1. (35 pts.)

20 pts. (a) Define the Helmholtz free energy \( A(T,V,N) \) and the Gibbs free energy \( G(T,P,N) \) based on the internal energy \( U(S,V,N) \). Write down the differential forms. Derive the Gibbs-Duhem relationship, \( 0 = SdT - VdP + Ndu \), starting from \( A \) and starting from \( G \).

15 pts. (b) The coefficient of adiabatic thermal expansion is defined by

\[
\beta_s = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{s,N}.
\]

Show that \( \beta_s = -\frac{c_v \kappa_T}{\nu T \beta} \), where \( c_v \) is the heat capacity at constant volume, \( \kappa_T \) is the isothermal compressibility, \( \nu \) is the number of particles per unit volume, and \( \beta \) is the thermal expansivity at constant pressure. Derive any Maxwell relations you need from the differential forms in (a).

2. (30 pts.) The cycle of a highly idealized gasoline engine can be approximated by the Otto cycle, at right. \( 1 \rightarrow 2 \) and \( 3 \rightarrow 4 \) are adiabatic compression and expansion, respectively, while \( 2 \rightarrow 3 \) and \( 4 \rightarrow 1 \) are constant volume processes. Treat the working medium as an ideal gas with constant \( \gamma = c_p / c_v \), where \( c_p \) and \( c_v \) are the heat capacity at constant pressure and volume respectively.

Remember that along adiabatic paths in an ideal gas with \( \gamma \) constant, \( PV^n = \text{const.} \)

Define and compute the efficiency of this cycle for \( \gamma = 1.4 \) and compression ratio \( r = V_1/V_2 = 10 \).

3. (35 pts.) Two bubbles in solution are connected by a thin "straw" of negligible volume compared to the volume of the bubbles (see at right). The ambient pressure is \( P_a \), the temperature is \( T \), and the surface energy per unit area is \( \gamma \).

10 pts. (a) Show that the pressure inside a single spherical bubble of radius \( r \), is

\[
P_i = P_a + 2\gamma r.
\]

10 pts. (b) Is the configuration \( r_1 = r_2 \) in stable equilibrium? Argue why or why not, starting from a consideration of what happens when \( r_2 \) is slightly smaller than \( r_1 \).

10 pts. (c) One could in principle use this system to determine \( \gamma \) by measuring \( r_1 \) and \( r_2 \) and then the final bubble radius \( r_f \) after one of the bubbles disappears entirely into the other. Relate \( \gamma \) to \( r_1, r_2, r_f \) and \( P_a \). Assume that the gas inside the bubbles is ideal and that both the total mass within the bubbles and the temperature remain constant during this process.

5 pts. (d) Comment on the result in the limits of large and small \( \gamma \). For \( \gamma = 30 \text{mN/m} \) (a typical value) and \( P_a \approx 1 \text{ atm} \), at what order of magnitude would you want to try this way of determining \( \gamma \) (\( r \approx 1 \text{ cm}, 1 \text{ mm}, 1 \text{\mu m} \ldots \)?) Remember that 1 atm = \( 10^5 \text{N/m}^2 \).