due date: Tuesday, April 2, 2024, please upload your solution as a pdf on Canvas

## Problem 1: Thermodynamic potentials of a surface (12 points)

The work required to change the area A of a surface by an infinitesimal amount dA is given by  $\delta W = \sigma \, dA$  where  $\sigma$  is the surface tension. Start from the first law  $dU = T \, dS + \sigma \, dA$  and derive the formulas for the thermodynamic potentials and their total differentials in terms of the natural variables.

- a) enthalpy,
- b) Helmholtz free energy,
- c) Gibbs free energy.

## Problem 2: Maxwell relations for a surface (12 points)

Using the thermodynamic potentials that you found in homework 9.1, derive the four Maxwell relations for a surface of area A under surface tension  $\sigma$ .

## Problem 3: Thermodynamic and caloric equations of state (16 points)

For a gas or liquid described in terms of pressure p, volume V, and temperature T, show that the thermodynamic equation of state (the relation between p, V, and T) and the caloric equation of state (the dependence of the internal energy U on the other variables) are not independent.

- a) Specifically show that  $(\partial U/\partial V)_T = -p + T(\partial p/\partial T)_V$
- b) Apply the above relation to the ideal gas and show that the internal energy must be volume-independent if  $pV = Nk_BT$ .

This problems requires a bit of creativity working with partial derivatives. Start from the differential of the entropy as function of U and V. Express the energy differential in terms of T and V. Now use the equality of the mixed second derivatives of the entropy with respect to T and V.