

Physics 607
Statistical Physics and Thermodynamics
Professor Valery Pokrovsky

Homework #3

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1 Problem #1

(1) Given the mass density of the medium, ρ , given by the expression

$$\rho = \frac{Nm}{V}$$

Using this relation we can take the partial derivative of pressure with respect to ρ keeping the entropy S constant. Using chain rule we can say that

$$\left(\frac{\partial p}{\partial \rho}\right)_S = \frac{(\partial S/\partial T)_p}{(\partial S/\partial T)_\rho} \left(\frac{\partial p}{\partial \rho}\right)_T$$

where we apply the cyclic chain rule to state that

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_S \left(\frac{\partial \rho}{\partial S}\right)_T &= -1 \\ \Downarrow \\ \left(\frac{\partial S}{\partial T}\right)_\rho &= - \left(\frac{\partial \rho}{\partial T}\right)_S \left(\frac{\partial S}{\partial \rho}\right)_T \end{aligned}$$

We note that ρ is only dependent on V which implies that

$$\left(\frac{\partial \rho}{\partial V}\right)_S = \left(\frac{\partial \rho}{\partial V}\right)_T$$

So, applying chain rule we find that

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_\rho &= - \left(\frac{\partial \rho}{\partial V}\right)_S \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial \rho}\right)_T \\ &= - \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial S}{\partial V}\right)_T \\ &= \left(\frac{\partial S}{\partial T}\right)_V \end{aligned}$$

Note we used the cyclic chain rule to find that the last partial derivative. We note the definitions for specific heat

$$\begin{aligned} C_p &= T \left(\frac{\partial S}{\partial T}\right)_p \\ C_V &= T \left(\frac{\partial S}{\partial T}\right)_V \end{aligned}$$

which implies that

$$\left(\frac{\partial p}{\partial \rho}\right)_S = \frac{C_p}{C_V} \left(\frac{\partial p}{\partial \rho}\right)_T$$

(2) Starting with the cyclic chain rule for the variables p , V , and T we have

$$\begin{aligned} -1 &= \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \\ \Downarrow \\ \left(\frac{\partial p}{\partial T}\right)_V &= - \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \end{aligned}$$

Therefore if we introduce the thermal expansion coefficient

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

and isothermic compressibility

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

we see that

$$\left(\frac{\partial p}{\partial T} \right)_V = -V\alpha(-V\kappa_T)^{-1} = \frac{\alpha}{\kappa_T}$$

- (3) We can find a relation to the quantities we introduced in part (2) to the specific heats of the system by noting that C_V is related to the change in energy through heat by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Now, if we treat E as a function of T and V by chain rule we have

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

which using the heat function we have

$$\begin{aligned} \delta Q &= \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV + pdV \\ &= C_V dT + \left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p dT + p \left(\frac{\partial V}{\partial T} \right)_p dT \\ &\Downarrow \\ \frac{\delta Q}{dT} - C_V &= C_p - C_V = \left(\left(\frac{\partial E}{\partial V} \right)_T + p \right) \left(\frac{\partial V}{\partial T} \right)_p \\ &= \left(T \left(\frac{\partial P}{\partial T} \right)_V - p + p \right) \left(\frac{\partial V}{\partial T} \right)_p \\ &= T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p \\ &= T \frac{\alpha}{\kappa_T} V \alpha = \frac{TV\alpha^2}{\kappa_T} \end{aligned}$$

2 Problem #2

- (1) For a glass of water at temperature $T = 300$ K placed into a heater with temperature $T = 363$ K and reaches thermal equilibrium. Assuming that the volume of the water remains constant implies that the change in energy is only dependent on the change in heat. This allows us to calculate the change in energy for the water in the glass using the specific heat

$$dQ = dE = CdT$$

Note we assume that C is a constant and independent of T allows us to calculate

$$\begin{aligned}\Delta S &= \int_{300}^{363} \frac{dQ}{T} \\ &= C \int_{300}^{363} \frac{dT}{T} \\ &= C \ln(T) \Big|_{300}^{363} \\ &= C \ln\left(\frac{363}{300}\right)\end{aligned}$$

We note that we assume that the heater reservoir is large enough to have the temperature remain constant. This allows us to directly calculate the change in entropy without integrating by noting that by conservation of energy the heat gained by the glass is the heat lost by the reservoir. We calculate this as

$$dQ = -C(363 - 300) = -63C$$

which implies that the change in entropy is calculated as

$$\Delta S = \frac{dQ}{T} = -C \frac{63}{363}$$

So the total change in entropy is given by

$$\Delta S_{tot} = C \left(\ln\left(\frac{363}{300}\right) - \frac{63}{363} \right) = 0.0171C$$

- (2) Now if we do the same process except with a two-stage heating with the first heater at $T = 333$ K and the second heater at $T = 363$ K. We note that the change in heat remains the same as the assumption that volume remains constant still holds. Which implies that the change in entropy of the cup can be calculated as

$$\begin{aligned}\Delta S &= \int_{300}^{333} \frac{dQ}{T} + \int_{333}^{363} \frac{dQ}{T} \\ &= \int_{300}^{363} \frac{dQ}{T} \\ &= C \ln\left(\frac{363}{300}\right)\end{aligned}$$

Note this verifies that the change in entropy is path independent. So we calculate the change in entropy of the two reservoirs by the same process

$$\begin{aligned}\Delta S_1 &= -C \frac{33}{333} \\ \Delta S_2 &= -C \frac{30}{363}\end{aligned}$$

so we calculate the total change in entropy

$$\Delta S_{tot} = C \left(\ln \left(\frac{363}{300} \right) - \frac{33}{333} - \frac{30}{363} \right) = 0.00888C$$

- (3) We note that the result from parts (1) and (2) that as we increase the number of steps between the initial and final temperatures, mathematically we write this as

$$\lim_{N \rightarrow \infty} \frac{\Delta T}{N}$$

In this limit the sum of the change in entropies of the reservoirs becomes $-C \ln(363/300)$ which makes the total change in entropy equal to zero.

3 Problem #3

(1) Given the energy of a monoatomic ideal gas given by $E = \frac{3}{2}NT$ we can calculate the efficiency of a cycle consisting of two isotherms and two isochores which follows the steps

- 1 to 2: Expansion from V_1 to V_2 at constant temperature T_2
- 2 to 3: Decrease in temperature from T_2 to T_1 at constant volume V_2
- 3 to 4: Compression from V_2 to V_1 at constant temperature T_1
- 4 to 1: Increase in temperature from T_1 to T_2 at constant volume V_1

To calculate the efficiency we use the relation between the work done on the environment versus the amount of heat used

$$\eta = \frac{-\Delta W}{\Delta Q}$$

Therefore, we need to calculate the work done by the cycle. We note that along the two isotherms T remains constant so all the heat energy is converted to work from V_1 to V_2 . So assuming we our gas is ideal we have an expansion from V_1 to V_2 at T_2 which has a change in heat as

$$\Delta Q_{12} = NT_2 \ln \left(\frac{V_2}{V_1} \right)$$

and for the other isotherm we contract from V_2 to V_1 at a temperature T_1 which yields

$$\Delta Q_{34} = NT_1 \ln \left(\frac{V_1}{V_2} \right)$$

Note it is assumed that $T_2 > T_1$. And as we stated both ΔQ_1 and ΔQ_2 are fully converted to work so

$$\begin{aligned}\Delta W_{12} &= -NT_2 \ln \left(\frac{V_2}{V_1} \right) \\ \Delta W_{34} &= -NT_1 \ln \left(\frac{V_1}{V_2} \right)\end{aligned}$$

Now for the isochores we note that V remains constant so there is no work done or

$$\Delta W_{23} = \Delta W_{41} = 0$$

but there is a change in heat which is the same as the total change in energy given by

$$\begin{aligned}\Delta Q_{23} &= \frac{3}{2}N(T_2 - T_1) \\ \Delta Q_{41} &= \frac{3}{2}N(T_1 - T_2)\end{aligned}$$

We note that ΔQ_{34} and ΔQ_{41} are negative and therefore are not heat added to the system. Therefore

$$\Delta Q = \Delta Q_{12} + \Delta Q_{23} = N \left(T_2 \ln \left(\frac{V_2}{V_1} \right) + \frac{3}{2}(T_2 - T_1) \right)$$

And we find the work done by

$$\Delta W = \Delta W_{12} + \Delta W_{34} = N(T_2 - T_1) \ln \left(\frac{V_2}{V_1} \right)$$

So we find the efficiency as

$$\begin{aligned}\eta &= \frac{(T_2 - T_1) \ln(V_2/V_1)}{T_2 \ln(V_2/V_1) + 3/2(T_2 - T_1)} \\ &= \frac{T_2 - T_1}{T_2 + 3(T_2 - T_1)/2 \ln(V_2/V_1)}\end{aligned}$$

We note that the Carnot cycle has an efficiency of

$$\eta_c = 1 - \frac{T_1}{T_2} = \frac{T_2 - T_1}{T_2}$$

we see that there is an extra term in the efficiency of the Sterling cycle given by

$$\frac{3(T_2 - T_1)}{2 \ln(V_2/V_1)}$$

which for our assumption $T_2 > T_1$ and $V_2 > V_1$ must be positive which makes $\eta < \eta_c$.

(2) For a refrigerator that works as a reversed Carnot cycle which goes through the following

- 1 to 2: Isothermal expansion at T_1
- 2 to 3: Reversible compression from T_1 to T_2
- 3 to 4: Isothermal compression at T_2
- 4 to 1: Reversible expansion from T_2 to T_1

Where we take $T_2 > T_1$. By driving the cycle in reverse (doing work onto the system) we take heat from from the T_2 reservoir and absorbed by the low temperature, T_1 , reservoir. For the Carnot cycle we coefficient of performance is given by

$$CoF = \frac{Q_{\text{cold}}}{Q_{\text{hot}} - Q_{\text{cold}}} = \frac{T_1}{T_2 - T_1}$$

so the CoF is less than one for $T_2 > 2T_1$.