

# UNIVERSITY OF OSLO

Weekly exercise W42: FYS2160, Thermodynamics and statistical physics

## 1 Principle of corresponding states

This exercise is closely related to the lab exercise on phase transitions of water that you will complete during October.

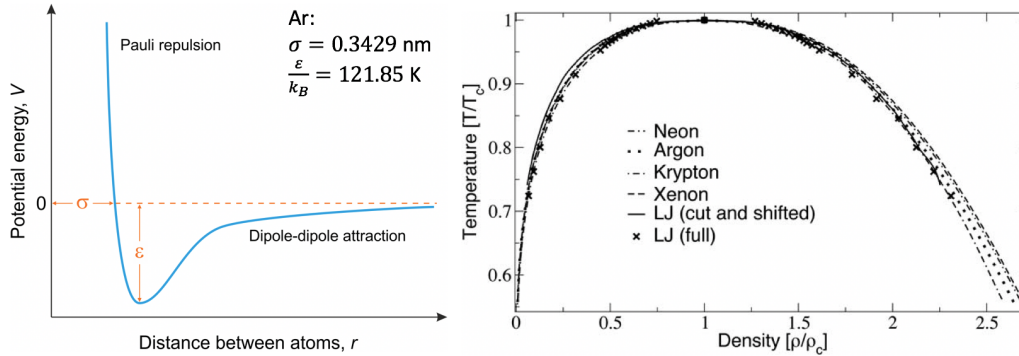


Figure 1: Left: Generic interaction potential between atoms or simple molecules. The most used interaction potential model  $U(\sigma, \epsilon, m)$  of this kind is called the Lennard-Jones (LJ) model. Inset are the values for Argon. Right: Liquid-gas coexistence curves of the LJ model and the noble gases neon, argon, krypton and xenon, rescaled by the critical temperature and density. Both the LJ model and the noble gas curves overlap. This signifies that using appropriate values of  $\sigma, \epsilon, m$  for the noble gases the LJ model and all the gases are equivalent.

Simple liquids and gases have atoms or molecules that can be characterized by their atomic or molecular mass,  $m$ , volume,  $v = \frac{4\pi\sigma^3}{3}$ , and strength of attractive interactions,  $\epsilon$ . The corresponding atomic/ molecular diameter,  $\sigma$ , and attractive energy,  $\epsilon$  are shown in Figure 1. In SI units  $[m] = \text{kg}$ ,  $[\sigma] = \text{m}$  and  $[\epsilon] = \text{kg m}^2 \text{s}^{-2}$ . All thermodynamic properties of solids, liquids or gases of such particles can be non-dimensionalised using only  $\sigma, \epsilon, m$  and the Boltzmann constant. For example the reduced temperature  $T_r = k_B T / \epsilon$  and the reduced density  $\rho_r = \rho \sigma^3$ .

a) Find the expressions for reduced pressure, time and enthalpy.

### Solution:

The SI unit of pressure is  $[P] = \text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$  which is the same as for  $\epsilon / \sigma^3$ , thus the dimensionless pressure is  $P_r = P \sigma^3 / \epsilon$ . Time is only present in  $\epsilon$ , thus  $t_r = t \sqrt{\epsilon / m} / \sigma$ . Enthalpy is an energy, thus  $H_r = H / \epsilon$ .

According to the principle of corresponding states the phase diagrams of all simple substances look like the phase diagrams of the Lennard-Jones fluid shown in Figure 2. This means that if we know three parameters necessary to non-dimensionalize all thermodynamic properties ( $\sigma, \epsilon, m$  or  $T_c, P_c, \rho_c$ , see next section) we can obtain values for all properties for all substances if we know the value for this property for one substance at the corresponding state.

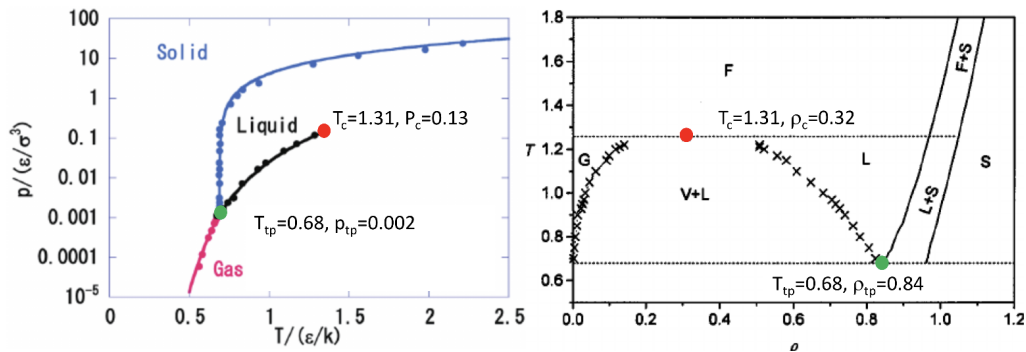


Figure 2: Phase diagrams of the Lennard-Jones model. **Left:** Pressure-temperature diagram. The lines in the diagram are called coexistence lines. The states specified by these lines are the states of equilibrium between two phases of the same substance. Boiling and condensation occurs at the black liquid-gas coexistence line. Melting and freezing occurs at the blue liquid-solid coexistence line. Sublimation occurs at the red solid-gas coexistence line. **Right:** Temperature-density diagram. The crosses are simulation data for the liquid-gas coexistence at temperatures below the critical temperature  $T_c$  and above the triple point temperature  $T_{tp}$ .

b) What are the densities and the pressures of the LJ liquid and gas in equilibrium at  $T_r = 1$ ?

**Solution:**

*Reading off the graphs I find that the density is  $\rho_r = 0.68$  and  $P_r \approx 0.02$ .*

c) In many simple liquids one finds that  $\frac{T_c}{T_{tp}} = \frac{5}{2} \pm \frac{1}{2}$ . Can the fact that  $\frac{T_c}{T_{tp}} \sim \text{constant}$  be derived from the principle of corresponding states?

**Solution:**

*The principle of corresponding states says that  $\frac{T_c}{T_{tp}} \sim \text{constant}$  but not which value such a constant has.*

d) Based on observations of some liquids, the Norwegian chemist Cato Maximillian Guldberg proposed in 1890 that the ratio between the normal boiling point temperature (at 1 atmosphere pressure),  $T_b$ , and the critical temperature,  $T_c$  was  $T_b/T_c \sim 2/3$ . Does this, so-called Guldberg rule, follow from the principle of corresponding states?

**Solution:**

*The normal boiling point temperature is given for  $P = 1 \text{ atm}$  which is not at a specific reduced pressure  $P_r = P/P_c$  because different substances have different critical pressures  $P_c$ .  $P_r = P/P_c$  for different substances the boiling point of different substances do not correspond to the same state. Therefore the Guldberg rule is not well defined in terms of the principle of corresponding states.*

It is found that for simple liquids the ratio  $H_v/RT_b \sim 10$  between the enthalpy of vaporization,  $H_v$  and the normal boiling point temperature,  $T_b$ . Over a much larger range of noble gases, organic and inorganic liquids and metals one finds  $H_v/RT_b \sim 12$  (see Figure 3). This has been named Trouton's rule.

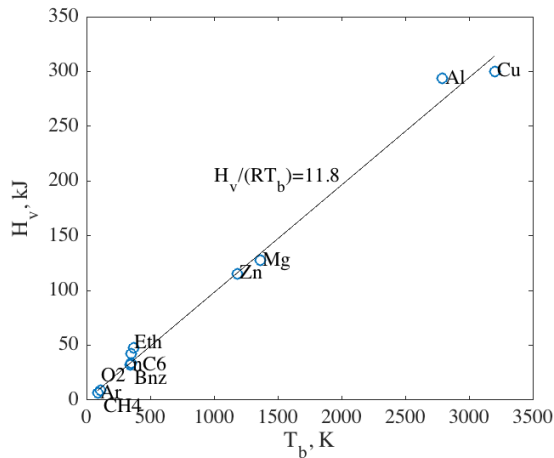


Figure 3: Trouton's rule: Enthalpy of vaporization,  $H_v$  and normal boiling point temperature,  $T_b$  are proportional.

e) Use Trouton's rule to estimate the heat of vaporization for water.

**Solution:**

$$H_v = R * (10 \rightarrow 12) \cdot 373.15 = 31 \rightarrow 37 \text{ kJ/mol.}$$

f) When measuring the enthalpy of vaporization one normally works at constant pressure with a fixed amount of substance. Use the thermodynamic identity for enthalpy to express Trouton's rule in terms of the entropy of vaporization,  $S_v$ .

**Solution:**

$$H_v/RT_b = S_v/R$$

g) It has been argued that Trouton's rule follows from the principle of corresponding states. Do you agree?

**Solution:**

*As for Guldbergs rule the boiling points of different substances are not corresponding states as they can be anywhere on the coexistence line between the triple point and critical point.*

h) Can you find an alternative explanation for Trouton's rule?

**Solution:**

*The change of phase from liquid to gas changes the order in a similar way for all substances: from particles being constrained to the attractive potentials of the other particles and with a liquid ordering (radial distribution function) to effectively an ideal gas. It follows that the change of entropy should be similar. Deviations from this rule are found especially in polar liquids like water and small alcohols that tend to have more local ordering and thus the change in order and  $S_v$  is larger upon vaporization.*

## 2 van der Waals equation of state

The van der Waals fluid is a mean field theory of a gas. It is a model system, just as the ideal gas, although it includes more features of realistic gases. The van der Waals gas includes two of the main effects of an attractive two-particle interaction between particles in the gas: a repulsive interaction that keeps particles apart, and an attractive long-range interaction that pulls particles together. These two effects leads to two changes in the Helmholtz free energy of the gas, as compared to an ideal gas: Instead of the volume  $V$  we introduce the effective volume,  $V - Nb$ , where the volume  $b$  is the excluded volume per particle, and we introduce an average binding energy,  $-a(N/V)^2$ . Helmholtz free energy for the van der Waals gas is:

$$F_{vdW} = -NkT \left( \ln \left( \frac{n_Q(V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V}, \quad (1)$$

where  $n_Q(T) = (2\pi mkT/h^2)^{3/2}$  is a function of  $T$  only.

a) Show that the pressure,  $P(N, V, T)$ , of the van der Waals gas is

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}. \quad (2)$$

**Solution:**

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, N}$$

This is the equation of state for the van der Waals gas. We introduce the quantities

$$P_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad kT_c = \frac{8a}{27b}. \quad (3)$$

These are in fact the critical pressure, volume and temperature of the van der Waals EOS. We can then introduce dimensionless quantities:

$$\hat{P} = P/P_c, \quad \hat{V} = V/V_c, \quad \hat{T} = T/T_c, \quad (4)$$

and similarly for the density

$$\hat{\rho} = 1/\hat{V} = \rho/\rho_c, \quad \rho_c = \frac{1}{3b}. \quad (5)$$

b) Show that the pressure of the van der Waals gas can be written as

$$\hat{P} = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}. \quad (6)$$

c) Plot the pressure  $\hat{P}$  as a function of  $\hat{V}$  for  $\hat{V}$  in the range from 0.4 to 6 for  $\hat{T} = 1.0, 0.95, 0.9$  and 0.8.

Solution:

