

PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #4 SOLUTIONS

(1) A strange material obeys the equation of state $E(S, V, N) = a S^7/V^4 N^2$, where a is a dimensionful constant.

- (a) What are the SI dimensions of a ?
- (b) Find the equation of state relating p , T , and $n = N/V$.
- (c) Find the coefficient of thermal expansion $\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ and the isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$. Express your answers in terms of p and T .
- (d) ν moles of this material execute a Carnot cycle between reservoirs at temperatures T_1 and T_2 . Find the heat Q and work W for each leg of the cycle, and find the cycle efficiency η .

Solution :

(a) Clearly $[a] = \text{K}^7 \text{m}^{12}/\text{J}^2$ where K are Kelvins, m are meters, and J are Joules.

(b) We have

$$T = + \left(\frac{\partial E}{\partial S} \right)_{V,N} = \frac{7aS^6}{N^2V^4}$$

$$p = - \left(\frac{\partial E}{\partial V} \right)_{S,N} = \frac{4aS^7}{N^2V^5}.$$

We must eliminate S . Dividing the second of these equations by the first, we find $S = 7pV/4T$, and substituting this into either equation, we obtain the equation of state,

$$p = c \cdot \left(\frac{N}{V} \right)^{1/3} T^{7/6},$$

with $c = \frac{6}{7^{7/6}} a^{-1/6}$.

(c) Taking the logarithm and then the differential of the above equation of state, we have

$$\frac{dp}{p} + \frac{dV}{3V} - \frac{7 dT}{6T} - \frac{dN}{3N} = 0.$$

Thus,

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} = \frac{7}{2T}, \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{3}{p}.$$

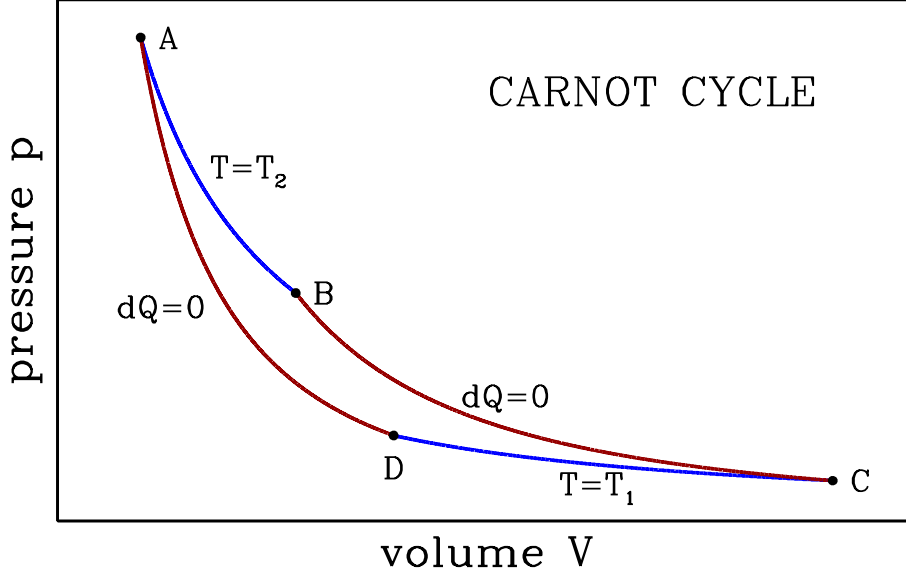


Figure 1: The Carnot cycle.

(d) From the results of part (b), we have that $dS = 0$ means $d(N^2V^4T) = 0$, so with N constant the equation for adiabats is $d(TV^4) = 0$. Thus, for the Carnot cycle of Fig. 1, we have

$$T_2 V_A^4 = T_1 V_D^4 \quad , \quad T_2 V_B^4 = T_1 V_C^4 .$$

We shall use this relation in due time. Another relation we shall use is obtained by dividing out the S^7 factor common in the expressions for E and for p , then substituting for p using the equation of state:

$$E = \frac{1}{4}pV = \frac{1}{4}cN^{1/3}V^{2/3}T^{7/6} .$$

AB: Consider the AB leg of the Carnot cycle. We use the equation of state along the isotherm to find

$$W_{AB} = \int_{V_A}^{V_B} dV p = \frac{3}{2}cN^{1/3}T_2^{7/6}(V_B^{2/3} - V_A^{2/3}) .$$

Since E depends on volume, unlike the case of the ideal gas, there is a change in energy along this leg:

$$(\Delta E)_{AB} = E_B - E_A = \frac{1}{4}cN^{1/3}T_2^{7/6}(V_B^{2/3} - V_A^{2/3}) .$$

Finally, the heat absorbed by the engine material during this leg is

$$Q_{AB} = (\Delta E)_{AB} + W_{AB} = \frac{7}{4}cN^{1/3}T_2^{7/6}(V_B^{2/3} - V_A^{2/3}) .$$

BC: Next, consider the BC leg. Clearly $Q_{BC} = 0$ since BC is an adiabat. Thus,

$$W_{BC} = -(\Delta E)_{BC} = E_B - E_C = \frac{1}{4}cN^{1/3}(T_2^{7/6}V_B^{2/3} - T_1^{7/6}V_C^{2/3}).$$

But the fact that BC is an adiabat guarantees $V_C^{2/3} = (T_2/T_1)^{1/6}V_B^{2/3}$, hence

$$W_{BC} = \frac{1}{4}cN^{1/3}V_B^{2/3}T_2^{1/6}(T_2 - T_1).$$

CD: For the CD leg, we can apply the results from AB, *mutatis mutandis*. Thus,

$$W_{CD} = \frac{3}{2}cN^{1/3}T_2^{7/6}(V_D^{2/3} - V_C^{2/3}).$$

We now use the adiabat conditions $V_C^{2/3} = (T_2/T_1)^{1/6}V_B^{2/3}$ and $V_D^{2/3} = (T_2/T_1)^{1/6}V_A^{2/3}$ to write W_{CD} as

$$W_{CD} = \frac{3}{2}cN^{1/3}T_1T_2^{1/6}(V_A^{2/3} - V_B^{2/3}).$$

We therefore have

$$Q_{CD} = \frac{7}{4}cN^{1/3}T_1T_2^{1/6}(V_A^{2/3} - V_B^{2/3}).$$

Note that both W_{CD} and Q_{CD} are negative.

DA: We apply the results from the BC leg, *mutatis mutandis*, and invoke the adiabat conditions. We find $Q_{DA} = 0$ and

$$W_{DA} = \frac{1}{4}cN^{1/3}V_A^{2/3}T_2^{1/6}(T_2 - T_1).$$

For the cycle, we therefore have

$$W_{\text{cyc}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \frac{7}{4}cN^{1/3}T_2^{1/6}(T_2 - T_1)(V_B^{2/3} - V_A^{2/3}).$$

and thus

$$\eta = \frac{W_{\text{cyc}}}{Q_{AB}} = 1 - \frac{T_1}{T_2}.$$

This is the same result as for an ideal gas, as must be the case as per the Second Law of Thermodynamics.

(2) The entropy of a thermodynamic system $S(E, V, N)$ is given by

$$S(E, V, N) = r E^\alpha V^\beta N^\gamma,$$

where r is a dimensionful constant.

(a) Extensivity of S imposes a condition on (α, β, γ) . Find this constraint.

- (b) Even with the extensivity condition satisfied, the system may violate one or more stability criteria. Find the general conditions on (α, β, γ) which are thermodynamically permissible.

Solution :

(a) Clearly we must have $\alpha + \beta + \gamma = 1$ in order for S to be extensive.

(b) The Hessian is

$$Q = \frac{\partial^2 S}{\partial X_i \partial X_j} = \begin{pmatrix} \alpha(\alpha - 1) S/E^2 & \alpha\beta S/EV & \alpha\gamma S/EN \\ \alpha\beta S/EV & \beta(\beta - 1) S/V^2 & \beta\gamma S/VN \\ \alpha\gamma S/EN & \beta\gamma S/VN & \gamma(\gamma - 1) S/N^2 \end{pmatrix}.$$

As shown in the notes, for any 2×2 submatrix of Q , obtained by eliminating a single row and its corresponding column, and written $\begin{pmatrix} a & b \\ b & c \end{pmatrix}$, we must have $a < 0$, $c < 0$, and $ac > b^2$. For example, if we take the upper left 2×2 submatrix, obtained by eliminating the third row and third column of Q , we have $a = \alpha(\alpha - 1)S/E^2$, $b = \alpha\beta S/EV$, and $c = \beta(\beta - 1)S/V^2$. The condition $a < 0$ requires $\alpha \in (0, 1)$. Similarly, $\beta < 0$ requires $\beta \in (0, 1)$. Finally, $ac > b^2$ requires $\alpha + \beta < 1$. Since $\alpha + \beta + \gamma = 1$, this last condition requires $\gamma > 0$. Obviously we must have $\gamma < 1$ as well, else either α or β would have to be negative. An examination of either of the other two submatrices yields the same conclusions. Thus,

$$\alpha \in (0, 1) \quad , \quad \beta \in (0, 1) \quad , \quad \gamma \in (0, 1) .$$

(3) For an ideal gas, find the difference $C_\varphi - C_V$ for the following functions φ . You are to assume N is fixed in each case.

- (a) $\varphi(p, V) = p^3 V^2$
 (b) $\varphi(p, T) = p e^{T/T_0}$
 (c) $\varphi(T, V) = VT^{-1}$

Solution :

In general,

$$C_\varphi = T \left(\frac{\partial S}{\partial T} \right)_\varphi .$$

Note that

$$dQ = dE + p dV .$$

We will also appeal to the ideal gas law, $pV = Nk_B T$. Below, we shall abbreviate $\varphi_V = \frac{\partial \varphi}{\partial V}$, $\varphi_T = \frac{\partial \varphi}{\partial T}$, and $\varphi_p = \frac{\partial \varphi}{\partial p}$.

(a) We have

$$dQ = \frac{1}{2} f N k_B dT + p dV ,$$

and therefore

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi .$$

Now for a general function $\varphi(p, V)$, we have

$$\begin{aligned} d\varphi &= \varphi_p dp + \varphi_V dV \\ &= \frac{Nk_B}{V} \varphi_p dT + \left(\varphi_V - \frac{p}{V} \varphi_p \right) dV , \end{aligned}$$

after writing $dp = d(Nk_B T/V)$ in terms of dT and dV . Setting $d\varphi = 0$, we then have

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi = \frac{Nk_B p \varphi_p}{p \varphi_p - V \varphi_V} .$$

This is the general result. For $\varphi(p, V) = p^3 V^2$, we find

$$C_\varphi - C_V = 3Nk_B .$$

(b) We have

$$dQ = \left(\frac{1}{2} f + 1 \right) N k_B dT - V dp ,$$

and therefore

$$C_\varphi - C_V = Nk_B - V \left(\frac{\partial p}{\partial T} \right)_\varphi .$$

For a general function $\varphi(p, T)$, we have

$$d\varphi = \varphi_p dp + \varphi_T dT \implies \left(\frac{\partial p}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_p} .$$

Therefore,

$$C_\varphi - C_V = Nk_B + V \frac{\varphi_T}{\varphi_p} .$$

This is the general result. For $\varphi(p, T) = p e^{T/T_0}$, we find

$$C_\varphi - C_V = Nk_B \left(1 + \frac{T}{T_0} \right) .$$

(c) We have

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi ,$$

as in part (a). For a general function $\varphi(T, V)$, we have

$$d\varphi = \varphi_T dT + \varphi_V dV \implies \left(\frac{\partial \varphi}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_V},$$

and therefore

$$C_\varphi - C_V = -p \frac{\varphi_T}{\varphi_V}.$$

This is the general result. For $\varphi(T, V) = V/T$, we find

$$C_\varphi - C_V = Nk_B.$$

(4) Find an expression for the energy density $\varepsilon = E/V$ for a system obeying the Dieterici equation of state,

$$p(V - Nb) = Nk_B T e^{-Na/Vk_B T},$$

where a and b are constants. Your expression for $\varepsilon(v, T)$ should involve an integral which can be expressed in terms of the exponential integral,

$$\text{Ei}(x) = \int_{-\infty}^x dt \frac{e^t}{t}.$$

Solution :

We have

$$\left(\frac{\partial E}{\partial V} \right)_{T,N} = T \left(\frac{\partial S}{\partial V} \right)_{T,N} - p = T \left(\frac{\partial p}{\partial T} \right)_{V,N} - p,$$

where we have invoked a Maxwell relation. For the Dieterici equation of state, then,

$$\left(\frac{\partial E}{\partial V} \right)_{T,N} = \frac{Nk_B T}{V - Nb} \cdot \frac{Na}{Vk_B T} \cdot e^{-Na/Vk_B T}.$$

Let $n = N/V$ be the density and $\varepsilon = E/N$ be the energy per particle. Then the above result is equivalent to

$$\frac{\partial \varepsilon}{\partial n} = -\frac{a}{1 - bn} e^{-na/k_B T}.$$

We integrate this between $n = 0$ and n , with $bn < 1$. Define the dimensionless quantity $\lambda = a/bk_B T$ and $t = \lambda(1 - bn)$. Then

$$\varepsilon(n, T) - \varepsilon(0, T) = -\frac{a e^{-\lambda}}{b} \int_{(1-bn)\lambda}^{\lambda} \frac{dt}{t} e^t = \left\{ \text{Ei}((1 - bn)\lambda) - \text{Ei}(\lambda) \right\} \frac{a e^{-\lambda}}{b}$$

In the zero density limit, the gas must be ideal, in which case $\varepsilon(0, T) = \frac{1}{2} f k_B T$. Thus,

$$\varepsilon(n, T) = \frac{1}{2} f k_B T - \left\{ \text{Ei} \left(\frac{(1 - bn)a}{bk_B T} \right) - \text{Ei} \left(\frac{a}{bk_B T} \right) \right\} \cdot \frac{a e^{-a/bk_B T}}{b}.$$

In terms of the volume per particle, write $v = V/N = 1/n$.