

Homework 3 (Due Tuesday, February 7th)

1. Show that when the coefficient of thermal expansion, α , is of the form, $\alpha = 1/(T + T_0)$, where T_0 is a constant, that $(\partial C_P/\partial P)_T = 0$.

2. The adiabatic volume expansivity may be defined as

$$\alpha_S = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_S$$

(a) Show that

$$\alpha_S = -\frac{C_V}{VT} \frac{K_T}{\alpha}$$

(b) Find α_S for an ideal gas.

3. For a given substance, the entropy per particle, $s = S/N$, is,

$$s = s_0 + R \ln \left(\frac{v - b}{v_0 - b} \right) + \frac{3R}{2} \ln(\sinh[c(u + a/v)])$$

where $v = V/N$ and $u = U/N$ are the volume and energy per particle, respectively. The parameters R, s_0, b, v_0, a and c are constants.

(a) Find the equation of state for this material, that is, obtain an equation for the pressure in terms of temperature and volume.

(b) Show that the heat capacity per particle at constant volume is,

$$c_V = \frac{3R/2}{1 - (3RcT/2)^2}$$

4. Consider a system with the equation of state

$$(P + f(V))(V - bN) = NkT$$

where b is a constant.

(a) In general $C_V = C_V(V, T)$; show that for this system C_V is independent of volume.

(b) Given that the isothermal compressibility for this system is

$$K_T = \frac{V - bN}{PV}$$

find $f(V)$ and show that the equation of state may be written as

$$P = \frac{NkT - \mathcal{E}}{V - bN}$$

where \mathcal{E} is a constant.

5. A given material has an equation of state

$$PV = AT^3$$

where A is a known constant. The internal energy is

$$E = BT^a \ln(V/V_0) + f(T)$$

where B , a , and V_0 are all constants and $f(T)$ is a function that only depends on the temperature. Find B and a . [Hint: Find a relation that relates $(\partial E/\partial V)_T$ to the pressure and match terms.]

Solutions

1. We first need to rearrange the derivatives as,

$$\begin{aligned}\left(\frac{\partial C_P}{\partial P}\right)_T &= \left(\frac{\partial}{\partial P} T \left(\frac{\partial S}{\partial T}\right)_P\right)_T \\ &= T \frac{\partial^2 S}{\partial P \partial T} \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P}\right)_T\right)_P\end{aligned}$$

Using the Maxwell relation,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$$

then

$$\begin{aligned}\left(\frac{\partial C_P}{\partial P}\right)_T &= T \left(\frac{\partial}{\partial T} (-V\alpha)\right)_P \\ &= -VT \left(\frac{\partial \alpha}{\partial T}\right)_P - \alpha T \left(\frac{\partial V}{\partial T}\right)_P \\ &= -VT \left(\frac{\partial \alpha}{\partial T}\right)_P - \alpha T (\alpha V)\end{aligned}$$

Finally, we insert our expression for α ,

$$\begin{aligned}\left(\frac{\partial C_P}{\partial P}\right)_T &= T \left(\frac{V}{(T+T_0)^2} - (1/(T+T_0))^2 V\right) \\ &= 0\end{aligned}$$

2. We want to rewrite the definition of α_S as,

$$\alpha_S = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S = \frac{-\left(\frac{\partial S}{\partial T}\right)_V}{V \left(\frac{\partial S}{\partial V}\right)_T} = \frac{\frac{-C_V}{T}}{V \left(\frac{\partial P}{\partial T}\right)_V}$$

Notice that in the numerator we used the definition of heat capacity while in the denominator we used a Maxwell relation. The last few steps are,

$$\alpha_S = \frac{\frac{-C_V}{T}}{-V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P} = -\frac{C_V}{VT} \frac{1}{(1/VK_T)(\alpha V)} = -\frac{C_V}{VT} \frac{K_T}{\alpha}$$

I must admit that I solved this by working backwards.

(b) For an ideal gas, $\alpha = 1/T$, $K_T = 1/P$ so $\alpha_S = -C_V/PV$. Notice that the adiabatic compressibility for an ideal gas is always negative. Since entropy increases with both temperature and volume, if entropy is fixed then temperature increases when volume is decreased (i.e., an adiabatic compression leads to an increase of temperature).

3. (a) Using

$$\left(\frac{\partial S}{\partial U}\right)_V = \left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T}$$

then

$$\frac{1}{T} = \frac{3}{2}Rc \frac{\cosh(cu + ca/v)}{\sinh(cu + ca/v)} = \frac{3}{2}Rc \coth(cu + ca/v)$$

Similarly, using

$$\left(\frac{\partial S}{\partial V}\right)_U = \left(\frac{\partial s}{\partial v}\right)_u = \frac{P}{T}$$

then

$$\begin{aligned} \frac{P}{T} &= \frac{R}{v-b} + \frac{3}{2}R \left(\frac{-ca}{v^2}\right) \frac{\cosh(cu + ca/v)}{\sinh(cu + ca/v)} \\ &= \frac{R}{v-b} - \frac{a}{Tv^2} \end{aligned}$$

so

$$\left(P - \frac{a}{v^2}\right)(v-b) = RT$$

which is the van der Waal equation of state. Note that the expression given in this exercise for s is *not* the only one that give this equation of state, there are many others.

(b) We want to find $c_v = T(\partial s/\partial T)_v = (\partial u/\partial T)_v$. The easiest route is probably to use the equation for temperature in a rather unconventional way,

$$\left(\frac{\partial}{\partial T}\right)_v T = \left(\frac{\partial}{\partial T}\right)_v \frac{1}{3Rc/2} \tanh(cu + ca/v)$$

or

$$1 = \frac{c}{3Rc/2} \operatorname{sech}^2(cu + ca/v) \left(\frac{\partial u}{\partial T}\right)_v$$

Using the identity,

$$\operatorname{sech}^2 x = 1 - \tanh^2 x = 1 - \frac{1}{\coth^2 x}$$

then

$$\begin{aligned} 1 &= \frac{1}{3R/2} \left[1 - \frac{1}{\coth^2(cu + ca/v)}\right] \left(\frac{\partial u}{\partial T}\right)_v \\ &= \frac{1}{3R/2} [1 - (3RcT/2)^2] \left(\frac{\partial u}{\partial T}\right)_v \end{aligned}$$

Finally,

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \frac{3R/2}{1 - (3RcT/2)^2}$$

Notice that c_v is a function of temperature and thus is *not* a constant.

4. (a) The result we want to establish is that

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

Since

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

then

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial}{\partial V}\right)_T T \left(\frac{\partial S}{\partial T}\right)_V = T \frac{\partial^2 S}{\partial V \partial T} = T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \\ &= T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_V = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

where we used a Maxwell relation to replace entropy with pressure. Finally, applying this general result to our present equation of state,

$$P = \frac{NkT}{V - bN} - f(V); \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V - bN}; \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

which establishes our result.

(b) From the definition of the isothermal compressibility,

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Evaluating the derivative

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{(V - bN)^2} - \frac{df}{dV}$$

gives

$$K_T = \frac{1}{\frac{VNkT}{(V - bN)^2} + V \frac{df}{dV}} = \frac{V - bN}{PV + f(V)V + V(V - bN) \frac{df}{dV}}$$

Comparing with the given expression for the compressibility implies

$$f + (V - bN) \frac{df}{dV} = 0$$

or

$$\frac{df}{f} = -\frac{dV}{V - bN}$$

so

$$\ln f = -\ln(V - bN) + C \quad \Rightarrow \quad f(V) = \frac{e^C}{V - bN}$$

where C is the constant of integration. Finally, putting this expression for $f(V)$ into the equation of state allows us to arrange terms such that

$$P = \frac{NkT}{V - bN} - f(V) = \frac{NkT}{V - bN} - \frac{e^C}{V - bN}$$

which gives the desired result by identifying the constant $\mathcal{E} = e^C$.

5. Starting with $dU = TdS - pdV$ we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

where a Maxwell relation is used to convert the derivative on the right hand side from entropy to pressure. Since we're given $U(V, T)$ and $p(V, T)$, we directly evaluate

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{BT^a}{V}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{3AT^2}{V}$$

so that

$$\frac{BT^a}{V} = T \left\{ \frac{3AT^2}{V} \right\} - \frac{AT^3}{V}$$

Comparing terms we see that $a = 3$ and $B = 2A$.

Note that if you started from the relation $U = TS - pV$ and write

$$dU = TdS + SdT - pdV - Vdp$$

it is *not* correct to write

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p - V \left(\frac{\partial p}{\partial V}\right)_T$$

The last term is not present because we know that $SdT = Vdp$ from Gibbs-Duhem so if the SdT term is absent, so is the Vdp term. Another way to see the problem with the above expression is that energy can only be a function of two independent variables, such as $U(S, V)$ or $U(T, V)$. That is, we cannot independently vary S , p , and V ; again, this is the origin of Gibbs-Duhem.