Molecular Physics
WS 07/08

1. Thermodynamics and Statistical Mechanics
(Chapt. 1-5, 19, 20)

1.1. Temperature

<u>Temperature T:</u>

indicates the direction of the flow energy (heat Q)

through a thermally conducting, rigid wall

$$A \xrightarrow{\text{energy}} B \Rightarrow T_A > T_B$$

<u>Thermal Equilibrium:</u>

no change of state when two objects A to B

are in thermal contact

<u>Equipartition Theorem:</u>

at a temperature T the average energy of

any quadratic degree of freedom of a molecule

is $\frac{1}{2} k_B T$

$\Rightarrow$ if a system contains N molecules, each with

f degrees of freedom, and there are no other

temperature-dependent forms of energy, then

its total thermal energy is

$$\boxed{U = N f \tfrac{1}{2} k_B T}$$

degrees of freedom:

mono atomic molecules $f = 1$ translation

diatomic molecules $f = 3$ $1 \times$ translation
$2 \times$ rotation

$\Rightarrow$ molecules determine how much heat can be stored !

Temperature and Brownian Motion
(1-dim.)

Fick's law

$$ j(x,t) = -D \frac{\partial c}{\partial x} \qquad (1) $$

microscopic origin: random Brownian motion of molecules

$\Rightarrow$ D contains molecular information !

Continuity equation:

$$ \frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} \qquad (2) $$

$1 + 2 \Rightarrow$

Diffusion equation

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

+ external potential $U(x)$:

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

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

with $g = 6\pi \eta_s a$ (Stokes)

↙ molecular size

molecular environment

$\Rightarrow$ $j = -D\frac{\partial c}{\partial x} - \frac{c}{g}\frac{\partial U}{\partial x}$

in thermal equilibrium:

$$c_{eq}(x) \sim e^{-U(x)/k_B T} \qquad j_{eq} = 0$$

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

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

↘ molecular information

1.2. Ideal and real gases

ideal gas equation

$$\boxed{pV = nRT} \qquad nR = Nk_B \Rightarrow \boxed{pV = Nk_B T}$$

↳ mole concentration

molecules dilute, no molecular interactions!

$\Rightarrow$ can be observed in reality $\Leftrightarrow$

molecular interactions must be short

range

mixtures of perfect gases:

$$p = \sum_i p_i \qquad p_i = \frac{n_i RT}{V}$$

mole fraction $\quad x_i = \frac{n_i}{n} \qquad n = \sum_i n_i$

$$p_i = x_i \, p$$

Real gases:

molecular interactions:

- repulsive interactions $\Rightarrow$ extremely short range
  $\qquad\qquad\qquad\qquad < $ molecular diameter

- attractive interactions: short range
  $$\sim \frac{1}{r^\alpha} \qquad \alpha \geqslant 3$$

- electrostatic interactions can be long range
  but are typically screened by
  counterions (Debye screening)

- hydrodynamic interactions are long range

proof for: all molecular interactions
are short range

typical interaction potentials of 2 molecules:
(→ multipole expansion)

$$U(r) = -c \frac{1}{r^n}$$

$$\rho := \frac{molecules}{volume}$$

calculate total interaction energy of one
molecule (with diameter σ) with all other
molecules in a space of size L

$$U_{tot} = \int_{\sigma}^{L} U(r) \, \rho \, 4\pi r^2 \, dr = -4\pi c \rho \int_{\sigma}^{L} r^{2-n} \, dr$$

$$= -\frac{4\pi c \rho}{(n-3)\sigma^{n-3}} \left[1 - \left(\frac{\sigma}{L}\right)^{n-3} \right]_{\bullet}$$

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

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

molecular interactions are short range

⇒ _gas at low pressures @ large molecule separations_
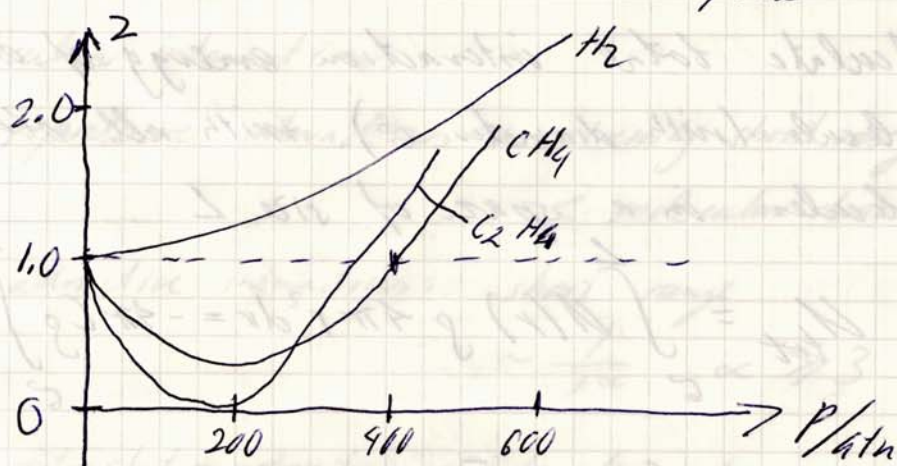
⇒ ⇒ _no interactions_

⇒ ideal gas

⇒ gas at moderate pressures ⇔ smaller molecule separations

⇒ attractive interactions

⇒ higher compressibility

⇒ gas at high pressures ⇔ molecules in close contact

⇒ repulsive interactions

⇒ lower compressibility

Compression factor Z $Z = \dfrac{V_{molar}}{V_{molar, ideal}}$

⇒ <u>Van der Waals equation</u>

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$
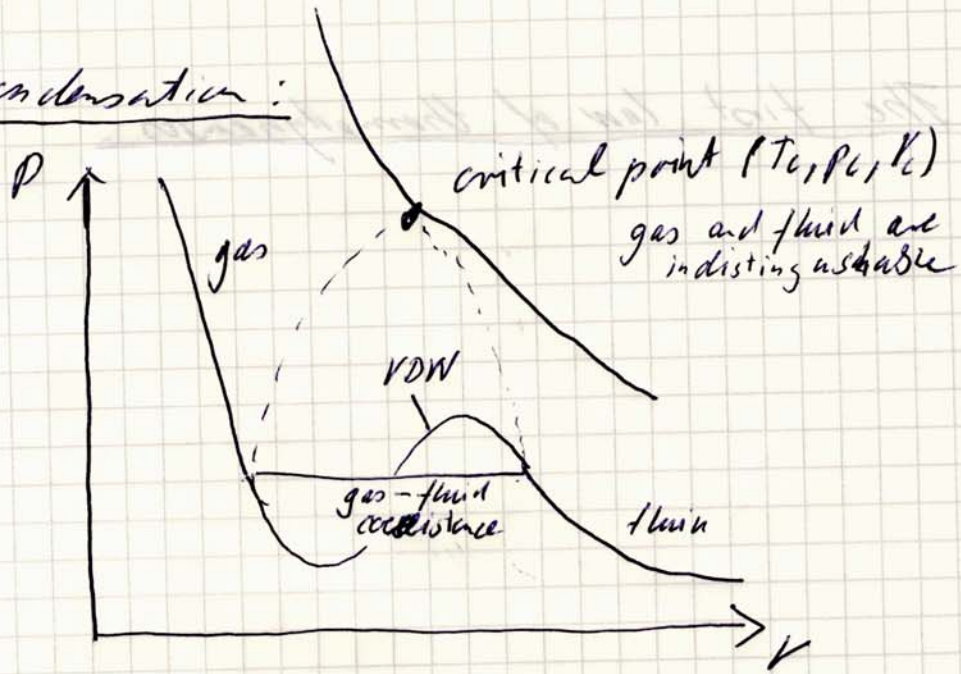
a, b: van der Waal

b: $n \cdot b \approx 4 \times$ total volume taken up

by the molecules

⇒ repulsion, hard core, excluded volume

a: attractive interactions ⇒ lower frequency

of collisions and thus lower impuls

transferred to the wall ⇒ higher compressibility

Condensation:

P [vertical axis]

gas

critical point (T_c, P_c, V_c)
gas and fluid are indistinguishable

VDW

gas—fluid
coexistence

fluid

→ V [horizontal axis]

1.3. Heat and Calorimetry

heat, molecular background:
the disorderly molecular motion called
thermal motion in the hot surroundings
stimulates the molecules in the cooler
system to move more and as a result
the energy of the system is increased

Energy distribution = Boltzmann distribution

number of molecules N_i in a sample of n molecules
that will be found in a state with an
energy E_i when it is part of a system in
thermal equilibrium at a temperature T

$$N_i = \frac{n e^{-E_i/k_B T}}{q}$$

partition function

$$q = \begin{cases} \int e^{-E/k_B T} \, dE & \text{classical} \\ \sum e^{-E_i/k_B T} & \text{quantum} \end{cases}$$