PHYSICS 210A : STATISTICAL PHYSICS
HW ASSIGNMENT #4 SOLUTIONS

(1) $\nu = 8$ moles of a diatomic ideal gas are subjected to a cyclic quasistatic process, the thermodynamic path for which is an ellipse in the (V, p) plane. The center of the ellipse lies at $(V_0, p_0) = (0.25\,\mathrm{m}^3, 1.0\,\mathrm{bar})$. The semimajor and semiminor axes of the ellipse are $\Delta V = 0.10\,\mathrm{m}^3$ and $\Delta p = 0.20\,\mathrm{bar}$.

(a) What is the temperature at $(V, p) = (V_0 + \Delta V, p_0)$?

(b) Compute the net work per cycle done by the gas.

(c) Compute the internal energy difference $E(V_0 - \Delta V, p_0) - E(V_0, p_0 - \Delta p)$.

(d) Compute the heat Q absorbed by the gas along the upper half of the cycle.

Solution :

(a) The temperature is $T = pV/\nu R$. With $V = V_0 + \Delta V = 0.35\,\mathrm{m}^3$ and $p = p_0 = 1.0\,\mathrm{bar}$, we have
$$T = \frac{(10^5\,\mathrm{Pa})(0.35\,\mathrm{m}^3)}{(8\,\mathrm{mol})(8.31\,\mathrm{J/mol\,K})} = 530\,\mathrm{K} \ .$$

(b) The area of an ellipse is π times the product of the semimajor axis lengths.
$$\oint p\,dV = \pi\,(\Delta p)(\Delta V) = \pi\,(0.20 \times 10^6\,\mathrm{bar})\,(0.10\,\mathrm{m}^3) = 6.3\,\mathrm{kJ} \ .$$

(c) For a diatomic ideal gas, $E = \frac{5}{2}pV$. Thus,
$$\Delta E = \tfrac{5}{2}\big(V_0\,\Delta p - p_0\,\Delta V\big) = \tfrac{5}{2}\,(-0.05 \times 10^5\,\mathrm{J}) = -13\,\mathrm{kJ} \ .$$

(d) We have $Q = \Delta E + W$, with
$$W = 2\,p_0\,\Delta V + \tfrac{\pi}{2}(\Delta p)(\Delta V) = 23\,\mathrm{kJ} \ ,$$

which is the total area under the top half of the ellipse. The difference in energy is given by $\Delta E = \frac{5}{2}\,p_0 \cdot 2\Delta V = 5\,p_0\,\Delta V$, so
$$Q = \Delta E + W = 7\,p_0\,\Delta V + \tfrac{\pi}{2}(\Delta p)(\Delta V) = 73\,\mathrm{kJ} \ .$$

(2) Consider a thermodynamic system for which $E(S, V, N) = aS^4/NV^2$.

(a) Find the equation of state $p = p(T, V, N)$.

(b) Find the equation of state $\mu = \mu(T, p)$.

(c) ν moles of this substance are taken through a Joule-Brayton cycle. The upper isobar lies at $p = p_2$ and extends from volume V_A to V_B. The lower isobar lies at $p = p_1$. Find the volumes V_C and V_D.

(d) Find the work done per cycle W_{cyc}, the heat Q_{AB}, and the cycle efficiency.

Solution :

(a) We can find

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

but we need to eliminate the inconvenient variable S from these equations. To do this, we construct the ratio p^3/T^4, in which the S factors manifestly cancel. One then finds $32a\,p^3V = NT^4$, i.e.

$$p(T, V, N) = (32a)^{-1/3}\left(\frac{N}{V}\right)^{1/3} T^{4/3} \ .$$

This means, for example, that the equation for an isotherm (at fixed N) is $pV^{1/3} = \text{const.}$, in contrast to the result for the ideal gas isotherm, $pV = \text{const.}$ Note also that p, being intensive, must be expressible as $p(T, V/N)$, which it is.

(b) To obtain $\mu(T, p)$, note that $2N\mu = -pV$, and from our result for $p(T, V/N)$ we have $V/N = T^4/32ap^3$. Thus,

$$\mu(T, p) = -\frac{T^4}{64a\,p^2} \ .$$

(c) The equilibrium adiabatic equation of state for this system is $dS = 0$. From (a), we see that at fixed N this means $pV^3 = \text{const.}$, so we must have $p_2V_B^3 = p_1V_C^3$ and $p_2V_A^3 = p_1V_D^3$. Hence

$$V_C = V_B \cdot \left(p_2/p_1\right)^{1/3} \quad , \quad V_D = V_A \cdot \left(p_2/p_1\right)^{1/3} \ .$$

(a) From part (a), the energy for our system is $E = \frac{1}{2}pV$. Along the upper (p_2) isochore,

$$W_{AB} = \int_A^B dV\, p_2 = p_2(V_B - V_A) \quad , \quad \Delta E_{AB} = E_B - E_A = \tfrac{1}{2}p_2\,(V_B - V_A) \quad ,$$

hence

$$Q_{AB} = \Delta E_{AB} + W_{AB} = \tfrac{3}{2}p_2\,(V_B - V_A) \ .$$

The work along the lower (p_1) isochore is

$$W_{CD} = p_1(V_D - V_C) = p_2\,(V_A - V_B)\left(\frac{p_1}{p_2}\right)^{2/3}.$$

Along the BC adiabat,

$$W_{BC} = \int\limits_{B}^{C} p\,dV = p_2 V_B^3 \int\limits_{V_B}^{V_C} \frac{dV}{V^3} = \tfrac{1}{2}p_2 V_B\left(1 - \frac{V_B^2}{V_C^2}\right) = \tfrac{1}{2}p_2 V_B\left[1 - \left(\frac{p_1}{p_2}\right)^{2/3}\right].$$

Similarly,

$$W_{DA} = \int\limits_{D}^{A} p\,dV = p_2 V_A^3 \int\limits_{V_D}^{V_A} \frac{dV}{V^3} = \tfrac{1}{2}p_2 V_A\left(\frac{V_A^2}{V_D^2} - 1\right) = \tfrac{1}{2}p_2 V_A\left[\left(\frac{p_1}{p_2}\right)^{2/3} - 1\right].$$

Adding up all the individual works, we get

$$W_{\text{cyc}} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$= \tfrac{3}{2}p_2(V_B - V_A)\left[1 - \left(\frac{p_1}{p_2}\right)^{2/3}\right].$$

Dividing by Q_{AB}, we obtain the efficiency,

$$\eta = \frac{W_{\text{cyc}}}{Q_{AB}} = 1 - \left(\frac{p_1}{p_2}\right)^{2/3}.$$

($\mathbf{3}$) A diatomic gas obeys the equation of state

$$p = \frac{RT}{v - b} - \frac{a}{v^2} + \frac{cRT}{v^3}\,,$$

where a, b, and c are constants.

    (a) Find the adiabatic equation of state relating temperature T and molar volume v.

    (b) What is the internal energy per mole, $\varepsilon(T, v)$?

    (c) What is the Helmholtz free energy per mole, $f(T, v)$?

Solution :

(a) Let ε be the molar internal energy and v the molar volume. We have already shown

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

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Thus, for our system,

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = \frac{a}{v^2} \quad \Rightarrow \quad \varepsilon(T, v) = \tfrac{5}{2}RT - \frac{a}{v} ,$$

where the first term is the result for the rarefied limit $v \to \infty$, where the gas presumably becomes ideal. Now if $s = S/\nu$ is the molar entropy ($\nu = N/N_A$ is the number of moles), then

$$T\, ds = d\varepsilon + p\, dv = \tfrac{5}{2}R\, dT + RT\,\frac{dv}{v - b} + cRT\,\frac{dv}{v^3} .$$

Dividing by T and then integrating, we have

$$s(T, v) = R\ln\left[T^{5/2}(v - b)\, e^{-c/2v^2}\right] + \text{const.} .$$

Thus, the equation of the adiabat is

$$T^{5/2}(v - b)\, e^{-c/2v^2} = \text{const.}$$

(b) We have already obtained the result

$$\varepsilon(T, v) = \tfrac{5}{2}RT - \frac{a}{v} .$$

(c) From $f = \varepsilon - Ts$, where $f = F/\nu$ is the Helmholtz free energy per mole, we have

$$f(T, v) = \tfrac{5}{2}RT - \frac{a}{v} - \tfrac{5}{2}RT\ln\left(\frac{bRT}{a}\right) - RT\ln\left(\frac{v - b}{b}\right) + \frac{cRT}{2v^2} - Ts_0 .$$

Here we have inserted constants with the proper dimensions in order to render our expression for f with the appropriate dimensions. Thus, the constant s_0 has dimensions of $\text{J/mol} \cdot \text{K}$, the same as the gas constant R. Since c/b^2 is dimensionless, there is more than one way to do this. Any resulting differences will show up in a different expression for s_0.

(4) Consider the thermodynamics of a solid in equilibrium with a vapor at temperature T and pressure p, but separated by a quasi-liquid layer of thickness d. Let the number density of the liquid be n_ℓ. The Gibbs free energy per unit area of the quasi-liquid layer is taken as

$$g_{qll}(T, p) = n_\ell\, \mu_\ell(T, p)\, d + \gamma(d) ,$$

where $\gamma(d)$ is an effective surface tension which interpolates between $\gamma(0) = \gamma_{sv}$ and $\gamma(\infty) = \gamma_{s\ell} + \gamma_{\ell v}$. The phenomenon of premelting requires $\gamma(0) > \gamma(\infty)$.

(a) Show that $\mu_{qll}(T, p) = \mu_\ell(T, p) + n_\ell^{-1}\gamma'(d) = \mu_s(T, p)$.

(b) Expand T relative to some point (T_m, p) along the melting curve to lowest order in $T - T_m$. Show $\Delta\mu(T, p) \equiv \mu_s(T, p) - \mu_\ell(T, p) = \ell_m(T - T_m)/T_m$, where ℓ_m is the latent heat of melting.

(c) Assume

$$\gamma(d) = \gamma_{sv} + (\gamma_{s\ell} + \gamma_{\ell v} - \gamma_{sv}) \cdot \frac{d^2}{d^2 + \sigma^2} \ ,$$

where σ is a molecular length scale. Assuming $d \gg \sigma$, find the dependence of the thickness d of the quasi-liquid layer on the reduced temperature $t \equiv (T_m - T)/T_m$.

Solution :

(a) The chemical potentials of a particle in the solid and the quasi-liquid layers must be the same. Since we use d for thickness, I will here use δ for differential. The Gibbs free energy of the quasi-liquid layer is $G_{qll}(d) = A g_{qll}(d)$, where A is the total surface area. The number of particles in the quasi-liquid layer is $N_{qll} = A n_{qll} d$. Thus, the chemical potential is potential is then

$$\mu_{qll} = \frac{\delta G_{qll}}{\delta N_{qll}} = \mu_\ell + n_\ell^{-1} \gamma'(d) \ .$$

(b) Expanding to first order, with $\Delta\mu = \mu_s - \mu_\ell$, we have

$$\Delta\mu(T, p) = \left(\frac{\partial\Delta\mu}{\partial T}\right)_p (T - T_m) = \frac{\ell_m}{T_m}(T - T_m) \quad ,$$

where ℓ_m is the latent heat of melting per molecule. This results in the desired expression $\Delta\mu(T, p) = \ell_m(T - T_m)/T_m$.

For a more rigorous derivation, expand to first order in both ΔT and Δp:

$$\Delta\mu(T, p) = \left(\frac{\partial\Delta\mu}{\partial T}\right)_p (T - T_m) + \left(\frac{\partial\Delta\mu}{\partial p}\right)_T (p - p_m) + \dots$$

$$= \frac{\ell_m}{T_m}(T - T_m) - \left(\frac{1}{n_\ell} - \frac{1}{n_s}\right)(p - p_m) + \dots \ .$$

The pressure shift can now be expressed in terms of the temperature shift by examining the slopes of the sublimation and melting lines, via the Clapeyron equation. This results in $\Delta\mu(T, p) = \kappa_v \ell_m(T - T_m)/T_m$, with

$$\kappa_v = 1 - \frac{(dp/dT)_{\text{subl}}}{(dp/dT)_{\text{melt}}} \ .$$

For water, $\kappa_v \approx 1$ and the correction is negligible.

(c) We now set

$$\Delta\mu = \frac{1}{n_\ell}\frac{\partial\gamma}{\partial d} = \frac{\gamma_{s\ell} + \gamma_{\ell v} - \gamma_{sv}}{n_\ell} \cdot \frac{2\sigma^2 d}{(\sigma^2 + d^2)^2} = \frac{\kappa_v \ell_m \,\Delta T}{T_m} \ .$$

For $d \gg \sigma$, we have

$$d(t) = \left(-\frac{2\sigma^2(\gamma_{s\ell} + \gamma_{\ell v} - \gamma_{sv})}{\ell_{\mathrm{m}}\, n_\ell} \right)^{1/3} t^{-1/3} \ ,$$

where $t \equiv (T - T_{\mathrm{m}})/T_{\mathrm{m}}$.