

# Structure of Matter I

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## Molecular Physics

### • Literature:

Atkins' Physical Chemistry  
Oxford Press

### • Requirements

- 50% of homework (handed out every Wednesday, return within one week)
- 1. exam (optional, counts if it improves total grade)  
December 21st, 7:30 - 9:00, Room 218
- 2. exam (required)  
February 4th, 7:50 - 9:00, Room 218

### Syllabus:

1. Thermodynamics and the properties of gases
- ~~2. Chemical equilibrium~~
2. Phase diagrams
3. Chemical equilibrium
4. Quantum theory
5. Molecular structure
6. Molecular symmetry
7. ~~Spin~~ Spectroscopy
8. Molecular interactions
9. Macromolecules and aggregates

# 1. Thermodynamics and the properties of gases

## 1. The perfect <sup>(ideal)</sup> gas

$P, V, n, T \Rightarrow$  state

equation of state :  $pV = nRT$  perfect gas law  
gas constant  $R = 8.31447 \frac{J}{Kmol}$

more than one atom :

<p>unspecific</p> <p>entropic forces,</p> <p>polymers,</p> <p>often collective</p>	<p><math>\leftrightarrow</math></p>	<p>specific</p> <p>molecular bonds,</p> <p>proteins</p> <p>often single molecule</p>
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e.g. solubility of a fatty acid

### Temperature:

collective phenomenon, Brownian energy of many particles, heat

diathermic : full thermal contact  
adiabatic : no thermal contact

Temperature and Brownian motion: (→ Doi, Edwards Theory of Polymer Dynamics page 47)

Fick's law

$$j(x,t) = -D \frac{\partial c}{\partial x}$$
 diffusive flux

microscopic origin: random Brownian motion of molecules

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x}$$
 continuity equation

both together

$$\Rightarrow \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$
 diffusion equation

+ external potential  $U(x) \Rightarrow$

$$F = -\frac{\partial U}{\partial x}$$

$$\Rightarrow v = -\frac{1}{\zeta} \frac{\partial U}{\partial x}$$
 drift velocity

$$\zeta = 6\pi\eta_s a$$
 (Stokes)

$$\Rightarrow j = -D \frac{\partial c}{\partial x} - \frac{c}{\zeta} \frac{\partial U}{\partial x}$$
  
-  $U(x)/kT$

in equilibrium:  $c_{eq}(x) \sim e^{-U(x)/kT}$   $j=0$

$$\Rightarrow -D \frac{\partial c_{eq}}{\partial x} - \frac{1}{\zeta} c_{eq} \frac{\partial U}{\partial x} = 0$$

$$\Rightarrow D = \frac{k_B T}{\zeta}$$
 Einstein relation

Equipartition theorem

Mean energy of each independent mode of a molecule of Brownian motion =  $\frac{1}{2} k_B T$

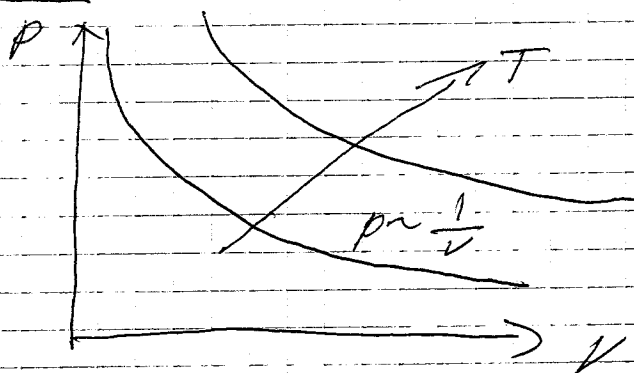
Zerth's law of thermodynamics:

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C then C is also in thermal equilibrium with A.

(Thermal equilibrium based on molecular interactions)

$PV = nRT \Rightarrow$  sets thermodynamic temperature scale

Isotherm:  $T = \text{const}$

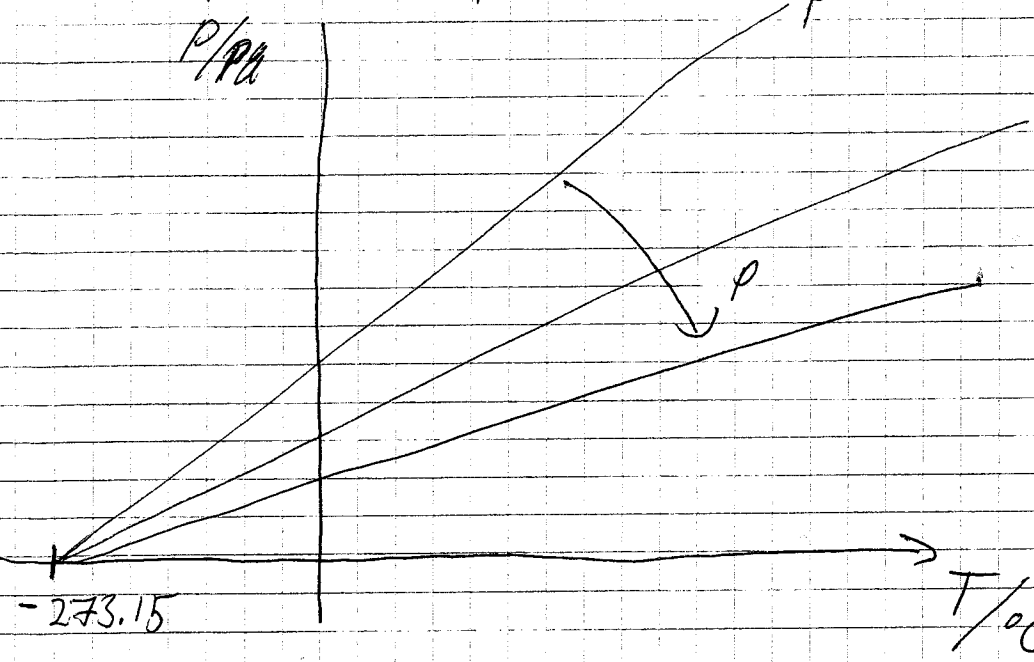


if a sample of gas is compressed to half its volume, then twice as many molecules ~~will~~ strike the walls

$\Rightarrow$  average force on the walls is doubled

only true for dilute gases when molecules are so far apart that specific molecular interactions can be ignored

isobars:  $p = \text{const}$



raising the temperature of a gas increases the speed of its molecules

mixtures of perfect gases

$p = \sum_i p_i$  / partial pressures (also true for real gas)

$p_i = \frac{n_i RT}{V}$

mole fraction  $x_j = \frac{n_j}{n}$       $n = \sum_j n_j$

$p_j = x_j p$

## 2. Real gases

molecular interactions:

repulsive interactions  $\Rightarrow$  extremely short range,  
< molecular diameter

attractive interactions  $\Rightarrow$  short range  
 $\sim \frac{1}{r^2} \propto r^{-3}$

only Coulomb interactions in vacuum are long range

(for details see: J. Israelachvili, Intermolecular + Surface Force  
page 6 + Chapter 9)

low pressures  $\Rightarrow$  large molecule separations  
 $\Rightarrow$  no interactions

moderate pressures  $\Rightarrow$  smaller molecule separations  
 $\Rightarrow$  attractive interactions  
 $\Rightarrow$  higher compressibility

high pressure  $\Rightarrow$  molecules in close contact  
 $\Rightarrow$  repulsive interactions  
 $\Rightarrow$  lower compressibility

Molecular interactions are short range:

typical interaction potentials of two molecules:

$$U(r) = -C \frac{1}{r^n} \quad (\text{note: multipole expansion})$$

region of space where the number density is  $\rho$

total interaction energy of one molecule ( $\sigma$ : diameter) with all the other molecules in a space of size  $L$ :

$$\begin{aligned} \text{total energy} &= \int_{\sigma}^L U(r) \rho 4\pi r^2 dr = -4\pi C \rho \int_{\sigma}^L r^{2-n} dr \\ &= \frac{-4\pi C \rho}{(n-3)\sigma^{n-3}} \left[ 1 - \left(\frac{\sigma}{L}\right)^{n-3} \right] \end{aligned}$$

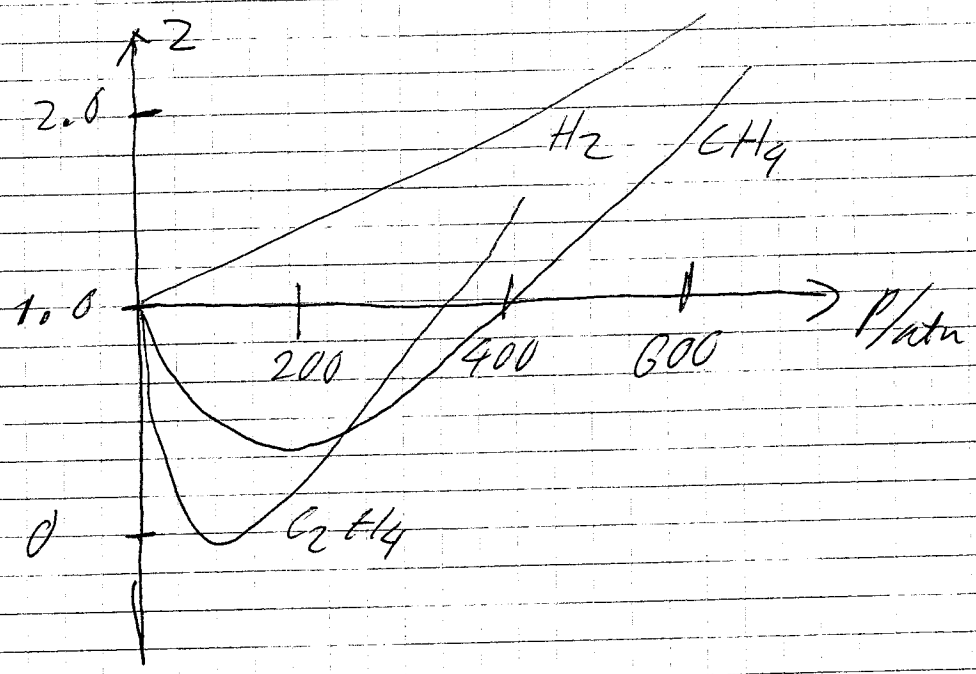
$$= \begin{cases} -4\pi C \rho / (n-3)\sigma^{n-3} & \text{for } n > 3 \quad L \rightarrow \infty \\ \infty & \text{for } n < 3 \quad L \rightarrow \infty \end{cases}$$

$\Rightarrow$  
$$U(r) = -C \frac{1}{r^n} \quad n > 3$$

$\Rightarrow$  short range

### compression factor Z

$$Z = \frac{V_{molar}}{V_{molar, ideal}}$$

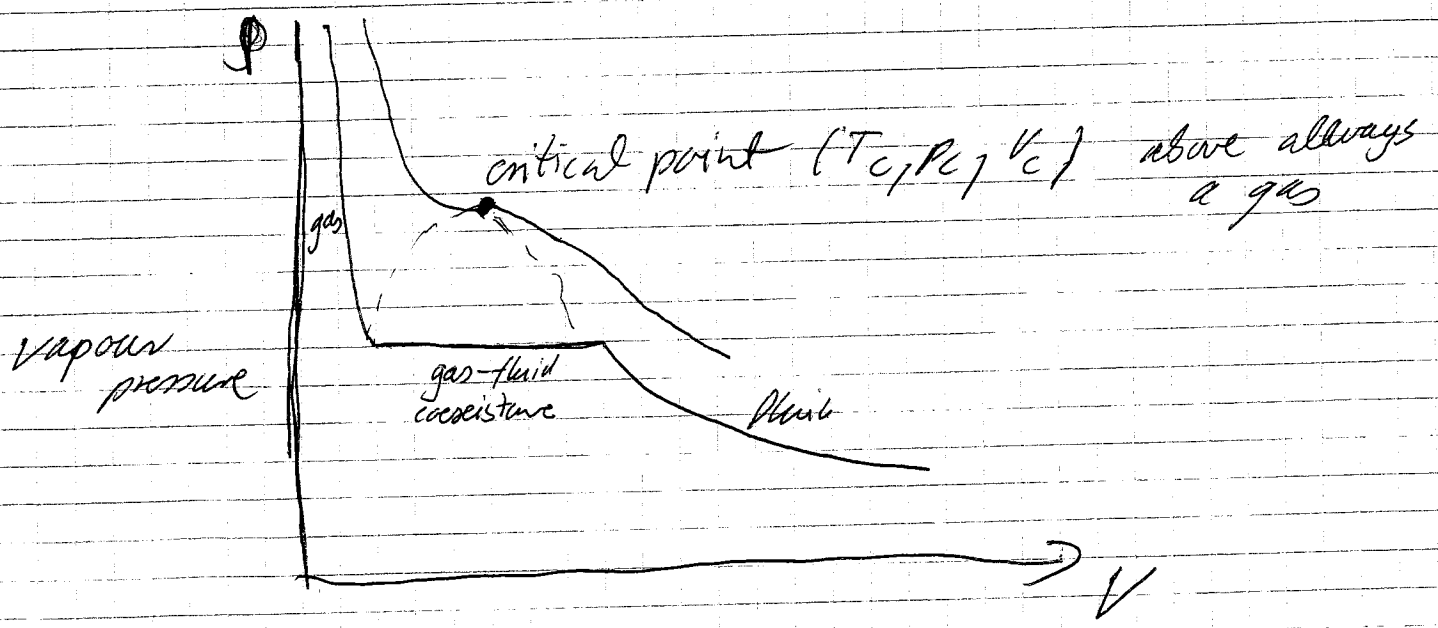


### Viral coefficients

$$P V_{molar} = RT (1 + B'p + C'p^2 + \dots)$$

power law expansion

### Condensation





# Van der Waals equation

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

a, b van der Waals coefficients

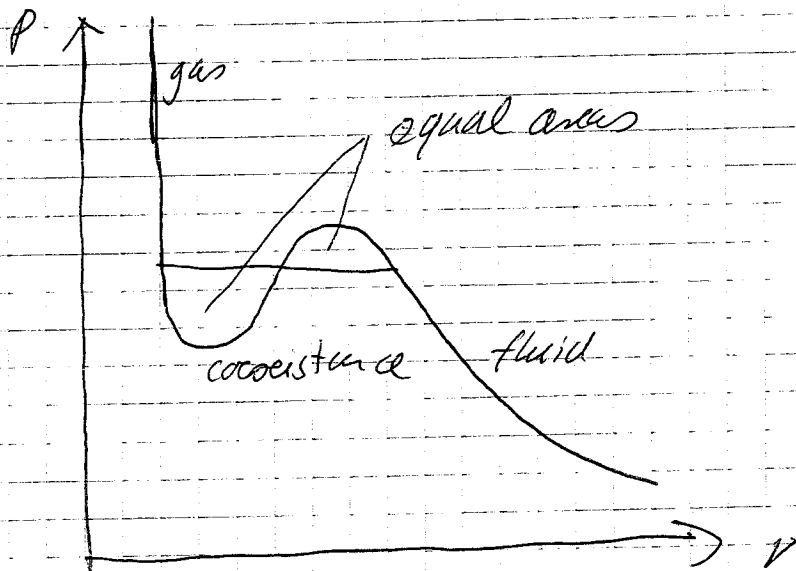
b:  $nb \approx 4 \times$  total volume taken up by the molecules

$\Rightarrow$  repulsion, hard core, excluded volume

a: attractive interactions lower frequency of collisions and impulses transferred to the walls

$\Rightarrow$  higher compressibility

limits: isotherms



## VdW and critical point

8

$$V_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

potential exercises:

1.2, 1.15, 1.20, 1.21, 1.23, 1.26

potential problems:

1.7, 1.15, 1.20, 1.29, 1.26, 1.27

## 3. The first law of thermodynamics

thermodynamics: study of transformations of energy, advantage: fundamental law, which do not require any molecular details.

open system: matter exchange possible } exchange of matter possible  
closed system: matter exchange inhibited }

isolated system: neither mechanical nor thermal exchange, no energy transfer

## Work and energy

The energy of a system is its capacity to do work. When work is done on an isolated system the capacity of the system to do work is increased, so the energy of the system is increased. When the system does work the energy of the system is reduced and it can do less work.