# Soft Matter Physics

Submission due: December 7, 2023, before the lecture starts.

## Exercise Sheet 7

### 7.1 Van der Walas interactions

- Which three forces contribute to the long range interaction between molecules (reaching several atoms in spacing) collectively known as the van der Waals force? Name them and state their typical distance dependence.
- Name the respective intermolecular force that is responsible for the condensation of:
  - He
  - $N_2$
  - HI
  - $Cl_2$
  - $BF_3$
  - $H_2O$

### 7.2 Van de Waals equation of state

The van der Waals equation of state can be expressed as

$$(P + a/\nu^2)(\nu - b) = k_\mathrm{B}T, \tag{1}$$

where $\nu$ is the volume of gas occupied by one molecule and $a$ and $b$ are gas-specific constants. Use the relation of an attractive pair interaction potential between gas molecules,

$$\omega\left(r\right) = \begin{cases} -C/r^n & \text{for } r \geq \sigma \\ \infty & \text{for } r < \sigma, \end{cases} \tag{2}$$

where $C$ and $\sigma$ are an energy coefficient and the so-called hard sphere diameter of a molecule, respectively, and derive equation 1.
Hints:

- Start with the chemical potential of a gas $\mu = \mu_\mathrm{cohesive} + k_\mathrm{B}T \cdot \ln[\rho/(1 - B\rho)]$, which neglects purely temperature-dependent contributions like the translational kinetic energy per molecule. Here, $\rho$ is the number density of the gas molecules and $B$ is the excluded volume per molecule.
- The cohesive energy being the sum of the interactions with all surrounding molecules may be obtained by counting the number of molecules in a spherical shell with radius $r$ and thickness d$r$ around a fixed molecule and integrating $\omega\left(r\right)$ over all these shells.
- Use the thermodynamic relation $\left(\frac{\partial \mu}{\partial P}\right)_T = \nu = \frac{1}{\rho}$ or $\left(\frac{\partial P}{\partial \rho}\right)_T = \frac{1}{\rho}\left(\frac{\partial \mu}{\partial \rho}\right)_T$.
- Assume $B \cdot \rho \ll 1$.

## 7.3 Van der Waals interactions between polarizable molecules

Results from experiments where water molecules were modeled as a van der Waals gas indicated the van der Waals constants $a = 5.536\ \mathrm{l^2\,bar\,mol^{-2}}$ and $b = 0.03049\ \mathrm{l\,mol^{-1}}$. Compare the energy coefficient $C' = \frac{C}{N_A^3}$, where $C$ is the energy coefficient similar to that in Task 7.2 and $N_A$ the Avogadro constant, obtained from the van der Waals equation of gases ($n = 6$), with the energy coefficient resulting from the interaction of two polar molecules in vacuum at $T = 293$ K. Therefor, use

- Electronic polarizability in terms of $4\pi\epsilon_0$: $\alpha_{H_2O} = 1.48 \cdot 10^{-30}\ \mathrm{m}^3$,
- Permanent dipole moment: $u_{H_2O} = 1.85$ D (D: Debye),
- Ionization potential: $I_{H_2O} = 12.6$ eV).

Hints:

- Use the van der Waals constants $a = \frac{2\pi C}{(n-3)\sigma^{n-3}}$ and $b = \frac{1}{3}\pi\sigma^3$ in order to derive an expression for the energy coefficient $C$ on the basis of experimental values.
- The total van der Waals energy coefficient is given as sum of the three energy coefficients from London, Debye, and Keesom interactions, with
  - $C_{\mathrm{disp}} = \frac{3\alpha_{H_2O}^2 I_{H_2O}}{4\cdot(4\pi\varepsilon_0)^2}$.
  - $C_{\mathrm{ind}} = \frac{2u_{H_2O}^2 \alpha_{H_2O}}{(4\pi\varepsilon_0)^2}$.
  - $C_{\mathrm{orient}} = \frac{u_{H_2O}^4}{3k_B T(4\pi\varepsilon_0)^2}$.

## 7.4 Van der Waals interaction between noble gas atoms

Calculate the boiling temperature $T_b$ of argon in three-dimensional space. Use the following parameters,

- Ionization potential: $I_{Ar} = 15.8$ eV
- Electronic polarizability in terms of $4\pi\epsilon_0$: $\alpha_{Ar} = 1.63 \cdot 10^{-30}\ \mathrm{m}^3$
- Atomic diameter: 0.376 nm)

Hints:

- The thermal energy compensates the binding energy arising from van der Walls interactions.
- While estimating the total thermal energy do not forget the equipartition theorem.
- Which of the three particular interactions contribute to the total van der Waals interaction in the case of a noble gas and which do not?
- For estimating the van der Waals binding energy use equation 2 (upper case, $n = 6$) and assume close packing of atoms.