

**PHYSICS 140A : STATISTICAL PHYSICS  
HW SOLUTIONS #2**

(1) A substance obeys the thermodynamic relation  $E = aS^4/VN^2$ .

- (a) Compute the heat capacity  $C_{V,N}$  in terms of  $N$ ,  $V$ , and  $T$ .
- (b) Compute the equation of state relating  $p$ ,  $V$ ,  $N$ , and  $T$ .
- (c) Compute the ratio  $C_{\varphi,N}/C_{V,N}$ , where  $C_{\varphi,N}$  is the heat capacity at constant  $\varphi$  and  $N$ , with  $\varphi = V^2/T$ .

**Solution :**

(a) We have

$$T = \left. \frac{\partial E}{\partial S} \right|_{V,N} = \frac{4aS^3}{VN^2} \Rightarrow S = \left( \frac{TVN^2}{4a} \right)^{1/3} .$$

Plugging this into the expression for  $E(S, V, N)$ , we obtain

$$E(T, V, N) = \frac{1}{4}(4a)^{-1/3} T^{4/3} V^{1/3} N^{2/3} ,$$

and hence

$$C_{V,N} = \left. \frac{\partial E}{\partial T} \right|_{V,N} = \frac{1}{3}(4a)^{-1/3} T^{1/3} V^{1/3} N^{2/3} .$$

(b) We have  $T(S, V, N)$  and so we must find  $p(S, V, N)$  and then eliminate  $S$ . Thus,

$$p = - \left. \frac{\partial E}{\partial V} \right|_{S,N} = \frac{aS^4}{V^2N^2} = \frac{1}{4}(4a)^{-1/3} T^{4/3} V^{-2/3} N^{2/3} .$$

Cubing this result eliminates the fractional powers, yielding the equation of state

$$256a p^3 V^2 = N^2 T^4 .$$

Note also that  $E = pV$  and  $C_{V,N} = 4pV/3T$ .

(d) We have  $dE = \delta Q - p dV$ , so

$$\delta Q = dE + p dV = C_{V,N} dT + \left\{ \left( \frac{\partial E}{\partial V} \right)_{T,N} + p \right\} dV .$$

Now we need to compute  $dV|_{\varphi,N}$ . We write

$$d\varphi = -\frac{V^2}{T^2} dT + \frac{2V}{T} dV ,$$

hence

$$dV|_{\varphi,N} = \frac{V}{2T} dT .$$

Substituting this into our expression for  $dQ$ , we have

$$C_{\varphi,N} = C_{V,N} + \left\{ \left( \frac{\partial E}{\partial V} \right)_{T,N} + p \right\} \frac{V}{2T} .$$

It is now left to us to compute

$$\left( \frac{\partial E}{\partial V} \right)_{T,N} = \frac{1}{12} (4a)^{-1/3} T^{4/3} V^{-2/3} N^{2/3} = \frac{1}{3} p .$$

We then have

$$C_{\varphi,N} = C_{V,N} + \frac{2pV}{3T} = \frac{3}{2} C_{V,N} .$$

Thus,

$$\frac{C_{\varphi,N}}{C_{V,N}} = \frac{3}{2} .$$

(2) A strange material satisfies  $E(S, V, N) = a S^6 / V^3 N^2$ .

- What are the SI dimensions of  $a$ ?
- Find the equation of state relating  $p$ ,  $T$ , and  $n = N/V$ .
- Find the coefficient of thermal expansion  $\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ . Express your answer in terms of  $T$ .
- Find the coefficient of isothermal compressibility  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$ . Express your answer in terms of  $p$ .

**Solution :**

(a) Since  $[S] = \text{J/K}$ , we have  $[a] = \text{K}^6 \text{m}^9 / \text{J}^5$ .

(b) We have

$$T = \left( \frac{\partial E}{\partial S} \right)_{V,N} = \frac{6aS^5}{V^3 N^2} , \quad p = - \left( \frac{\partial E}{\partial V} \right)_{S,N} = \frac{3aS^6}{V^4 N^2} .$$

The combination  $T^6/p^5$  eliminates  $S$ , and we obtain the equation of state,

$$192a p^5 V^2 = N^2 T^6 .$$

(c) At constant  $p$  and  $N$ , we have  $\ln V = 3 \ln T + \text{const}$ . Thus, the coefficient of thermal expansion is

$$\alpha_p = \left( \frac{\partial \ln V}{\partial T} \right)_{p,N} = \frac{3}{T} .$$

(d) At constant  $T$  and  $N$ , we have  $\ln V = -\frac{5}{2} \ln p + \text{const.}$  Thus, the isothermal compressibility is

$$\kappa_T = - \left( \frac{\partial \ln V}{\partial p} \right)_{T,N} = \frac{5}{2p} .$$

(3)  $\nu$  moles of the substance in problem 2 execute a Carnot cycle between reservoirs at temperatures  $T_1$  and  $T_2$ . The top isotherm extends from volume  $V_A$  to  $V_B$ . Find the heat  $Q$  and work  $W$  for each leg of the cycle, and compute the cycle efficiency. *Suggestion: It is useful to use §2.6.6 of the Lecture Notes as a template.*

**Solution :**

From the results of problem (2), we have

$$E = \frac{1}{3} p V = \frac{1}{3} \left( \frac{N^2 V^3 T^6}{192a} \right)^{1/5} .$$

Thus, under isothermal conditions,

$$dE|_T = \frac{1}{5} \left( \frac{N^2 T^6}{192a} \right)^{1/5} \frac{dV}{V^{2/5}} = \frac{1}{5} p dV .$$

Thus, along an isotherm, we have

$$W_{\text{if}} = \int_{V_i}^{V_f} dV p = 5 (E_f - E_i)$$

$$Q_{\text{if}} = E_f - E_i + W_{\text{if}} = 6 (E_f - E_i) .$$

Along an adiabat, we have  $TV^3 = \text{const.}$  and  $E/T = \text{const.}$ , so

$$E_B = \left( \frac{V_B}{V_A} \right)^{3/5} E_A , \quad E_C = \frac{T_1}{T_2} \left( \frac{V_B}{V_A} \right)^{3/5} E_A , \quad E_D = \frac{T_1}{T_2} E_A ,$$

where AB is an isotherm at  $T_2$ , BC is an adiabat, CD is an isotherm at  $T_1$ , and DA is an adiabat. We now have

$$W_{\text{AB}} = 5(E_B - E_A) = 5 \left\{ \left( \frac{V_B}{V_A} \right)^{3/5} - 1 \right\} E_A$$

$$Q_{\text{AB}} = 6(E_B - E_A) = 6 \left\{ \left( \frac{V_B}{V_A} \right)^{3/5} - 1 \right\} E_A$$

$$W_{\text{BC}} = E_C - E_B = \left( 1 - \frac{T_1}{T_2} \right) \left( \frac{V_B}{V_A} \right)^{3/5} E_A$$

$$Q_{\text{BC}} = 0$$

and

$$\begin{aligned}
 W_{\text{CD}} &= 5(E_{\text{D}} - E_{\text{C}}) = 5 \frac{T_1}{T_2} \left\{ 1 - \left( \frac{V_{\text{B}}}{V_{\text{A}}} \right)^{3/5} \right\} E_{\text{A}} \\
 Q_{\text{CD}} &= 6(E_{\text{D}} - E_{\text{C}}) = 6 \frac{T_1}{T_2} \left\{ 1 - \left( \frac{V_{\text{B}}}{V_{\text{A}}} \right)^{3/5} \right\} E_{\text{A}} \\
 W_{\text{DA}} &= E_{\text{A}} - E_{\text{D}} = \left( \frac{T_1}{T_2} - 1 \right) E_{\text{A}} \\
 Q_{\text{DA}} &= 0
 \end{aligned}$$

Adding up the work along the four legs of the Carnot cycle, we have

$$W = 6 \left( 1 - \frac{T_1}{T_2} \right) \left\{ \left( \frac{V_{\text{B}}}{V_{\text{A}}} \right)^{3/5} - 1 \right\} E_{\text{A}} ,$$

and the efficiency is

$$\eta = \frac{W}{Q_{\text{AB}}} = 1 - \frac{T_1}{T_2} ,$$

which is the same result as for an ideal gas. Were the efficiency different from that of the ideal gas Carnot cycle running between the same two reservoirs, one could use one of the engines to drive the other run as a refrigerator and thereby violate the Second Law of Thermodynamics, *i.e.* transferring heat from the cold reservoir to the warm reservoir during a cycle. The fact that this is impossible requires that the efficiencies are exactly the same.

(4) An interacting diatomic gas obeys the equation of state

$$p(v - b) = RT e^{-a/v} ,$$

where  $v = N_{\text{A}}V/N$  is the molar volume.

(a) Show that  $E(T, V, N) = \frac{1}{2}fNk_{\text{B}}T$ , the same as for an ideal gas.

(b) Find the molar specific heat  $c_p$  as a function of the specific volume  $v$ .

**Solution :**

(a) We know that

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p ,$$

where  $\varepsilon$  and  $v$  are molar energy and molar volume, respectively. For our system, the RHS of the above equation vanishes, hence  $\varepsilon = \varepsilon(T)$ . In the dilute limit we know the answer,

and since  $\varepsilon$  is independent of volume, this is true for arbitrary molar volumes. Thus,  $\varepsilon(T) = \frac{1}{2}fRT$ , i.e.  $E = \frac{1}{2}fNk_{\text{B}}T$ .

(b) We have

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_p = \left( \frac{\partial \varepsilon}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p .$$

The first term on the RHS yields  $\frac{1}{2}fR$ . To evaluate the second term, we appeal to the equation of state at constant pressure, which yields, upon taking the differential,

$$\begin{aligned} p dv &= R e^{-a/v} dT + \frac{RTa}{v^2} e^{-a/v} dv \\ &= \frac{RT}{v-b} e^{-a/v} dv . \end{aligned}$$

Thus,

$$\left( \frac{\partial v}{\partial T} \right)_p = \frac{(v-b)v^2/T}{v^2 - av + ab}$$

We then have

$$c_p = \frac{1}{2}fR + \frac{Rv^2 e^{-a/v}}{v^2 - av + ab} .$$

Note that  $c_p(v \rightarrow \infty) = (\frac{1}{2}f + 1)R$ , which is the ideal gas value.