MSE-483 ADVANCED PHASE TRANSFORMATIONS

FALL 2024

QUESTION 1 : IDEAL GAS

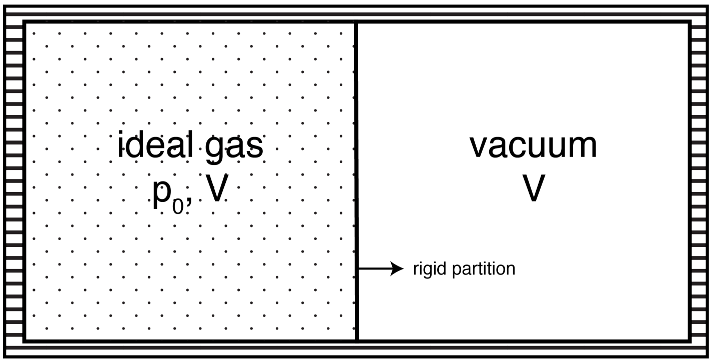

Figure 1

A container of total volume $2V$ contains two chambers of equal size separated by a rigid partition. One of the chambers is filled with one mole of ideal gas with an initial pressure, p_0, and volume V. The other half of the container is empty (i.e. contains vacuum). A schematic picture of the container is shown in fig. 1. The rigid partition is suddenly removed and the gas expands to fill the entire container

1. Assume the walls of the container are adiabatic:
   (a) What is the work performed by the gas during expansion?
   (b) Estimate the change in internal energy (ΔU) due to the removal of the wall.
   (c) What is the final temperature (T_1) of the gas?
2. Instead of adiabatic walls, what if the container was made of diathermic walls? Estimate the work, change in internal energy and final temperature of the gas.

QUESTION 2 : CALLEN 1.8-6

For a particular gas it is found that if the volume is kept constant at the value V_0 and the pressure is changed from p_0 to an arbitrary pressure p, the heat transfer (q) into the system is:

$$q = A(p - p_0)$$

where A is a positive constant. In addition it is known that the adiabats of the system are of the form:

$$pV^\gamma = \text{constant}$$

where $\gamma > 0$. Calculate an expression for the internal energy of the gas at any arbitrary point (p, V). Express the internal energy, $U(p, V)$, in terms of p_0, V_0, A, γ, and $U_0 = U(p_0, V_0)$

QUESTION 3 : MORE FUN WITH IDEAL GASES

Figure 2 shows one mole of an ideal gas in the bottom compartment of a diathermal container that is held in an environment at 298K. The ideal gas is separated from the top of the container by a frictionless piston (with surface area 1 m^2). A constant weight of 100 kg is placed on the piston. A circuit with a resistor and a generator passes through the compartment with the gas. A frictionless pulley system converts the mechanical work of dropping a weight of mass M =10 kg by a height of 10m into an electric current that passes through the resistor. The specific heats of an ideal gas are given by $C_V = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$. You can assume that the environment is very large and stays at constant temperature and pressure.

1. Calculate the entropy change of the gas after it equilibrates with the environment
2. Calculate the entropy change of the universe after the gas equilibrates with the enviroment.

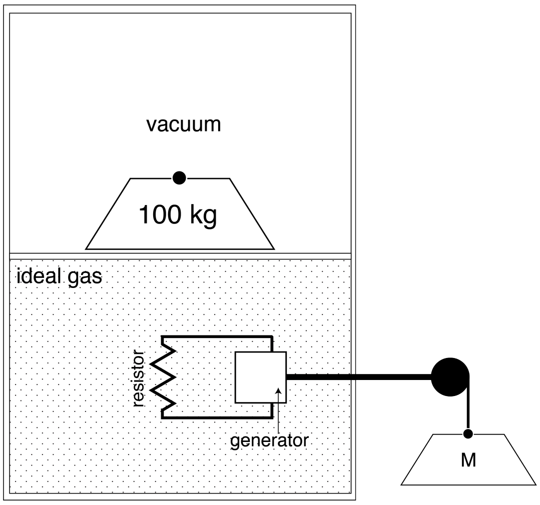

Figure 2

Question 4 : Legendre transforms and Characteristic potentials

An electrically polarizable material is placed between the plates of a capacitor under ambient temperature and pressure as shown in fig. 3. Applying a voltage across the capacitor plates results in an electric field of magnitude $\vec{E}$ across the material. Let the induced polarization in the material be denoted as $\vec{\mathcal{P}}$

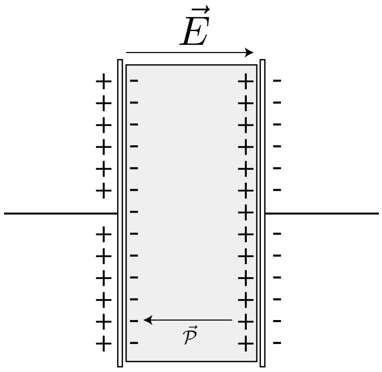

Figure 3

1. List all the relevant state variables of the *polarizable material*. Be sure to indicate the pairs of variables that are *conjugate* to each other.
2. What are the state variables of the polarizable material that are controlled experimentally?
3. Write down an expression for dU (where U is the internal energy of the polarizable material) in terms of the state variables of the material.
4. Write down the expression for the characteristic potential of the material under these boundary conditions
5. Calculate the equations of state for the material based on the characteristic potential.

Question 5 : Massieu functions

During class, we derived the Legendre transforms of the internal energy $U(S, V)$. Similar Legendre transforms can also be derived for the entropy $S(U, V)$. Start from the fundamental relation in thermodynamics:

$$dS = \frac{dU}{T} + \frac{p}{T}dV$$

1. Identify the natural variables of S and the variables that are conjugate to the natural variables.
2. Define the three Legendre transforms of the entropy $S(U, V)$. *HINT : The three Legendre transforms of $U(S, V)$, transformed the internal energy into three different characteristic potentials: $H(S, p)$, $F(T, V)$ and $G(T, p)$*
3. Write the differential form of each Legendre transform

The Legendre transformations in the entropy representation are called Massieu functions - named after François Massieu who developed them in 1869.

QUESTION 6

A rod having initial length L_0 is elongated to a length L_1 by applying a force f under isothermal conditions. The temperature of the rod is T_0. The state variables of the rod are related by the following equation:

$$L = L_0 + \alpha(T - T_0) + \beta f$$

where $L, T,$ and f are the length, temperature and force applied on the rod. α, β, T_0, L_0 are constants.

1. What are the thermodynamic state variables of the rod that are controlled experimentally?
2. Write down an expression for the characteristic potential of the rod and derive the equations of state.
3. Show that :
$$\left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial L}{\partial T}\right)_f$$
4. The rod is elongated reversibly from a length L_0 to L_1.
   (a) What is the work done on the rod during elongation?
   (b) How much heat is exchanged between the rod and the environment?
5. The rod is elongated by applying a constant force of magnitude $f = \frac{L_1 - L_0}{\beta}$
   (a) Is this process reversible or irreversible?
   (b) What is the work done on the rod by the environment?
   (c) Calculate the heat exchanged between the rod and the environment.

QUESTION 7

Consider a solid that is placed in an environment where we control the temperature (T), pressure (p), and magnetic field (H) across it.

1. How many independent response functions can be defined for this system? Write down expressions for each response function. Give them different Greek letter names. Ensure that each response function is independent of system size.
2. The solid at constant T and p and zero applied magnetic field is suddenly placed in a magnetic field of magnitude H_1. Derive an expression for the change in internal energy of the solid after it has reached equilibrium at the same temperature and pressure, but in a magnetic field of H_1. Write the change in internal energy in terms of measurable state variables and response functions.

QUESTION 8

The characteristic potential (A) for a block of material at constant length and temperature is given by:

$$A(T, L) = (L - L_0)^4(\lambda + T\theta) + \kappa T^2 \tag{1}$$

where the length of the material is L, temperature is T, $L_0, \lambda, \theta, \kappa$ are constants. The constants are such that $\lambda > 0$ and $\theta < 0$. The free energy is found to characterize the behavior of the material at low temperatures.

1. What is the sign of κ?
2. Derive an equation for the force on the rod as a function of the length of the rod. Express the force in terms of the constants $\theta, \lambda, \kappa, L_0$, temperature ($T$) and length ($L$).
3. Derive an expression for the characteristic potential (G) of the material at constant temperature and force (F). The free energy should be expressed in terms of its natural variables F, T and material constants ($\theta, \lambda, \kappa, L_0$).
4. Use the characteristic potential, $G(T, F)$ to calculate the length of the material when no force is applied to it at a temperature T.
5. The force and length of a material are proportional to each other in linear elastic materials, i.e. $F \propto (L - L_0)$. Is the material with the free energy function shown in eq. (1) a linear elastic material? If not, propose a free energy function ($B(T, L)$) that could represent a linear elastic material.

QUESTION 9

Consider a binary mixture with N_A atoms of the chemical element A, N_B atoms of the chemical element B mixed together at a temperature T and pressure p.

1. Write down the expression for the characteristic potential of this system.
2. Express the Hessian of this characteristic potential with respect to the experimentally controlled state variables.
3. Use the Maxwell relations to identify the independent terms in the Hessian matrix
4. Recall that response functions are typically defined as proportional to the partial derivative of an extensive variable with respect to an intensive variable. Let $\chi_{ij} = \frac{\partial N_i}{\partial \mu_j}$. Express the Hessian in terms of suitably defined response functions that are "easy" to measure.