

UNIVERSITY OF OSLO

Obligatory assignment 2: FYS2160, Thermodynamics and statistical physics, Fall 2019

Due: October 08. 2019

1 Stretching of a rubber band

Consider an elastic rubber band with a length $L(T, P)$ that changes with temperature T and tension P . Equivalently, we can say that the tension P depends on the length L and temperature T . One may find that the tension in the band changes with T and L according to the empirical slopes

$$\begin{aligned}g(L) &= \left(\frac{\partial P}{\partial T}\right)_L = \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L}\right)^3\right] \\f(T, L) &= \left(\frac{\partial P}{\partial L}\right)_T = \frac{aT}{L_0} \left[1 + 2\left(\frac{L_0}{L}\right)^3\right],\end{aligned}\tag{1}$$

where L_0 is the length of the un-stretched band (independent of temperature) and $a > 0$ is an empirical constant.

1.1 Using the empirical slopes, derive the equation of state $P(T, L)$, that relates the tension P in the rubber band with its temperature T and length L .

The rubber band obeys the thermodynamic relations that are analogous to those of a gas. However, work is done on the rubber band by stretching it, hence the sign in the work is opposite to that of the gas, $\delta W = +PdL$. The first law of thermodynamics for an infinitesimal reversible deformation reads as

$$dU = TdS + PdL,\tag{2}$$

where U is the internal energy and S is the entropy of the elastic band.

1.2 Show that the thermodynamic identity of the Helmholtz free energy $F(T, L, N)$ leads to the following Maxwell relation

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_L\tag{3}$$

1.3 From the equation of state $P = Tg(L)$, it follows that $(\partial P/\partial T)_L = P/T$. Using this together with the above Maxwell relation, show that the internal energy of the band depends only on T , just like for an ideal gas. (show that $(\partial U/\partial L)_T = 0$)

1.4 The heat capacity at constant length L is then related to changes in the internal energy at fixed L as $dU = C_L dT$. Assume that C_L is constant. Suppose the band is stretched adiabatically and reversibly ($Q_{rev} = 0$), i.e. isentropically ($dS = 0$), from L_0 at an initial temperature T_i to the final length L_f . What is its final temperature T_f ?

1.5 The stretched rubber band with the final length L_f is released, so that it contracts freely to its equilibrium unstretched length L_0 . If no heat and no work is exchanged with its surrounding

during this contraction, find the changes in its temperature and entropy. What is the analogue process for a gas?

2 Principle of corresponding states

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

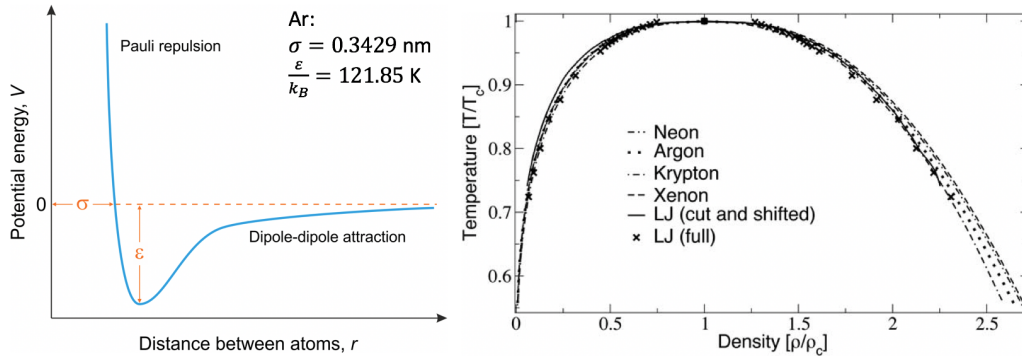


Figure 1: Left: Generic interaction potential between atoms or simple molecules. The most used interaction potential model $U(\sigma, \epsilon, m)$ of this kind is called the Lennard-Jones (LJ) model. Inset are the values for Argon. Right: Liquid-gas coexistence curves of the LJ model and the noble gases 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 σ, ϵ, 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 characterised by their atomic or molecular mass, m , volume, $v = \frac{4\pi\sigma^3}{3}$, and strength of attractive interactions, ϵ . The corresponding atomic/ molecular diameter, σ , and attractive energy, ϵ 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 σ, ϵ, m and the Boltzmann constant. For example the reduced temperature $T_r = k_B T / \epsilon$ and the reduced density $\rho_r = \rho \sigma^3$.

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

According to the principle of corresponding states, all simple fluids behave similarly in terms of their reduced temperature, pressure and volume. The phase diagrams of all simple liquids and gasses look like the phase diagrams of the Lennard-Jones fluid shown in Figure 2, the thermodynamic variables are given in dimensionless units. This means that if we know three parameters necessary to non-dimensionalise all thermodynamic properties (σ, ϵ, m or T_c, P_c, ρ_c , see Problem 3), we can data collapse the coexistence curves into universal curves. It means that different substances that occupy the same state in the phase diagram corresponding to their reduced variables, will have the same behavior.

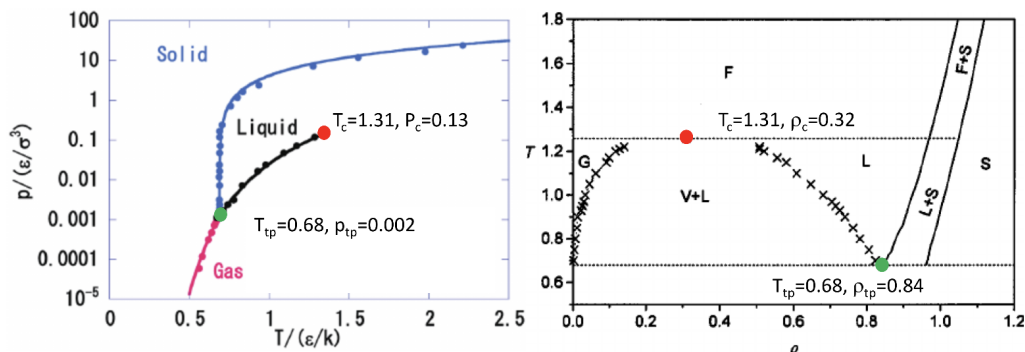


Figure 2: Phase diagrams of the Lennard-Jones model. **Left:** Pressure-temperature diagram. The lines in the diagram are called coexistence lines. The states specified by these lines are the states of equilibrium between two phases of the same substance. Boiling and condensation occurs at the black 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} .

2.2) What are the densities and the pressures of the LJ liquid and gas in equilibrium at $T_r = 1$? (Use Fig. 2)

2.3) 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?

2.4) 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?

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.

Note: The enthalpy of vaporization is the same as the latent heat at the liquid-gas phase transition. The entropy of vaporization is the same as the jump in entropy ΔS at the liquid-gas phase transition.

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

2.6) 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 .

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

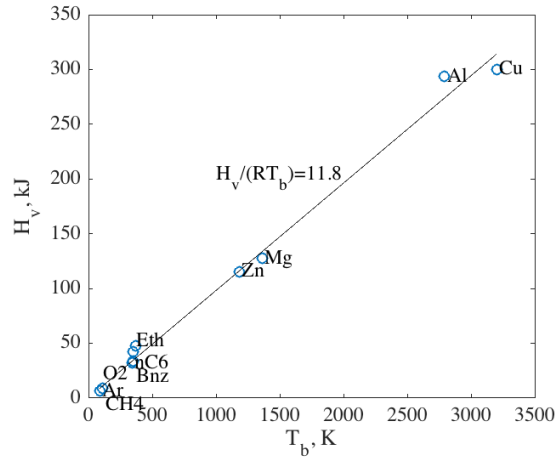


Figure 3: Trouton's rule: Enthalpy of vaporization, H_v and normal boiling point temperature, T_b are proportional.

2.8) Can you find an alternative explanation for Trouton's rule using the entropy change during vaporization?

3 Phase coexistence of N_2 - van der Waals equation

In this project we will study the gas-liquid phase equilibrium of nitrogen using the van der Waals equation of state.

The van der Waals fluid is a mean field theory of a gas of weakly interacting particles. 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:

$$F_{wdW} = -NkT \left(\ln \left(\frac{n_Q(V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V}, \quad (4)$$

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

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

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}. \quad (5)$$

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

$$P_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad kT_c = \frac{8a}{27b} \quad (6)$$

which are the critical pressure, volume and temperature of the van der Waals model. We can then introduce dimensionless quantities:

$$\hat{P} = P/P_c, \quad \hat{V} = V/V_c, \quad \hat{T} = T/T_c, \quad (7)$$

and similarly for the density

$$\hat{\rho} = 1/\hat{V} = \rho/\rho_c, \quad \rho_c = \frac{1}{3b}. \quad (8)$$

3.2) Show that the reduced pressure of the van der Waals gas follows the universal equation of state (principle of corresponding states)

$$\hat{P} = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}. \quad (9)$$

3.3) 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.

Notice that the volume is not a unique function of the pressure for some range of values. This means that we generally cannot find $\hat{V}(\hat{P})$.

3.4) Show that the pressure also can be expressed using the density instead of the volume:

$$\hat{P} = \frac{8\hat{\rho}\hat{T}}{3 - \hat{\rho}} - 3\hat{\rho}^2. \quad (10)$$

3.5) Plot the pressure \hat{P} as a function of $\hat{\rho}$ for $\hat{\rho}$ in the range from 0.0 to 2.0 for $\hat{T} = 0.8, 0.9, 0.95$ and 1.0

3.6) Now we would like to relate the van der Waals fluid to a nitrogen (N_2) gas. Use the critical parameters $P_c=33.6$ atm, $V_c=0.089$ l/mol and $T_c=126$ K to plot, using the van der Waals equation of state the PV isotherms of N_2 for $T = 77, 100, 110, 115, 120, 125$ K. You have now applied the principle of corresponding states.

3.7) Use the Maxwell equal area construction (see figures 5.21 and 5.23 in Schroeder) to determine the liquid volume $V_l(T)$ and gas volume $V_g(T)$ at the temperatures 100, 110, 115, 120 and 125 K. Do this "by hand", using your eyes to judge when the areas are equal. Plot $V_g(T) - V_l(T)$ as function of T to determine the critical temperature. Why do you get this value of the critical temperature?

3.8) Extra challenge (optional): Find a numerical solution to the Maxwell construction and use this to determine the critical temperature, volume and pressure.