PY541 Problem Set 2: Due Thursday, September 26, 2002 in class

1) Consider quasi-static processes in which a gas goes between points A and B, as shown in the diagram below, by several different paths. In general, some heat is adsorbed from or emitted to the environment. Assume that, in the case of an adiabatic process, the pressure and volume are related by:

$$P = V^{-7/5}. \tag{1}$$

At A, $V = 1m^3$, $P = 1$ Atm. and at B, $V = 2m^3$ and $P = .3789$ Atm. Calculate the amount of work done on the gas and the amount of heat adsorbed by the gas for the following 3 paths, shown in the diagram:
a) The pressure decreases linearly with volume while heat is applied.
b) The volume first increases at fixed P, while heat is added, and then the pressure decreases at fixed V, heat being extracted.
c) The pressure is reduced at fixed volume first, then the volume is increased at fixed P.

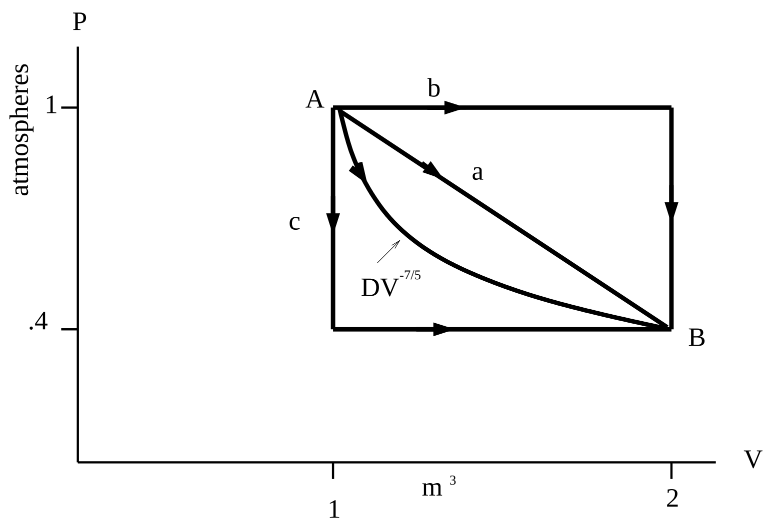

FIG. 1.

Note that this example shows that the "amount of heat contained in the gas" *is not* a well-defined concept since we can take the gas from A to B by adding different amounts of heat.

2) Although this assumption was not neccessary to solve problem 1, assume for this problem that the gas obeys the ideal gas equation of state, $PV = NkT$ and that its energy is given by $E = (5/2)NkT$.
a) Consider a heat engine which runs forward on path b then backward on path c. Assume that on the constant P part of path b the gas is adsorbing heat from a high temperature reservoir and on the constant V part of path b it is emitting heat to a low temperature reservoir and conversely when it runs backwards on path c. Assume that the high temperature reservoir is at the highest temperature that the gas reaches during the cycle and that the low temperature reservoir is at the lowest temperature that the gas reaches during the cycle. Calculate its efficiency.
b) Now suppose the heat engine runs forward on the adiabat and back on path c. Make the same assumptions as above about heat adsorption and emission on path c) and assume that no heat is adsorbed or emitted by either reservoir during the adiabatic part of the path. Calculate the efficiency in this case.
c) Explain why a path running forward on c and backward on a would not correspond to a heat engine.

3) Derive further thermodynamic stability conditions by considering a relatively small (but still macroscopic) part of a larger system. Now assume that this part has a fixed volume but can exchange particles and energy with the rest of the system. Assume that the rest of the system is so large that its chemical potential and temperature remain fixed during these processes. You may also assume, for simplicity, that there is only one type of particle. In this way derive the following inequalities:

$$C_{V,N} \equiv \left(\frac{\partial E}{\partial T}\right)_{V,N} \geq 0$$

$$\left(\frac{\partial\mu}{\partial N}\right)_{V,S} \geq 0$$

$$T\left(\frac{\partial\mu}{\partial N}\right)_{V,S} \geq C_{V,N}\left(\frac{\partial\mu}{\partial S}\right)_{V,N}^2 . \tag{2}$$

4) Show that the thermodynamic inequalities derived in class:

$$C_V \geq 0$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_V \left(\frac{\partial^2 E}{\partial V^2}\right)_S \geq \left(\frac{\partial^2 E}{\partial S \partial V}\right)_V^2 , \tag{3}$$

imply that the isothermal compressibility, $K_T \equiv -V\left(\frac{\partial V}{\partial P}\right)_T$ obeys:

$$K_T \geq 0.$$

(You may assume $T > 0$.)

5) A certain approximate calculation predicts that the Helmholtz free energy of an interacting gas should be:

$$A(T,V) = -NkT\ln[T^{3/2}(V - Nb)d/(N)] - aN^2/V, \tag{4}$$

where b, a and d are positive constants.

a) Calculate the equation of state, $P(V,T)$ that is implied by this approximate Helmholtz free energy.

b) Calculate the isothermal compressibility, K_T for this approximate Helmholtz free energy and show that the thermodynamic inequality derived in problem 4 is violated for a certain range of P,V and T. (This is basically a defect of the approximation although it is possible to make a certain amount of sense out of it anyway, as we shall see later.) Hint: You may find section 11.2 of Pathria helpful.

c) Calculate C_V and C_P using this Helmholtz free energy. There are thermodynamic inequalities $C_V > 0$ and $C_P > 0$. I derived the first one in class. The second one follows from problem 4) above and Eq. (1.68) of Plishke and Bergersen. Check whether the inequalities $C_V > 0$, $C_P > 0$ are consistent with this approximate Helmholtz free energy.