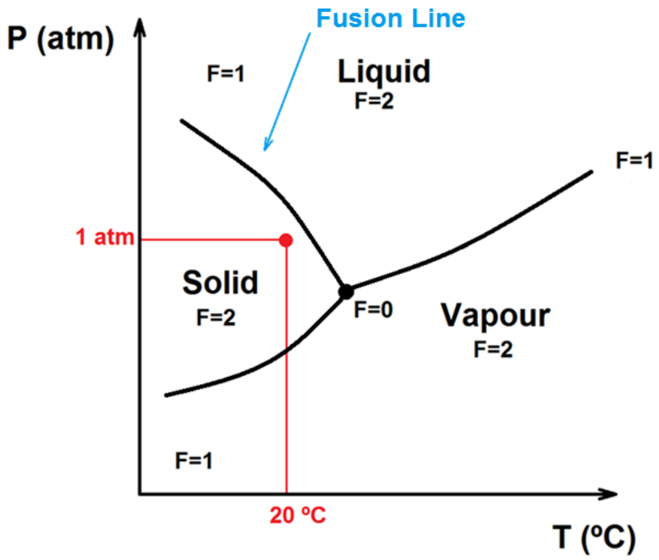
Homework 7 solution

Exercise 1. Baroplastics

Baroplastic materials are transformed from solid state to liquid state under the application of pressure at reasonably low temperatures. With this property, a plastic material can be molded into different shapes with the help of pressure. This new class of materials has been proposed to replace traditional thermoplastic materials for their low-temperature and low-pressure processing, and faster production. These materials are mainly investigated as a future avenue for recyclable polymers. The goal would be to recycle polymer waste by applying pressure at room temperature and thereby achieving a liquid that can be further processed. In this problem, we will consider a baroplastic material as a pure substance.

a) Based on the provided information, what does a pressure-temperature (p-T) phase diagram of a typical baroplastic material look like? Make sure to label regions of the 3 phases (solid, liquid, vapor).



b) Do you know of any material (not a baroplastic) that has a similar phase diagram?

The phase diagram of water is similar. The similar unusual property is the negative rather than positive slope of the fusion line (see diagram above).

c) Indicate in the diagram the degrees of freedom according to the phase rule.

The degrees of freedom are noted with the letter F in the phase diagram above.
For the derivation: Since we have a single component system, $n = 1$ and therefore

$$F = n + 2 - \phi = 3 - \phi$$

For the pure phases (solid, liquid and vapor), we have $\phi = 1$ (phase coexistence of one phase) and thus $F = 2$. This means that the pure phases each form a two-dimensional region in the p-T diagram.
Along the coexistence lines (the fusion, sublimation and evaporation lines), we have $\phi = 2$ phases that coexist and thus $F = 1$. This explains why two phases coexist along a line, namely because it is a one-dimensional subset of the p-T plane.

Finally, at the triple point, we have $\phi = 3$ phases that coexist and thus $F = 0$. This explains why the triple point is just a point, a zero-dimensional subset of the p-T plane.

d) Indicate on the phase diagram that you have drawn, what is the key phase line that matters for a baroplastic. Please explain what the relationship between the slope of the phase line and the performance of the materials is. Specifically explain how that phase line is related to the optimization of the baroplastic material to potentially reduce the molding cost.

The important slope for a baroplastic material is the **fusion** line.
To evaluate if we have a performant baroplastic material, we need to see the behaviour of this coexistence line. We know that the slope of the phase coexistence line is related to the heat of fusion L and volume change by the Clausius Clapeyron relation

$$\frac{dP}{dT} = \frac{L}{T(v^{liquid} - v^{solid})}$$

Since we need to provide the heat L every time we recycle a baroplastic, having a small L and thus small slope $|\frac{dP}{dT}|$ (in absolute value) of the coexistence line would make it easier to liquefy the plastic at room temperature by the application of pressure.

e) Indicate in your diagram where the atmospheric temperature and pressure are. Explain where it should be for an ideal baroplastic material to be useful in practice.

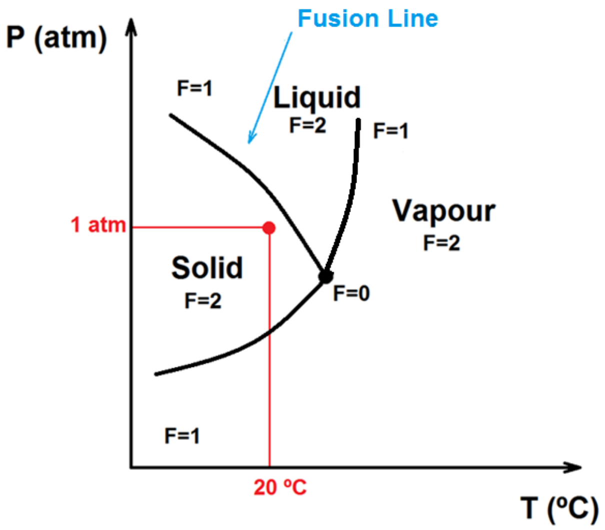
The atmospheric pressure and temperature point is indicated in red. Clearly, the point needs to be in the solid phase if we want the material to be usable under standard conditions.
Furthermore, it would be desirable to have it close to the fusion line so that these materials can be processed at near room temperature and atmospheric pressure conditions. It should also be above the triple point so that while processing we remain away from the gas phase to avoid further complications.

For the second part of this exercise, we shall consider hypothetical experimental measurements for a candidate baroplastic and try to understand it thermodynamically.

f) Assume that a group of researchers has reported the following relations for the slopes of a p-T diagram for a new baroplastic material.

$$0 < \left(\frac{dp}{dT}\right)_{sublimation} < \left(-\frac{dp}{dT}\right)_{fusion} < \left(\frac{dp}{dT}\right)_{vaporization} \quad (1)$$

Draw the p-T phase diagram with the given properties.



The slope of the vaporization line is unusually high.

h) Given the second phase diagram that you have drawn, please derive a relationship between the experimental results in eq. (1) and the molar entropies of the three phases of the materials that the researchers have discovered.
We can relate the measured slopes to the molar entropies and volumes using the Clausius-Clapeyron relation

$$\frac{dP}{dT} = \frac{S^{\alpha} - S^{\beta}}{v^{\alpha} - v^{\beta}}$$

For the two condensed phases, namely the solid and liquid phase, the molar volume is negligible compared to the gas phase.

$$v^{gas} \gg v^{solid}, v^{solid}$$

For the sublimation line we can thus write

$$\left(\frac{dP}{dT}\right)_{sublimation} = \frac{s^{gas} - s^{solid}}{v^{gas} - v^{solid}} \approx \frac{s^{gas} - s^{solid}}{v^{gas}}$$

Similarly, for vaporization, we obtain

$$\left(\frac{dP}{dT}\right)_{vaporization} = \frac{s^{gas} - s^{liquid}}{v^{gas} - v^{liquid}} \approx \frac{s^{gas} - s^{liquid}}{v^{gas}}$$

Finally, for the fusion line, we obtain

$$\left(\frac{dP}{dT}\right)_{fusion} = \frac{s^{liquid} - s^{solid}}{v^{liquid} - v^{solid}}$$

Note that we cannot simplify the molar volumes here, since both the liquid and solid phases typically have densities on the same order of magnitude.

i) What is the most unusual property? Do you think that this material is possible or that the researchers made a mistake in determining their phase diagram?

Based on the reported slopes, we have

$$\left(\frac{dP}{dT}\right)_{sublimation} < \left(\frac{dP}{dT}\right)_{vaporization}$$

Using the results from the previous exercise, this can be written as:

$$\frac{\cancel{s^{gas}} - s^{solid}}{\cancel{v^{gas}}} < \frac{\cancel{s^{gas}} - s^{liquid}}{\cancel{v^{gas}}}$$

$$s^{solid} > s^{liquid}$$

The entropy for the solid phase is larger than the liquid phase, which is highly unlikely!