.
- ✓ The ideal-gas equation is valid for all gases if a sufficiently low pressures and a high temperature are the conditions. However, error becomes large as the pressure increases.

*Good agreement ( $P \sim 1$  bar)*

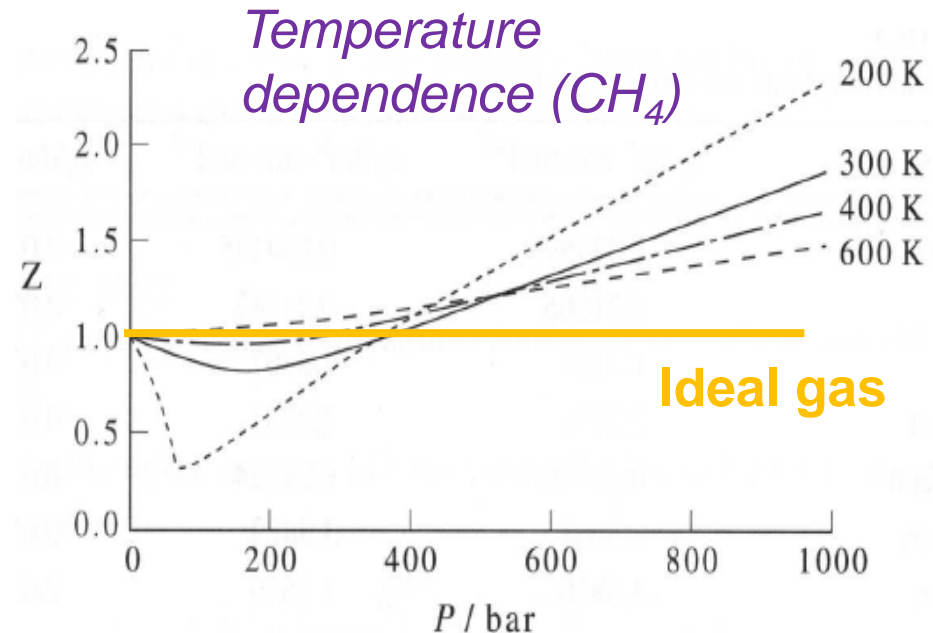
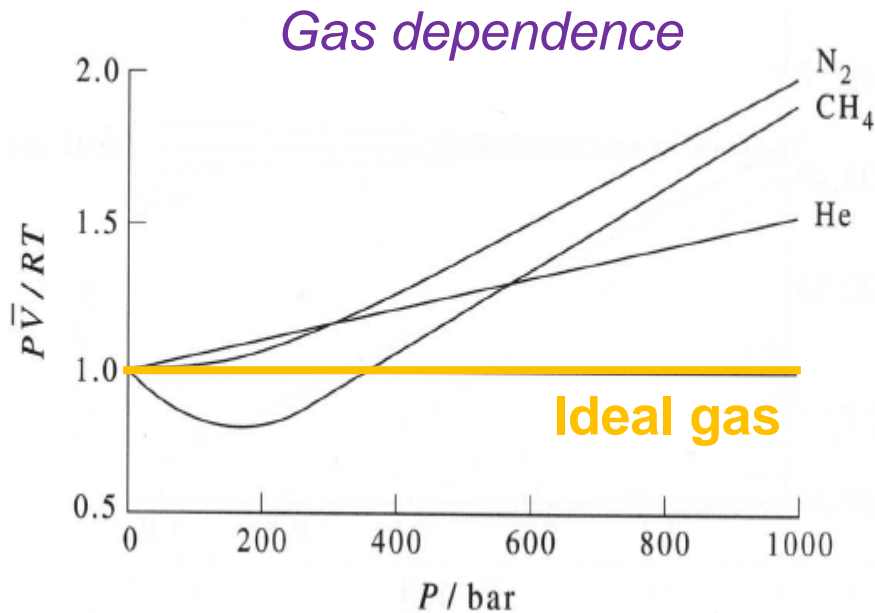
*Bad agreement ( $P > 10$  bar)*



# 1.X.2. Gas equation

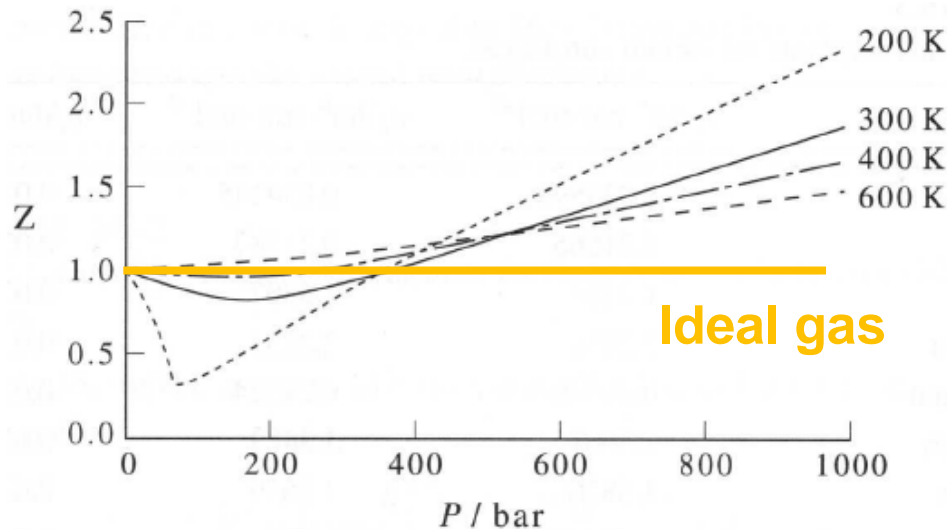
## - \$16: compressibility factor -

- ✓ The compressibility factor  $Z = \frac{P\bar{V}}{RT} = \frac{PV}{nRT}$  is often used to quantify the **non-ideality** of real gas. ( $\bar{V} = \frac{V}{n}$  is molar volume)
- ✓ If  $Z = 1$ , it means that the gas behaves as an ideal gas, which is achieved with low  $P$ .



# 1.X.2. Gas equation

## - \$16: reasons of differences between ideal gas and real gas-



\*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

- ✓ [low temperatures] The molecules are moving less rapidly and so are more influenced by their attractive forces of inter-molecular interaction. Because of the attractive forces, the molecules are drawn together, thus making  $\bar{V}_{real} < \bar{V}_{ideal}$ , which in turn makes  $Z < 1$ .
- ✓ [high temperatures] The molecules are moving rapidly enough that their attraction is much smaller than their kinetic energies ( $U_{binding} \ll U_{kinetic}$ ).
  - ✓ [high-pressure] The molecules are influenced primarily by their repulsive forces, which work at short range like when the inter-molecular distance is close to the sum of molecular radii. This repulsive effect may be considered as the effect of molecular size, which is neglected in ideal gas.

## 1.X.2. Gas equation

### - §16.2: The van der Waals equation as equation of state-

- ✓ One of the most famous one is the van der Waals equation:

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

where  $\bar{V}$  is molar volume ( $\bar{V} = \frac{V}{n}$ ).

- ✓ The constant parameters  $a$  and  $b$  are called *van der Waals constants*.
  - $a$  reflects how strongly the molecules of a gas attract each other.
  - $b$  reflects the size of molecules, related to the repulsive force for short ranges.

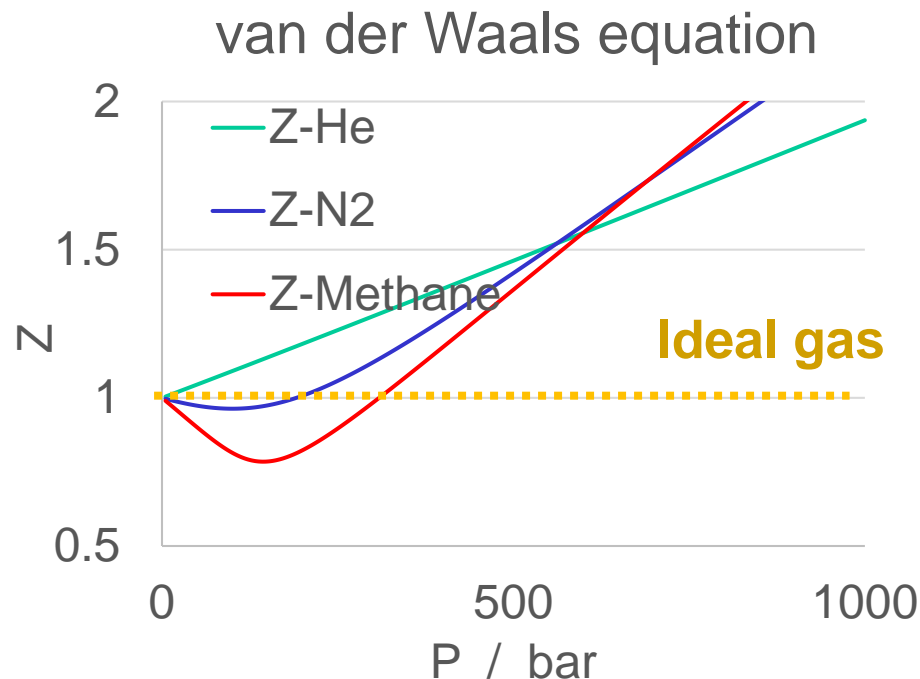
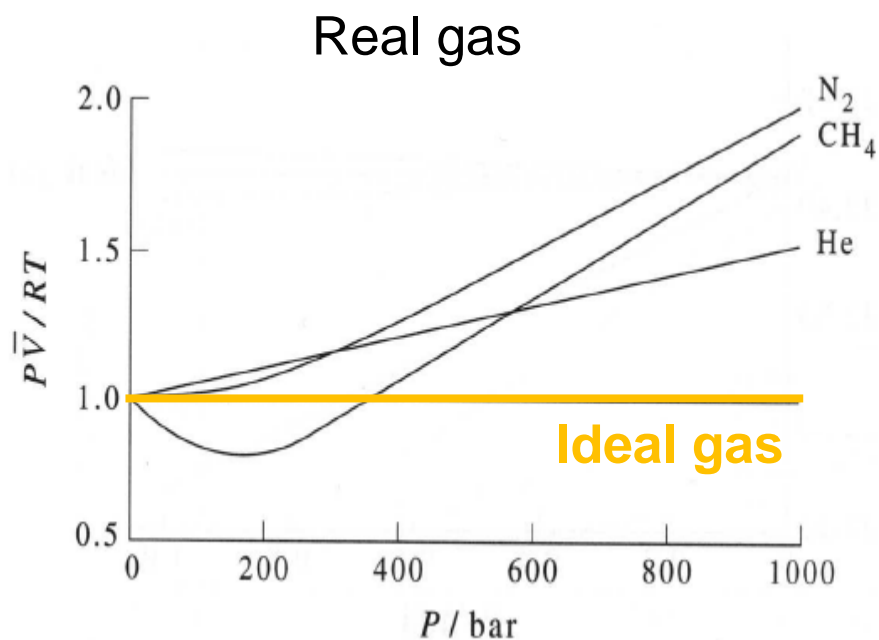
Species	$a$ [ $10^{-7} \text{ m}^6 \text{ Pa mol}^{-2}$ ]	$b$ [ $10^{-7} \text{ m}^3 \text{ mol}^{-1}$ ]
He	0.03460	0.2373
Ne	0.2166	0.1738
Ar	1.348	0.3183
O <sub>2</sub>	1.382	0.3186
Methane (CH <sub>4</sub> )	2.303	0.4307
Benzene (C <sub>6</sub> H <sub>6</sub> )	18.88	1.197

# 1.X.2. Gas equation

## - §16.2: van der Waals equation, with several gas species -

- ✓ Although van der Waals equation is still less accurate at high pressures,  $Z$ -factor's dependence on  $P$  is qualitatively well described.

Comparison on gas species dependence of  $Z$  factor.





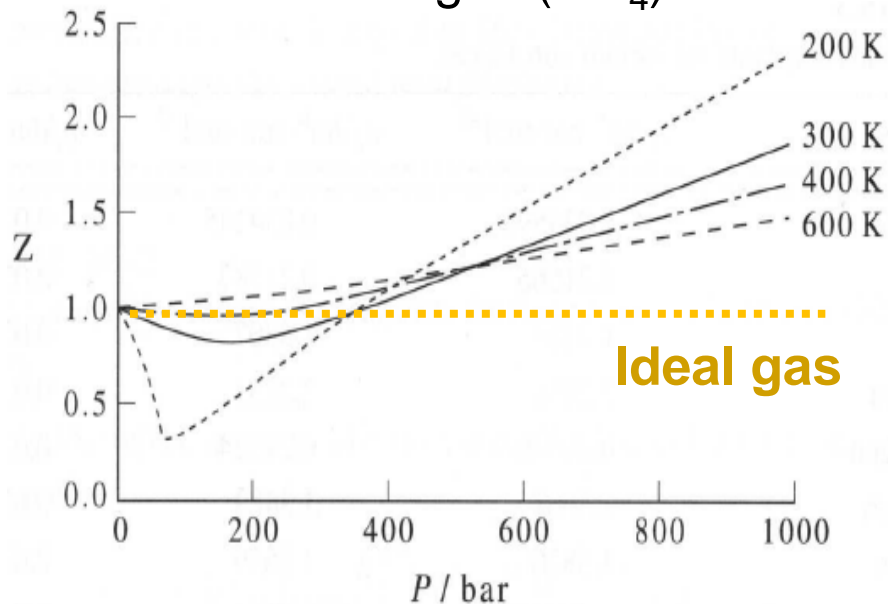
# 1.X.2. Gas equation

## - \$16.2: van der Waals equation, temperature dependence-

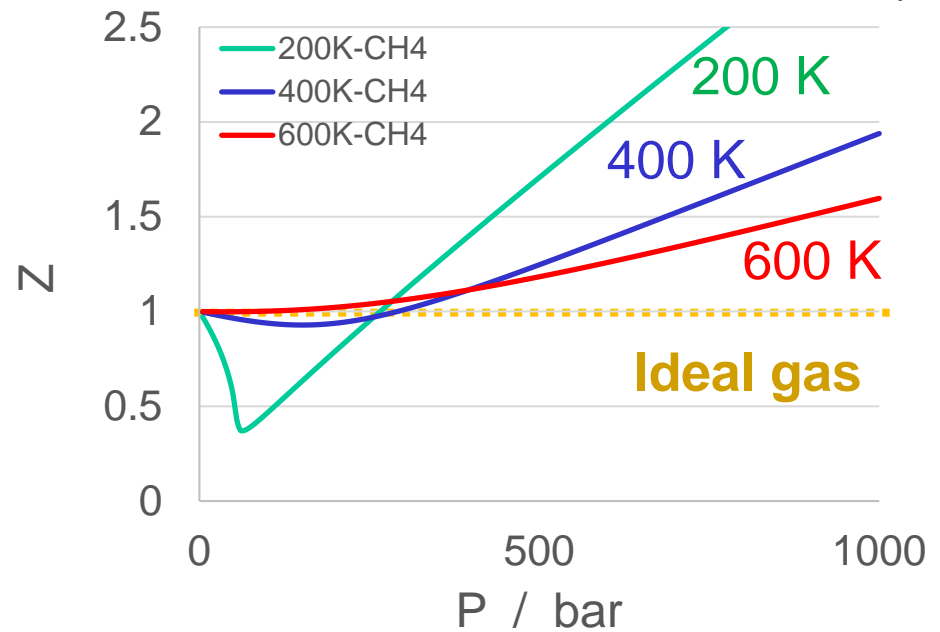
- ✓ Although van der Waals equation is still less accurate at high pressures,  $Z$ -factor's dependence on  $P$  is qualitatively well described.

Comparison on temperature dependence of  $Z$  factor.

Real gas ( $\text{CH}_4$ )



van der Waals equation ( $\text{CH}_4$ )



# 1.X.2. Gas equation

## - \$16.2: van der Waals equation, comparison with others-

(1) Van der Waals equation  
(dot-dashed line)

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

(2) Redlich-Kwong equation  
(long dashed line)

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)}$$

(2) Peng-Robinson equation  
(short dashed)

$$P = \frac{RT}{\bar{V} - \beta} - \frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)}$$

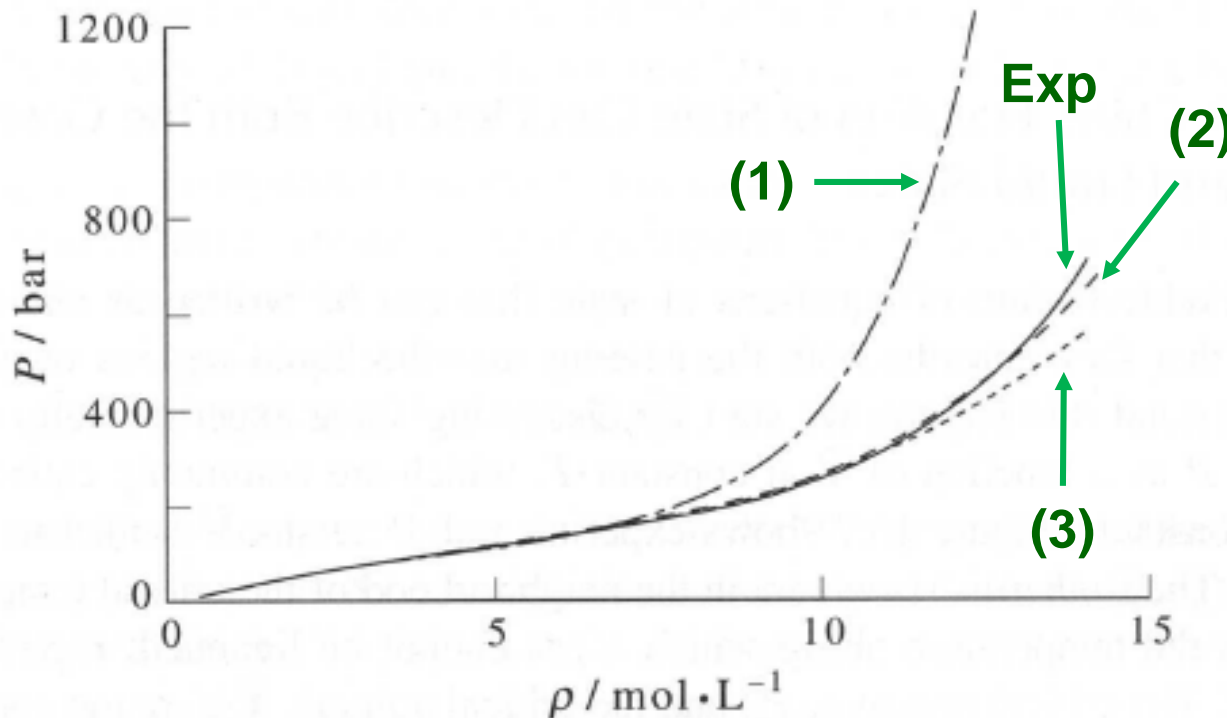


Figure: Experimental pressure versus density data for ethane at 400 K (solid) with veracious theoretical equations.

\*1 bar =  $1 \times 10^5$  Pa

## 1.X.2. Gas equation

- §16.3: vdW equation describes both gaseous and liquid states -

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$



- ✓ The van der Waals equation can be written as a cubic equations of  $\bar{V}$ :

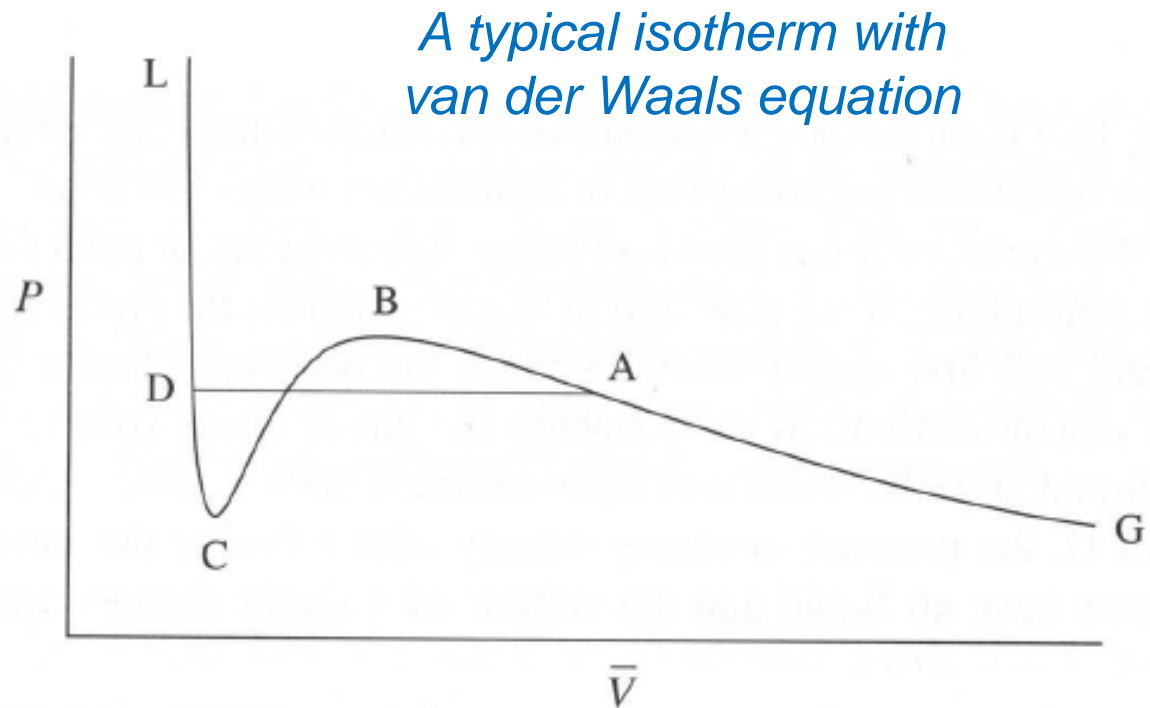
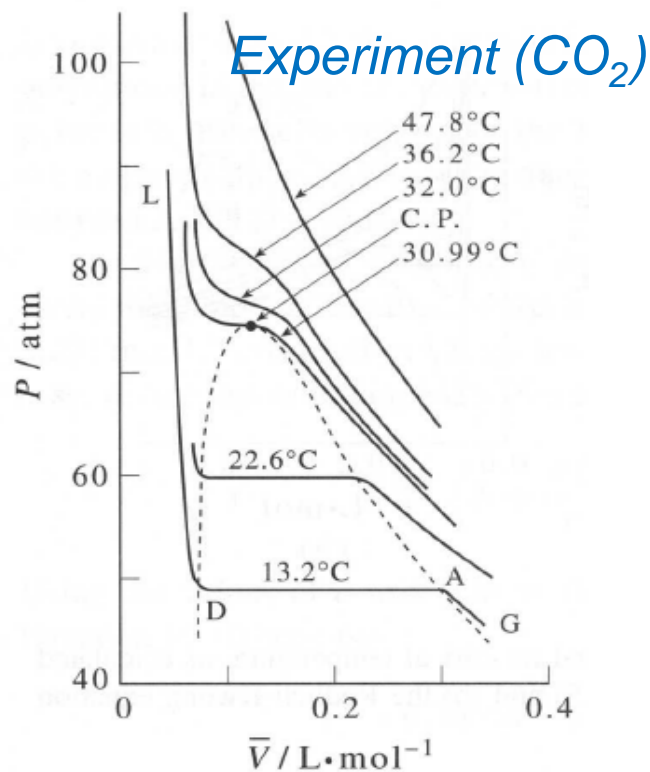
$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

- ✓ In general, if the equation of state can be written as a cubic equation of  $\bar{V}$ , there are 3 volumes for a specific pressure value. Then, **the equation can reproduce both the gaseous and the liquid states of a substance.**
  - ✓ Note that ideal-gas equation cannot describe a condensed phase (liquid or solid) because it does not involve inter-atomic interaction, which is vital to form liquid and solid.
- ✓ Appearance of liquid phase can be seen in pressure-volume isotherms.

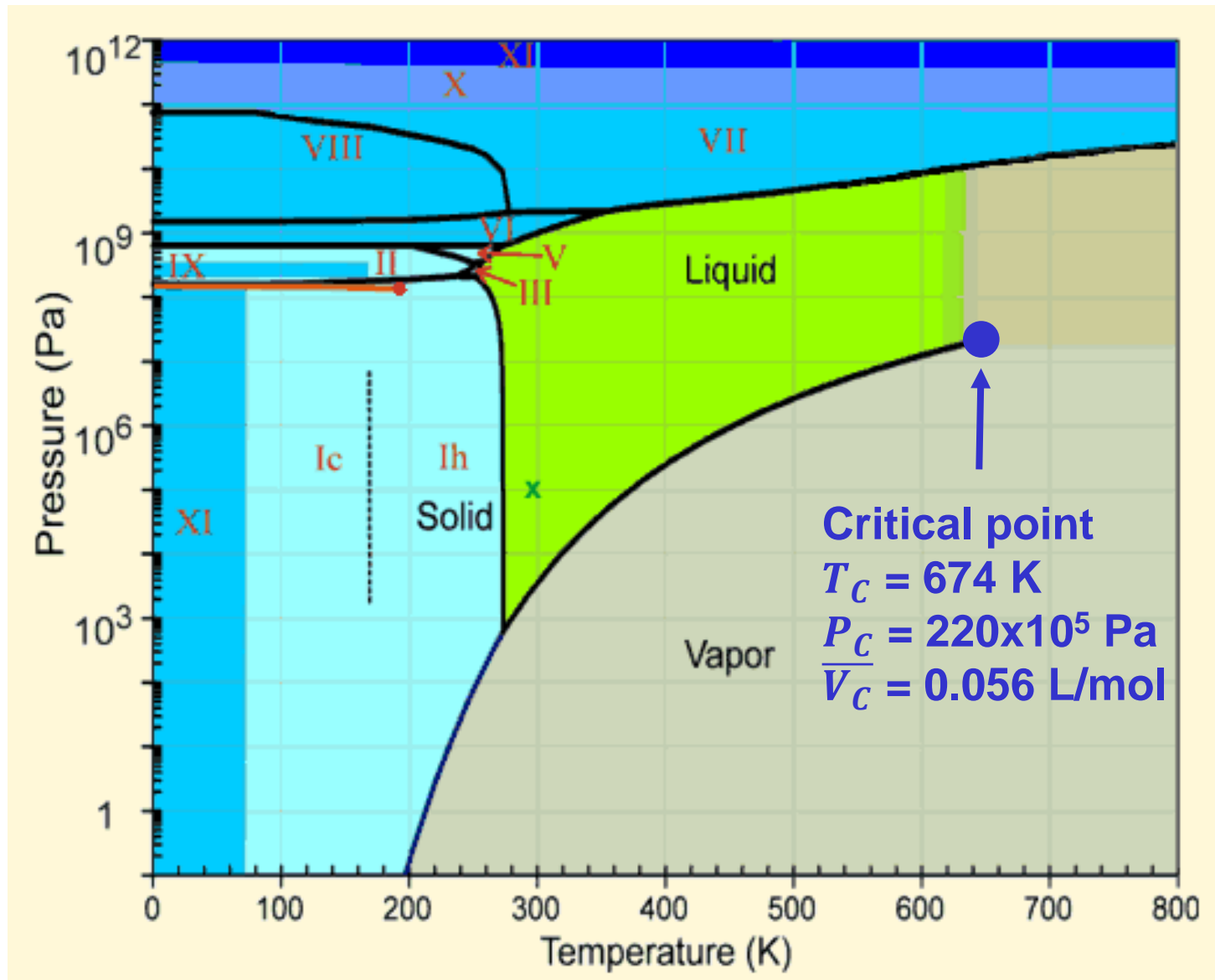
## 1.X.2. Gas equation

### - \$16.3: vdW equation describes both gaseous and liquid states -

- ✓ In isotherms of a cubic equations of  $\bar{V}$ , we may have 3 different  $\bar{V}$  values for a certain  $P$ , mathematically. This is achieved when the temperature is lower than the **critical temperature**.
  - ✓ L-D: the change of pressure of the liquid as a function of volume
  - ✓ D-A: liquid-gas coexistence curve
  - ✓ A-G: the change of pressure of the gas as a function of volume



# (Appendix) phase diagram of water



## (Appendix) critical point

- ✓ The liquid-gas coexistence curve ends abruptly at the critical point, where the difference between the liquid and gaseous phases are not distinct.
- ✓ If both temperature and pressure are larger than the critical point values, the liquid and the vapor phase simply merge into a single fluid phase, which is called *supercritical fluid*.

Species	$T_c/K$	$P_c/\text{bar}$	$P_c/\text{atm}$	$\bar{V}_c/\text{L}\cdot\text{mol}^{-1}$	$P_c\bar{V}_c/RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443
Water	647.126	220.55	217.66	0.05595	0.2295

# (Appendix) supercritical water

To supercritical state of water (increasing temperature with a constant volume)  
The critical temperature of water is 374°C.

\*<http://www.youtube.com/watch?v=29oy1UCHJIE>



## 1.X.2. Gas equation

### - §16.3: vdW equation describes both gaseous and liquid states -

- ✓ We can correlate the van der Waals equation and the quantities at the critical point:  $T = T_C$ ,  $P = P_C$  and  $\bar{V} = \bar{V}_C$ .
- ✓ Since a cubic equation should have a sole real solution at the critical point
$$(\bar{V} - \bar{V}_C)^3 = \bar{V}^3 - 3\bar{V}_C\bar{V}^2 + 3\bar{V}_C^2\bar{V} - \bar{V}_C^3 = 0$$

- ✓ Then compare this equation with the van der Waals equation:

$$3\bar{V}_C = b + \frac{RT_C}{P_C}, \quad 3\bar{V}_C^2 = \frac{a}{P_C}, \quad \text{and} \quad \bar{V}_C^3 = \frac{ab}{P_C} . \quad \text{Accordingly,}$$

$$\bar{V}_C = 3b, \quad P_C = \frac{a}{27b^2}, \quad T_C = \frac{8a}{27bR} \quad \text{and}$$

$$a = \frac{27(RT_C)^2}{64P_C}, \quad b = \frac{RT_C}{8P_C}$$

>> Accordingly van der Waals constants are determined in this way solely dependent on these experimental quantities at the critical point.



## 1.X.2. Gas equation

### - §16.7: vdW equation is written in terms of molecular parameters -

- ✓ To make it more accurate, we may describe inter-molecular interaction using a “**potential model**”, such as Morse potential.
- ✓ The important and famous model, which basically works well for inert gasses, are Lennard-Jones (LJ) model:

$$u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}$$

where the first term is for repulsive and the second term for attractive interactions;  $r$  is the inter-molecular distance,  $c_{12}$  and  $c_6$  are model parameters (constants) characteristic of each substance.

- ✓ In this LJ potential model,  $\frac{c_6}{r^6}$  term has a physical background: so called “*London Dispersion forces*”, which can be derived by quantum mechanics.
- ✓ The  $\frac{c_{12}}{r^{12}}$  is rather empirical: to introduce the repulsive interaction when two atoms get close each other and the electron cores start to overlap. (like the molecular size effect)

## 1.X.2. Gas equation

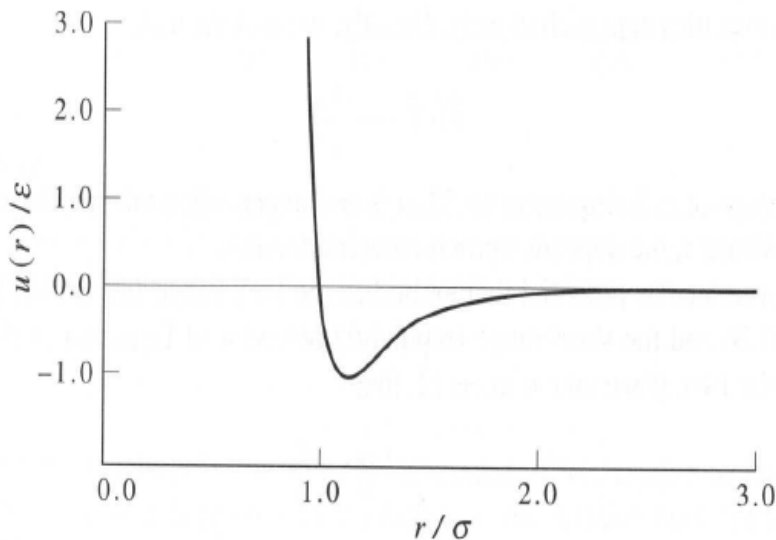
- \$16.7: vdW equation is written in terms of molecular parameters -

✓ Lennard-Jones (LJ) model:  $u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}$

where the first term is for repulsive and the second term for attractive interactions;  $r$  is the inter-molecular distance,  $c_{12}$  and  $c_6$  are model parameters (constants) characteristic of each substance.

$$u(r)/\varepsilon = 4 \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

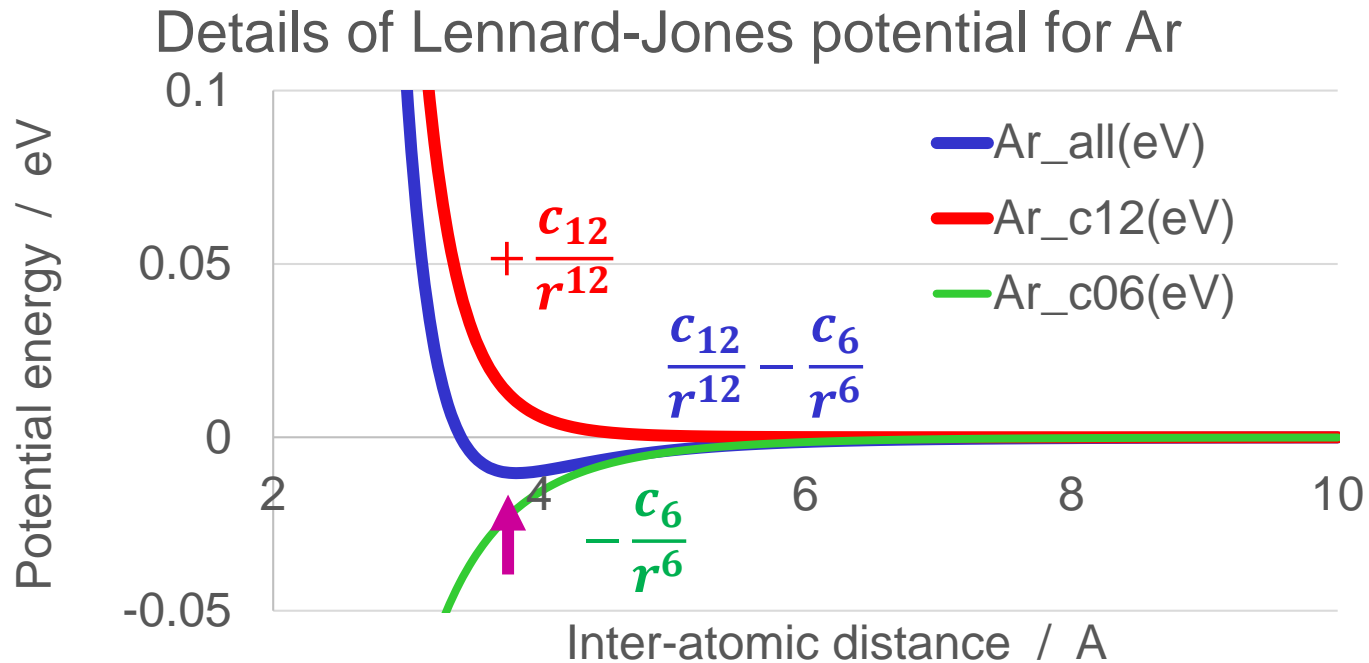
$$c_{12} = 4\varepsilon\sigma^{12} \quad c_6 = 4\varepsilon\sigma^6$$



Species	$(\varepsilon/k_B)/\text{K}$	$\sigma/\text{pm}$	$(2\pi\sigma^3 N_A/3)/\text{cm}^3 \cdot \text{mol}^{-1}$
He	10.22	256	21.2
Ne	35.6	275	26.2
Ar	120	341	50.0
Kr	164	383	70.9
Xe	229	406	86.9
H <sub>2</sub>	37.0	293	31.7
N <sub>2</sub>	95.1	370	63.9
O <sub>2</sub>	118	358	57.9
CO	100	376	67.0
CO <sub>2</sub>	189	449	114.2
CF <sub>4</sub>	152	470	131.0
CH <sub>4</sub>	149	378	68.1
C <sub>2</sub> H <sub>4</sub>	199	452	116.5
C <sub>2</sub> H <sub>6</sub>	243	395	77.7
C <sub>3</sub> H <sub>8</sub>	242	564	226.3
C(CH <sub>3</sub> ) <sub>4</sub>	232	744	519.4

## 1.X.2. Gas equation

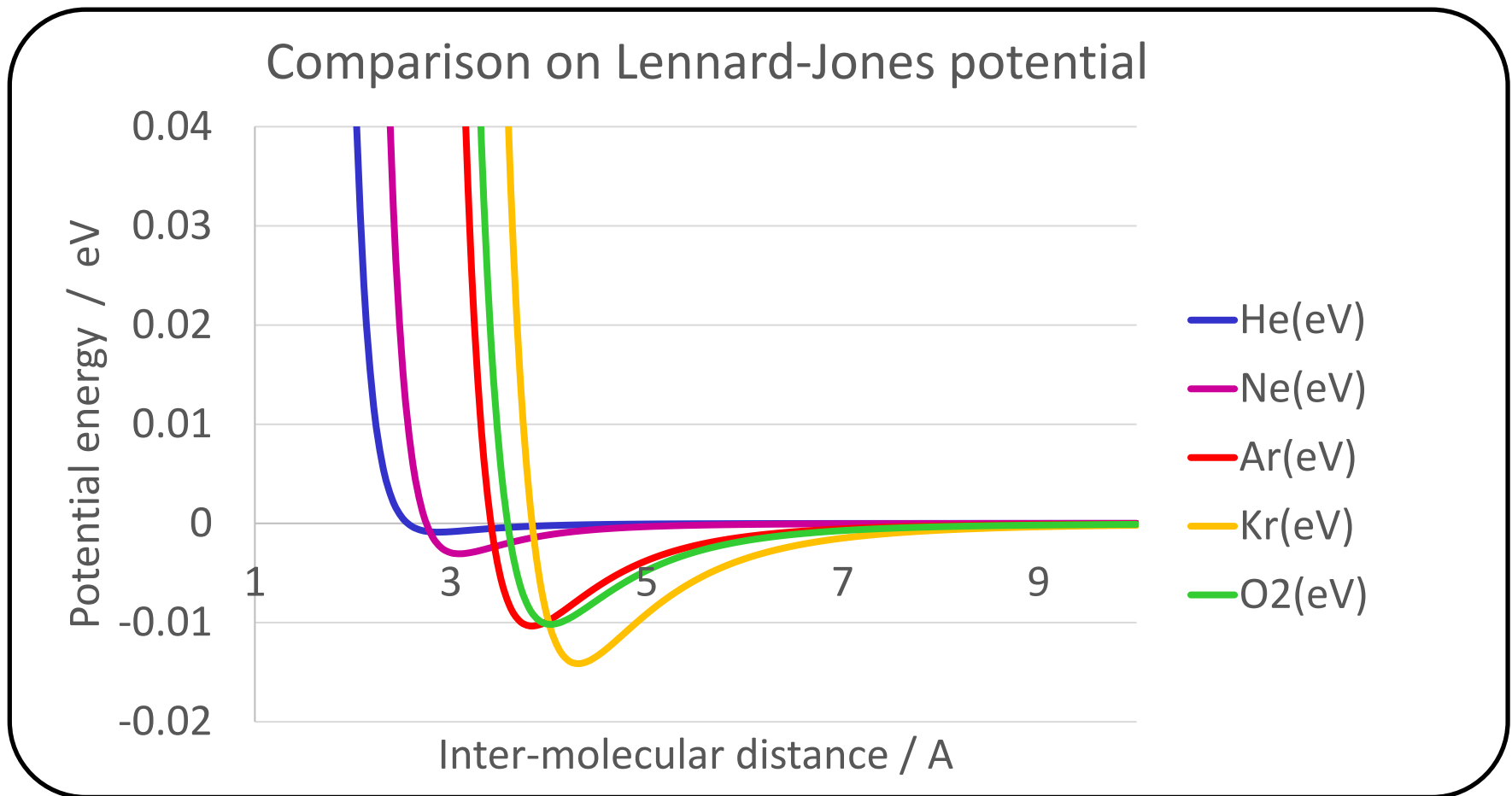
- §16.7: vdW equation is written in terms of molecular parameters -



- ✓  $\frac{c_{12}}{r^{12}}$  repulsive term dominates the overall shape for shorter inter-atomic distances, while  $-\frac{c_6}{r^6}$  attractive term for longer inter-atomic distances.
- ✓ There is a minimum at  $\sim 3.8 \text{ \AA}$ . If the temperature is enough low, Ar may form a crystal or  $\text{Ar}_2$  molecule with the inter-atomic distance of  $\sim 3.8 \text{ \AA}$ .
  - ✓ However, as the energy gain by this interaction is small ( $\sim 0.01 \text{ eV/bond}$ ), they may not form molecules or solid at high temperatures due to the “entropy effect”.

## 1.X.2. Gas equation

- \$16.7: vdW equation is written in terms of molecular parameters -



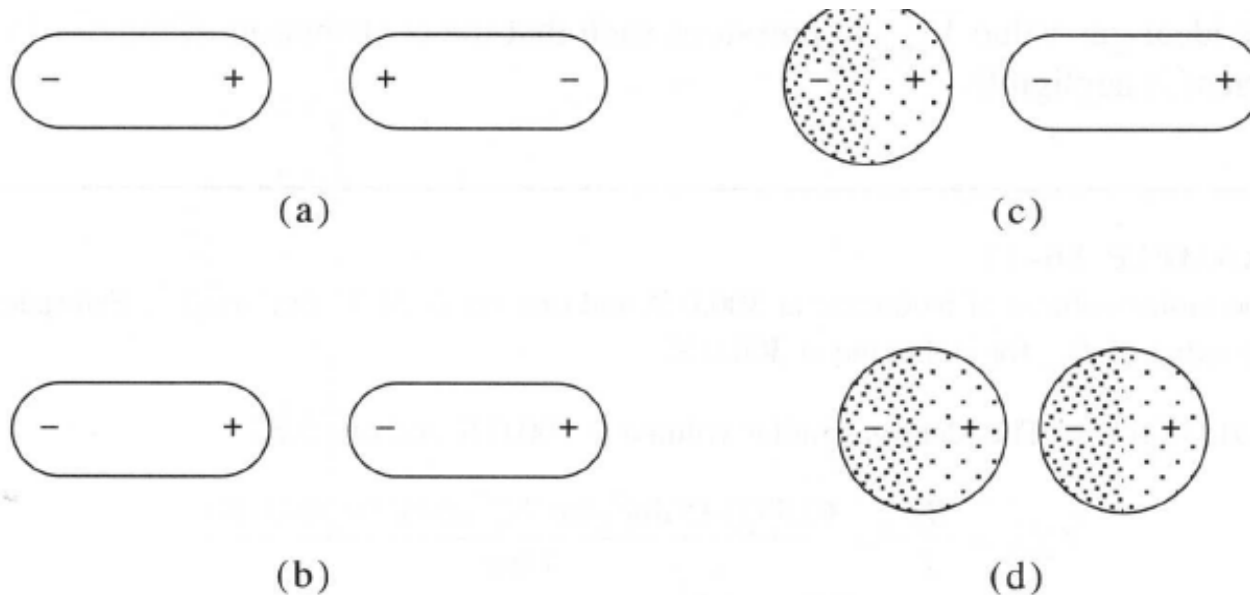
- ✓ In comparison among inert gases, it is clear that large radii reflect in escalation of potential energy at a longer inter-molecular (inter-atomic) distance.

## 1.X.2. Gas equation

- §16.7: vdW equation is written in terms of molecular parameters -

$$u(r) = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6}$$

✓ In this LJ potential model,  $\frac{c_6}{r^6}$  term has a physical background: so called “*London Dispersion forces*”, which can be derived by quantum mechanics.



**FIGURE 16.16**

Two permanent dipoles oriented (a) head-to-head and (b) head-to-tail. The head-to-tail orientation is energetically favorable. (c) A molecule with a permanent dipole moment will induce a dipole moment in a neighboring molecule. (d) The instantaneous dipole-dipole correlation shown here is what leads to a London attraction between all atoms and molecules.

## 1.X.2. Gas equation

### - \$16.7: vdW equation is written in terms of molecular parameters -

- ✓ If we use “virial expansion”, we can correlate the van der Waals equation and the Lennard-Jones potential model.

- ✓ The “virial expansion” of state expresses the compressibility factor as a polynomial in  $1/\bar{V}$ :

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \frac{B_{4V}(T)}{\bar{V}^3} + \dots$$

- ✓ Here, the coefficients in this expansion are functions of temperature only and are called “*virial coefficients*”. An, for example,  $B_{2V}(T)$  is called “*the second virial coefficient*”.

- ✓ The van der Waals equation can be expanded in a form of virial expansion:

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right) \frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots$$

- ✓ For the Lennard-Jones potential mode, we simplify it as:

$$u(r) = -\frac{c_6}{r^6} \text{ when } r > \sigma \text{ and } u(r) = \infty \text{ when } r < \sigma$$

Then, if we take a virial expansion and compare with the vdW case:

$$a = \frac{2\pi N_A^2 c_6}{3\sigma^2}, \quad b = \frac{2\pi\sigma^3 N_A}{3\sigma^2}$$

## 1.X.2. Gas equation

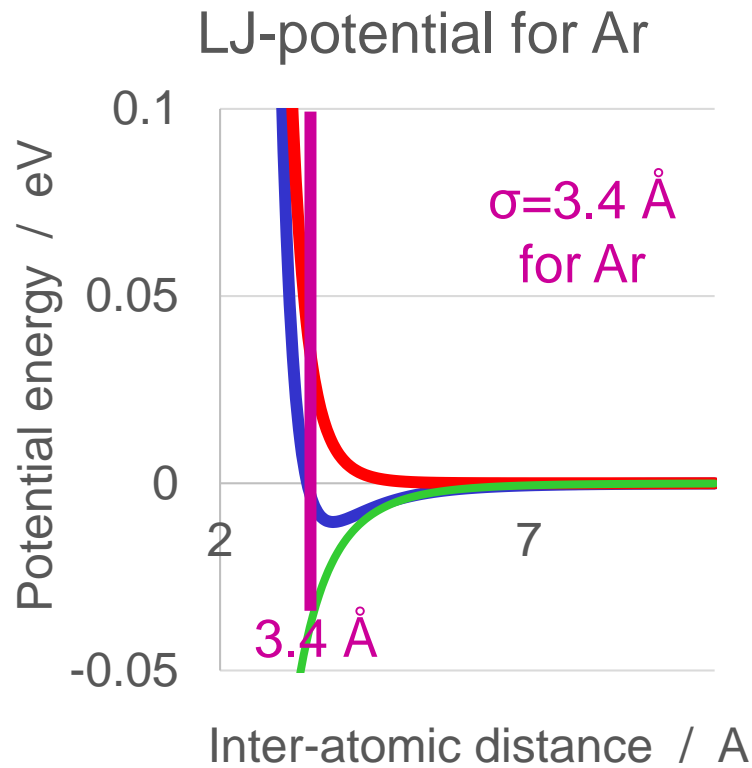
- §16.7: vdW equation is written in terms of molecular parameters -

For the Lennard-Jones potential model, we simplify it as:

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Then, if we take a virial expansion and compare with the vdW case:

$$a = \frac{2\pi N_A^2 c_6}{3\sigma^2} \qquad b = \frac{2\pi\sigma^3 N_A}{3\sigma^2}$$



- ✓ We see that
  - (1)  $a$  is directly proportional to  $c_6$ , coefficient of the attractive force term ( $-\frac{c_6}{r^6}$ ) in the LJ potential model, and
  - (2)  $b$  is equal to four times the volume of the molecule (hard sphere model).
- ✓ Indeed,  $a$  reflects how strongly the molecules of a gas attract each other in vdW equation.

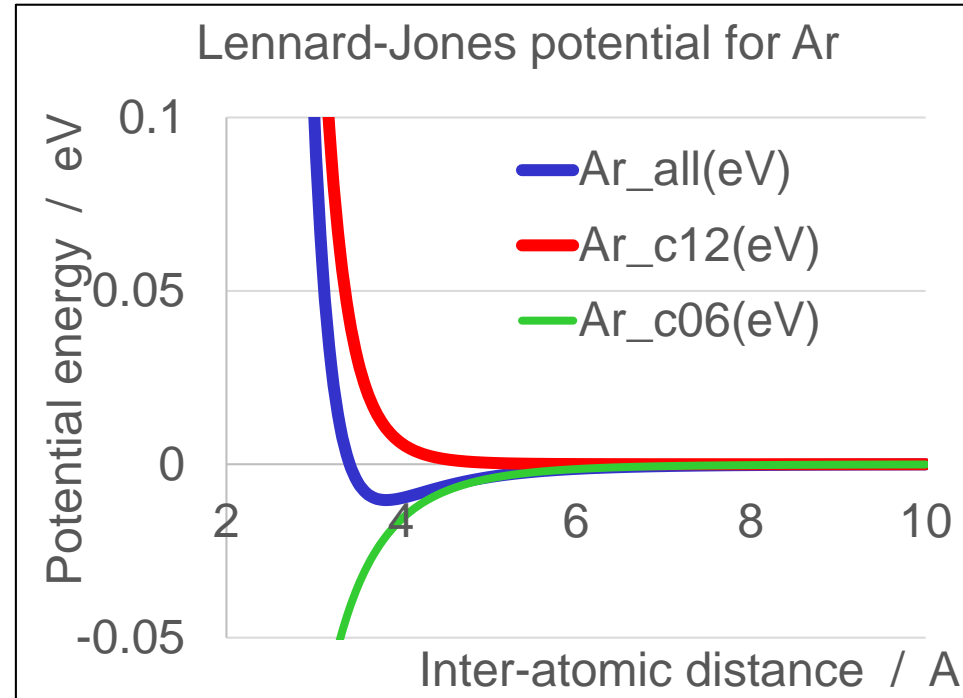
# 1.X.2. Gas equation

## - (Appendix) Molecular dynamics simulation -

Because we know how to evaluate potential energy now, why don't we check atoms motion using Newton's equation of motion??

$$F_x = -\frac{\partial U_{pot}}{\partial x}, F_y = -\frac{\partial U_{pot}}{\partial y}, F_z = -\frac{\partial U_{pot}}{\partial z}$$

$$\mathbf{F} = m\mathbf{a}$$



This is the idea of (classical) molecular dynamics (MD) simulation. As this is based on classical mechanics, quantum effects cannot be involved. However,

- ✓ Atoms and molecules do not normally show significant quantum effects (while electrons do).
- ✓ Quantum effects may be incorporated into the potential energy model, so-called “**potential mode**”.



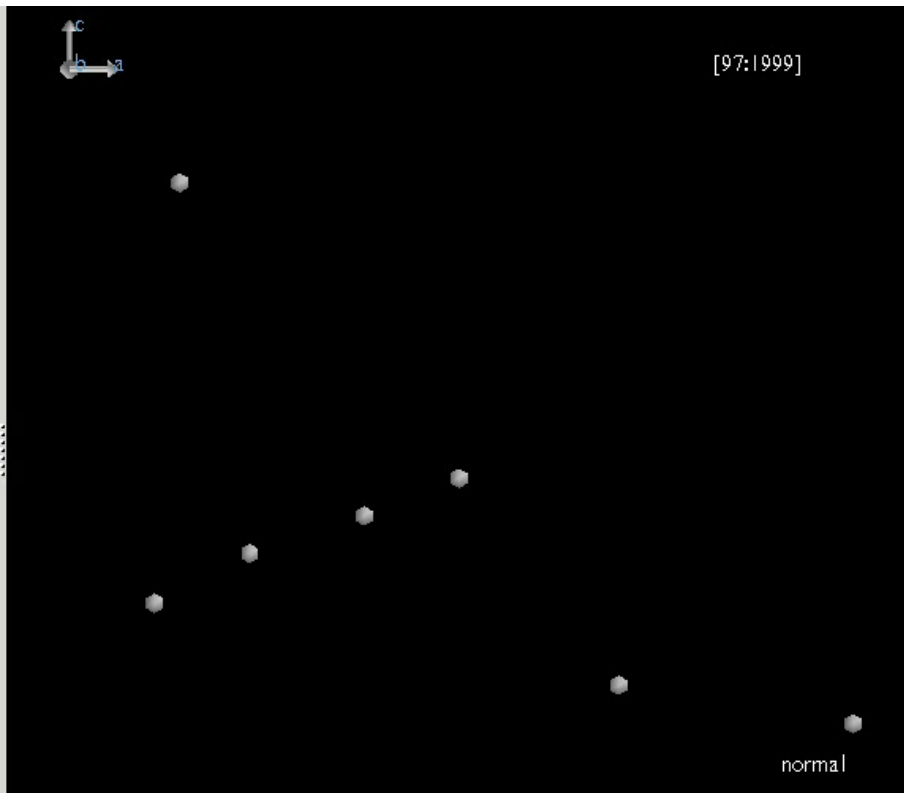
## 1.X.2. Gas equation

### - (Appendix) Molecular dynamics simulation for ideal gas-

If we consider no interaction between molecules, it becomes ideal gas.

- ✓ Ar
- ✓ Constant volume condition:  $V/n = 0.025 \text{ m}^3 (=25 \text{ L})$
- ✓ Left: ( $\sim 0.33 \text{ atm}$ ,  $100 \text{ K}$ ), Right: ( $\sim 2.00 \text{ atm}$ ,  $600 \text{ K}$ )
- ✓  $0.1 \text{ ps/frame}$  in the movie.

### Ideal gasses



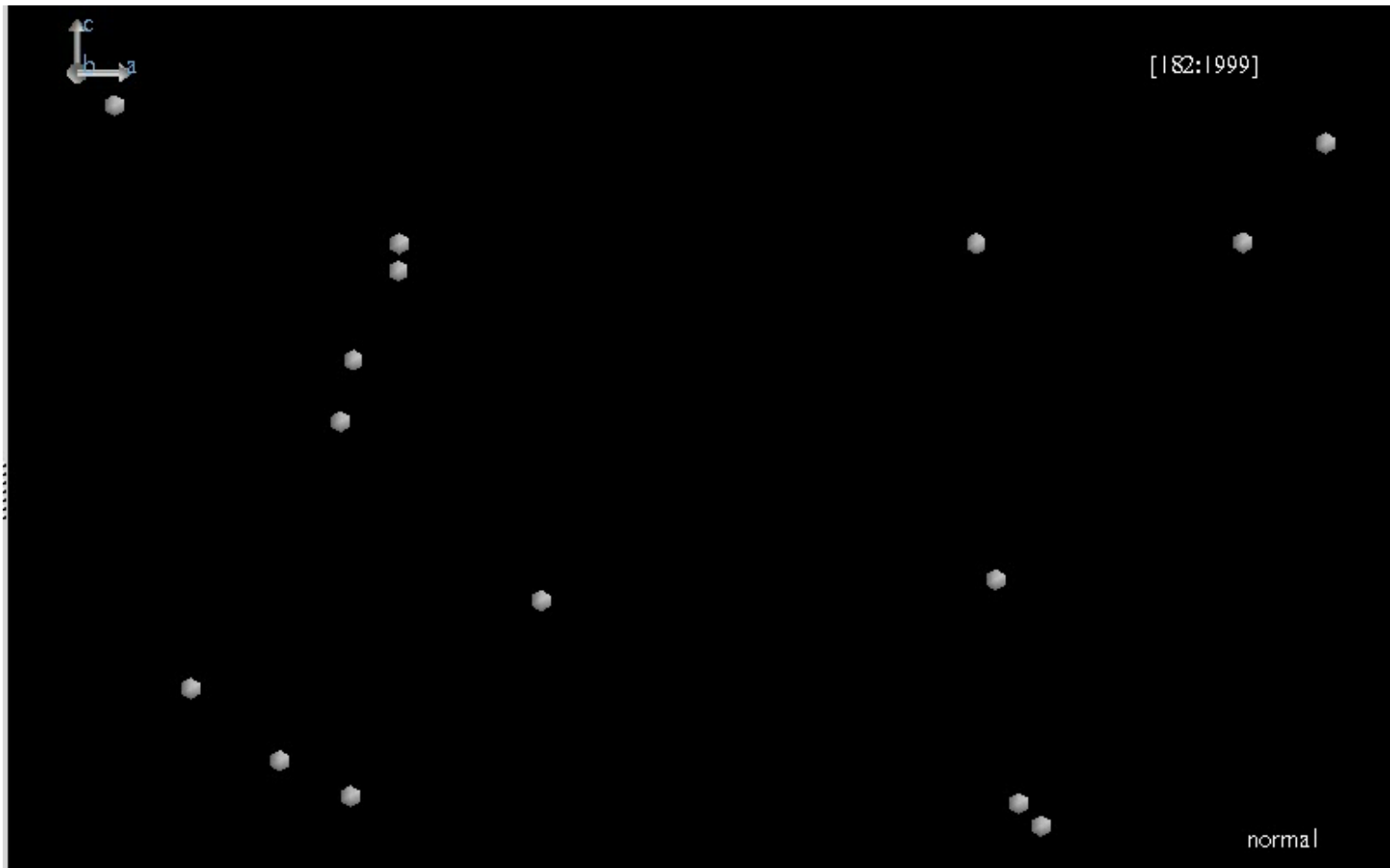
## 1.X.2. Gas equation

### - (Appendix) Molecular dynamics simulation for vdW -

If we use Lennard-Jones potential, the gas behaviors similar to vdW gas.

- ✓ Ar
- ✓ Constant volume condition:  $V/n = 0.025 \text{ m}^3 (=25 \text{ L})$ ; 100 K
- ✓ LJ potential (with parameters given before)

vdW  
gas

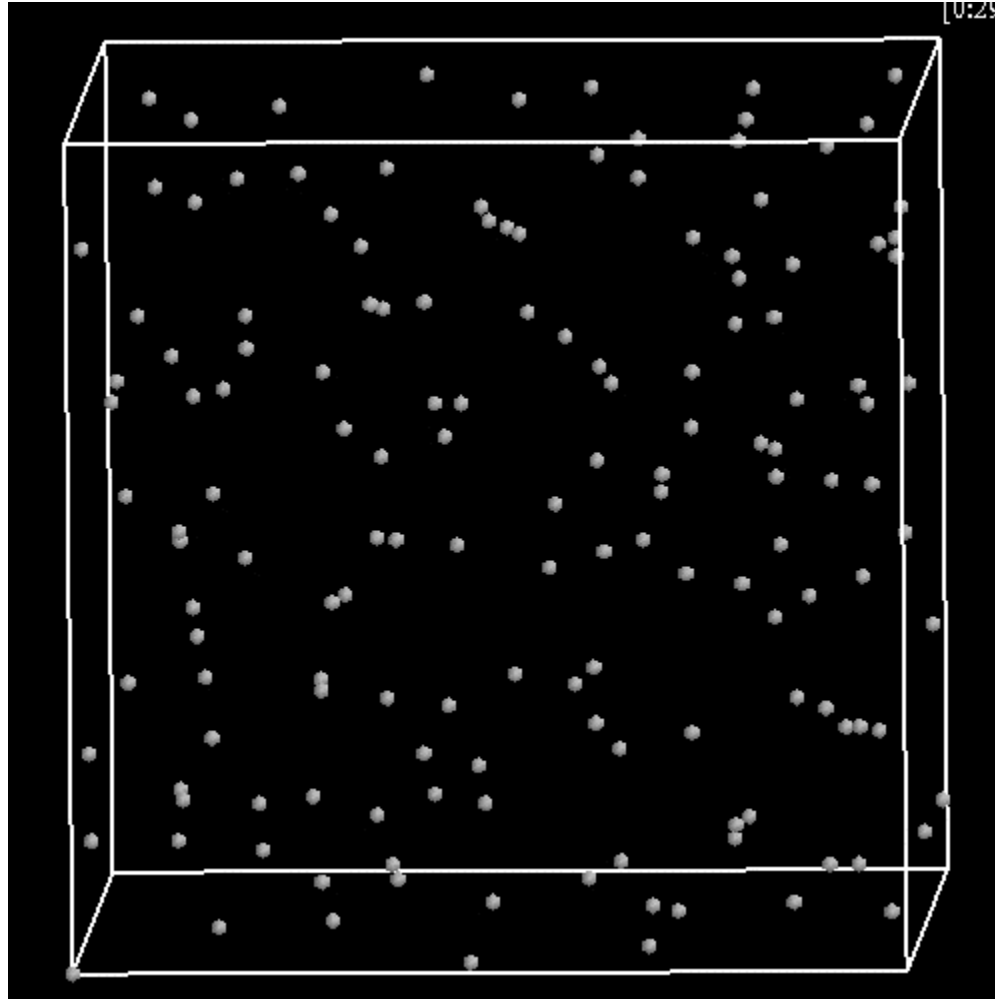


## 1.X.2. Gas equation

- (Appendix) MD for ideal gas: high pressure (~50 atm) -

- ✓ Ar
- ✓ Constant volume condition:  $V/n = 0.0005 \text{ m}^3 (=0.5 \text{ L})$ , 100 K
- ✓ High pressure: 50 atm

**Ideal gas**

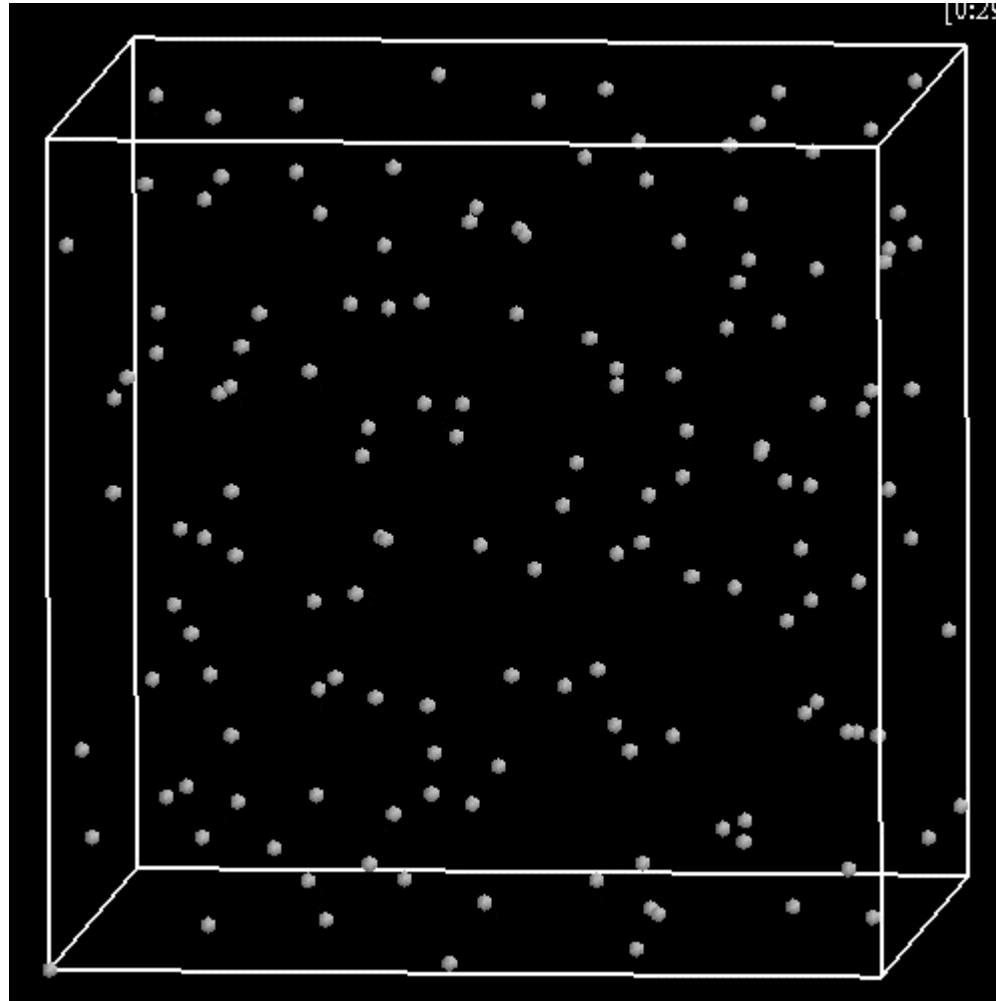


## 1.X.2. Gas equation

### - (Appendix) MD for vdW gas: high pressure (~50 atm) -

- ✓ Ar
- ✓ Constant volume condition:  $V/n = 0.0005 \text{ m}^3 (=0.5 \text{ L})$ , 100 K
- ✓ High pressure: 50 atm

vdW gas

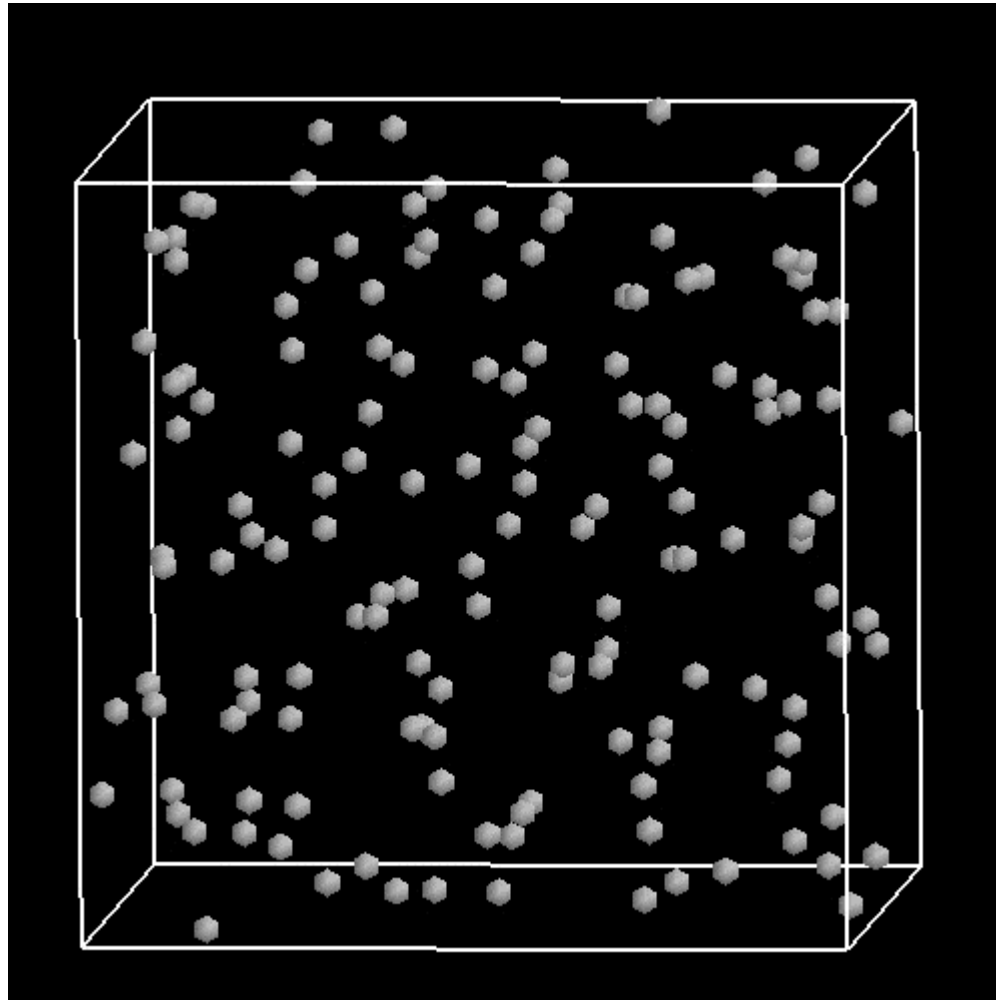


## 1.X.2. Gas equation

### - (Appendix) MD for vdW gas: very high pressure (~400 atm) -

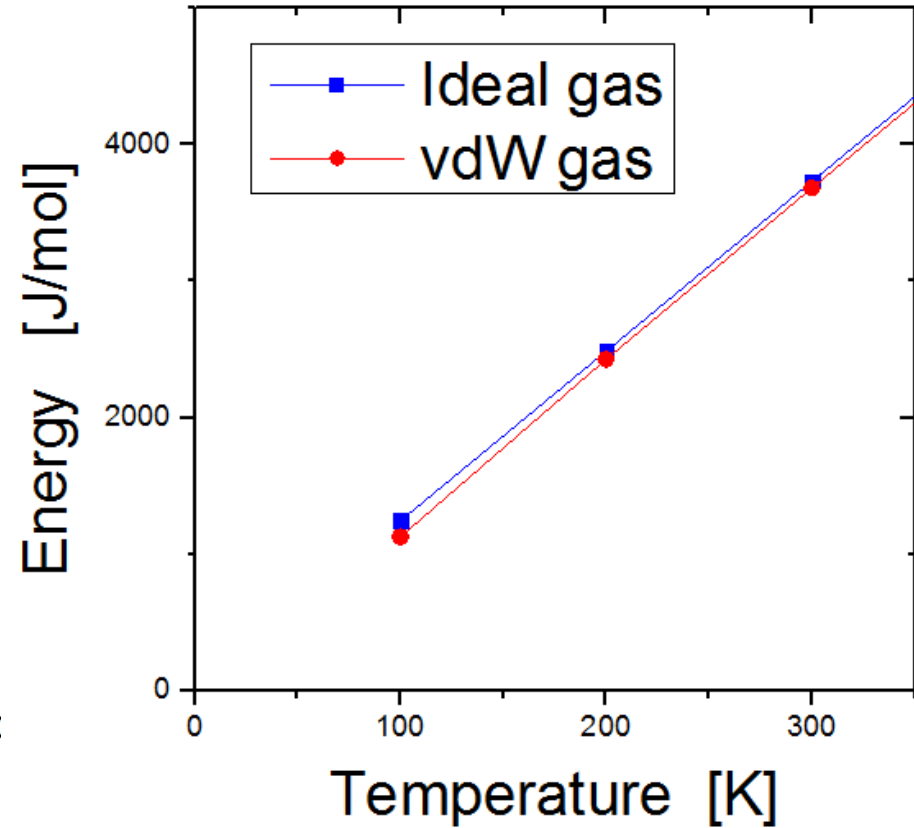
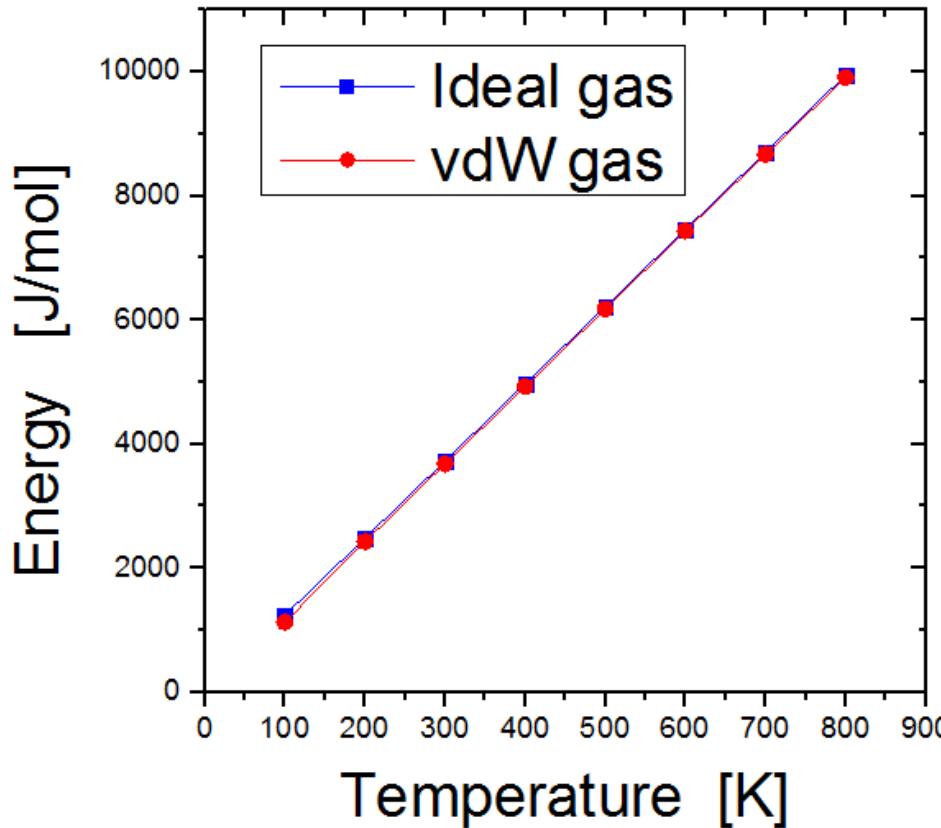
- ✓ Ar
- ✓ Constant volume condition:  $V/n = 0.00006 \text{ m}^3 (=0.06 \text{ L})$ , 100 K
- ✓ High pressure: 400 atm

vdW gas



## 1.X.2. Gas equation

### - (Appendix) MD results: comparison in energy-

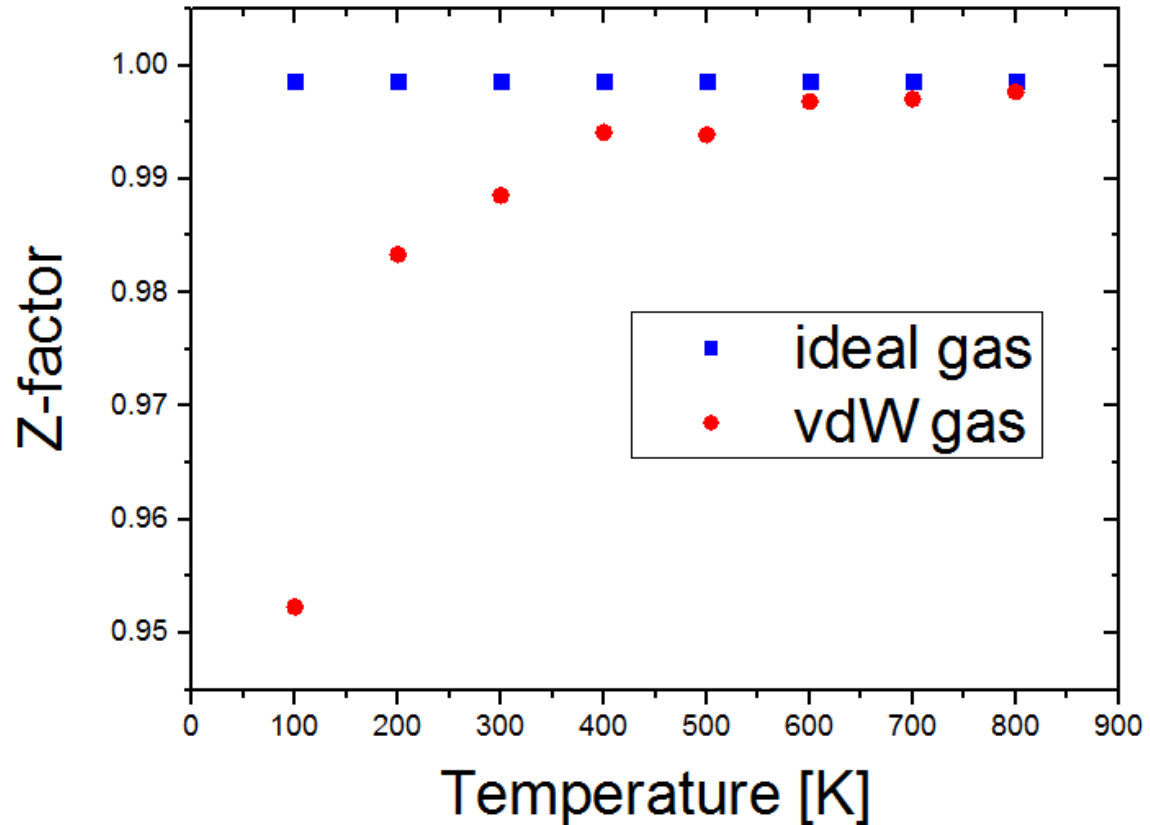


- ✓ The ideal gas energy totally agrees with  $U = \frac{3}{2}nRT$
- ✓ The vdW gas also shows similar energy; however, at low temperatures, because the binding energy contributes significantly, some difference from ideal gas data is observable.

## 1.X.2. Gas equation

### - (Appendix) MD results: comparison in Z factor-

$$Z = \frac{P\bar{V}}{RT} = \frac{PV}{nRT}$$



- ✓ As expected, at high temperatures, even vdW gas behaves like ideal gas.
- ✓ However, at low temperature, there is some difference, due to inter-molecular interaction, including the molecular size effect.