PHYSICS 140A : STATISTICAL PHYSICS
HW ASSIGNMENT #7 SOLUTIONS

(1) Using the chain rule from multivariable calculus (see §2.16 of the lecture notes), solve the following:

(a) Find $(\partial N/\partial T)_{S,p}$ in terms of T, N, S, and $C_{p,N}$.

(b) Experimentalists can measure $C_{V,N}$ but for many problems it is theoretically easier to work in the grand canonical ensemble, whose natural variables are (T, V, μ). Show that

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,z} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z} \bigg/ \left(\frac{\partial N}{\partial z}\right)_{T,V} ,$$

where $z = \exp(\mu/k_B T)$ is the fugacity.

Solution :

(a) We have

$$\left(\frac{\partial N}{\partial T}\right)_{S,p} = \frac{\partial(N,S,p)}{\partial(T,S,p)} = \frac{\partial(N,S,p)}{\partial(N,T,p)} \cdot \frac{\partial(N,T,p)}{\partial(T,S,p)} = -\frac{NC_{p,N}}{TS} .$$

(b) Using the chain rule,

$$\begin{aligned} C_{V,N} = \frac{\partial(E,V,N)}{\partial(T,V,N)} &= \frac{\partial(E,V,N)}{\partial(T,V,z)} \cdot \frac{\partial(T,V,z)}{\partial(T,V,N)} \\ &= \left[\left(\frac{\partial E}{\partial T}\right)_{V,z} \left(\frac{\partial N}{\partial z}\right)_{T,V} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z}\right] \cdot \left(\frac{\partial z}{\partial N}\right)_{T,V} \\ &= \left(\frac{\partial E}{\partial T}\right)_{V,z} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z} \bigg/ \left(\frac{\partial N}{\partial z}\right)_{T,V} . \end{aligned}$$

(2) Consider the equation of state,

$$p = \frac{R^2 T^2}{a + vRT} ,$$

where $v = N_A V/N$ is the molar volume and a is a constant.

(a) Find an expression for the molar energy $\varepsilon(T, v)$. Assume that in the limit $v \to \infty$, where the ideal gas law $pv = RT$ holds, that the gas is ideal with $\varepsilon(v \to \infty, T) = \frac{1}{2} f RT$.

(b) Find the molar specific heat $c_{V,N}$.

Solution :

(a) We fix N throughout the analysis. As shown in §2.10.2 of the lecture notes,

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

Defining the molar energy $\varepsilon = E/\nu = N_{\rm A}E/N$ and the molar volume $v = V/\nu = N_{\rm A}V/N$, we can write the above equation as

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_{T} = T\left(\frac{\partial p}{\partial T}\right)_{v} - p = p\left[\left(\frac{\partial \ln p}{\partial \ln T}\right)_{v} - 1\right].$$

Now from the equation of state, we have

$$\ln p = 2\ln T - \ln(a + vRT) + 2\ln R\,,$$

hence

$$\left(\frac{\partial \ln p}{\partial \ln T}\right)_{v} = 2 - \frac{vRT}{a + vRT}\,.$$

Plugging this into our formula for $\left(\frac{\partial \varepsilon}{\partial v}\right)_T$, we have

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_{T} = \frac{a\,p}{a + vRT} = \frac{aR^2T^2}{(a + vRT)^2}\,.$$

Now we integrate with respect to v at fixed T, using the method of partial fractions. After some grinding, we arrive at

$$\varepsilon(T, v) = \omega(T) - \frac{aRT}{(a + vRT)}\,.$$

In the limit $v \to \infty$, the second term on the RHS tends to zero. This is the ideal gas limit, hence we must have $\omega(T) = \frac{1}{2}fRT$, where $f = 3$ for a monatomic gas, $f = 5$ for diatomic, *etc.* Thus,

$$\varepsilon(T, v) = \tfrac{1}{2}fRT - \frac{aRT}{a + vRT} = \tfrac{1}{2}fRT - \frac{a}{v} + \frac{a^2}{v(a + vRT)}\,.$$

(b) To find the molar specific heat, we compute

$$c_{V,N} = \left(\frac{\partial \varepsilon}{\partial T}\right)_{v} = \tfrac{1}{2}fR - \frac{a^2 R}{(a + vRT)^2}\,.$$

(3) A van der Waals gas undergoes an adiabatic free expansion from initial volume $V_{\rm i}$ to final volume $V_{\rm f}$. The equation of state is given in §2.10.3 of the lecture notes. The number of particles N is held constant.

(a) If the initial temperature is $T_{\rm i}$, what is the final temperature $T_{\rm f}$?

(b) Find an expression for the change in entropy ΔS of the gas.

Solution :

(a) This part is done for you in §2.10.5 of the notes. One finds

$$\Delta T = T_{\rm f} - T_{\rm i} = \frac{2a}{fR}\left(\frac{1}{v_{\rm f}} - \frac{1}{v_{\rm i}}\right) .$$

(b) Consider a two-legged thermodynamic path, consisting first of a straight leg from $(T_{\rm i}, V_{\rm i})$ to $(T_{\rm i}, V_{\rm f})$, and second of a straight leg from $(T_{\rm i}, V_{\rm f})$ to $(T_{\rm f}, V_{\rm f})$. We then have

$$\Delta S = \overbrace{\int\limits_{V_{\rm i}}^{V_{\rm f}} dV \left(\frac{\partial S}{\partial V}\right)_{T_{\rm i},N}}^{\Delta S_1} + \overbrace{\int\limits_{T_{\rm i}}^{T_{\rm f}} dT \left(\frac{\partial S}{\partial T}\right)_{V_{\rm f},N}}^{\Delta S_2} .$$

Along the first leg we use

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

and we then find

$$\Delta S_1 = R \ln\left(\frac{v_{\rm f} - b}{v_{\rm i} - b}\right) .$$

Along the second leg, we have

$$\Delta S_2 = \int\limits_{T_{\rm i}}^{T_{\rm f}} dT \left(\frac{\partial S}{\partial T}\right)_{V_{\rm f},N} = \int\limits_{T_{\rm i}}^{T_{\rm f}} dT \, \frac{C_{V_{\rm f},N}}{T} = \tfrac{1}{2} fR \int\limits_{T_{\rm i}}^{T_{\rm f}} \frac{dT}{T} = \tfrac{1}{2} fR \ln\left(\frac{T_{\rm f}}{T_{\rm i}}\right) .$$

Thus,

$$\Delta S = R \ln\left(\frac{v_{\rm f} - b}{v_{\rm i} - b}\right) + \tfrac{1}{2} fR \ln\left[1 + \frac{2a}{fRT_{\rm i}}\left(\frac{1}{v_{\rm f}} - \frac{1}{v_{\rm i}}\right)\right] .$$