# Assignment 1

Tyler Shendruk

October 11, 2010

## 1 Kadar Ch. 1 Problem 8

Hard core gas with an equation of state $P(V - Nb) = Nk_{\mathrm{B}}T$ which has a $C_V$ that is independent of T.

### 1.1 Problem 8.a

Construct a Maxwell equation for $\frac{\partial S}{\partial V}\big|_{T,N}$. The question makes a point that $N$ is constant so we don't mention it anymore. Start using Helmholtz free energy where we assume there is no change in species:

$$dF = -SdT - PdV \tag{1}$$

$$-S = \left.\frac{\partial F}{\partial T}\right|_V \qquad \text{and} \qquad -P = \left.\frac{\partial F}{\partial V}\right|_T \tag{2}$$

and so by equivalence of partials

$$\begin{aligned} \left.\frac{\partial}{\partial V}\left(\left.\frac{\partial F}{\partial T}\right|_V\right)\right|_T &= \left.\frac{\partial}{\partial T}\left(\left.\frac{\partial F}{\partial V}\right|_T\right)\right|_V \\ \left.\frac{\partial S}{\partial V}\right|_T &= \left.\frac{\partial P}{\partial T}\right|_V \end{aligned} \tag{3}$$

Substituting the equation of state in for $P$ we find

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V = \frac{\partial}{\partial T}\left[\frac{Nk_{\mathrm{B}}T}{V - Nb}\right]_V$$

$$\boxed{\left.\frac{\partial S}{\partial V}\right|_T = \frac{Nk_{\mathrm{B}}}{V - Nb}} \tag{4}$$

### 1.2 Problem 8.b

Show that $E$ is a function of $T$ (and $N$) only. To do this we will show that $\partial E/\partial V|_T = 0$. Start with the $1^{\text{st}}$ Law and remember Eq. (4) .

$$\begin{aligned}
dE &= TdS - PdV \\
\left.\frac{\partial E}{\partial V}\right|_T &= T\left.\frac{\partial S}{\partial V}\right|_T - P \\
&= T\left.\frac{\partial P}{\partial T}\right|_V - P \\
&= T\frac{Nk_{\mathrm{B}}}{V - Nb} - P \\
&= P - P
\end{aligned}$$

$$\boxed{\left.\frac{\partial E}{\partial V}\right|_T = 0} \tag{5}$$

And so $E$ depends only on $T$ (and $N$): $E(V, T, N) \Rightarrow E(T, N)$.

The other (perhaps better) way to see this is to fully extend $dS$ which gives

$$\begin{aligned}
dE &= TdS - PdV \\
&= T\left[\left.\frac{\partial S}{\partial V}\right|_T dV + \left.\frac{\partial S}{\partial T}\right|_V dT\right] - PdV
\end{aligned}$$

We then use Eq. (4) and the definition of a heat capacity

$$C_x \equiv T\left.\frac{\partial S}{\partial T}\right|_x \tag{6}$$

to find

$$\begin{aligned}
dE &= \left[\frac{Nk_{\mathrm{B}}T}{V - Nb}dV + C_V dT\right] - PdV \\
&= PdV - C_V dT - PdV
\end{aligned}$$

$$\boxed{dE = C_V dT}. \tag{7}$$

This might be clearer since here we explicitely have that any variation of $E$ is only a function of a $dT$.

### 1.3 Problem 8.c

Show the ratio of heat capacities ($\gamma$) is $1 + Nk_{\mathrm{B}}/C_V$. To do this we start by considering $C_V$ and substitute the first law as $đQ = dE - pdV$ into the definition.

$$C_V = \left.\frac{đQ}{dT}\right|_V = \left.\frac{dE - PdV}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V - P\left.\frac{dV}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V - 0 = \left.\frac{dE}{dT}\right|_V$$

which means

$$dE = C_V dT \tag{8}$$

In light of this, let's consider $C_p$

$$\begin{aligned}
C_P &= \left.\frac{đQ}{dT}\right|_P \\
&= \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{C_V dT + PdV}{dT}\right|_P \\
&= \left.\frac{C_V dT}{dT}\right|_P + \left.\frac{PdV}{dT}\right|_P = C_V + P\left.\frac{dV}{dT}\right|_P
\end{aligned}$$

Use the equation of state ($V = Nk_\mathrm{B}T/P + Nb$) in the second term:

$$\begin{aligned}
C_P &= C_V + P\left.\frac{dV}{dT}\right|_P \\
&= C_V + P\frac{d}{dT}\left[\frac{Nk_\mathrm{B}T}{P} + Nb\right]_P \\
&= C_V + P\frac{Nk_\mathrm{B}}{P} \\
&= C_V + Nk_\mathrm{B}
\end{aligned}$$

Then

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{C_V + Nk_\mathrm{B}}{C_V} = 1 + \frac{Nk_\mathrm{B}}{C_V}} \tag{9}$$

## 1.4 Problem 8.d

Show that an adiabatic change satisfies the equation $p(V - Nb)^\gamma =$ a constant.

$$dE = đQ - PdV$$

But if the process is adiabatic $đQ = 0$ and we know that $dE = C_V dT$ for a hard sphere gas (Eq. (8) in the last section) and we have the equation of state for $P$. Therefore,

$$\begin{aligned}
C_V dT &= 0 - PdV \\
0 &= C_V dT + \frac{Nk_\mathrm{B}T}{V - Nb}dV \\
0 &= C_V\frac{dT}{T} + Nk_\mathrm{B}\frac{dV}{V - Nb}
\end{aligned}$$

Integrate this and remembering Eq. (9) . Also notice that in the following, $K$ will denote the integration constant and $K^*$ will say that the constant has absorbed some other constant or constants or has been operated on in some way such that it remains an arbitary constant.

$$\begin{aligned}
C_V \ln T + Nk_\mathrm{B}\ln(V - Nb) &= K \\
\ln T + \left(\frac{Nk_\mathrm{B}}{C_V}\right)\ln(V - Nb) &= K^* \\
\ln T + (\gamma - 1)\ln(V - Nb) &= K \\
T\,(V - Nb)^{\gamma - 1} &= K^*.
\end{aligned}$$

Now using the equation of state we can substitute in for $T$ as $T = \frac{P(V-Nb)}{Nk_{\mathrm{B}}}$.

$$\begin{aligned} T\left(V-Nb\right)^{\gamma-1} &= K \\ P\frac{\left(V-Nb\right)}{Nk_{\mathrm{B}}}\left(V-Nb\right)^{\gamma-1} &= K \\ P\left(V-Nb\right)\left(V-Nb\right)^{\gamma-1} &= K^{*} \end{aligned}$$

$$\boxed{P\left(V-Nb\right)^{\gamma} = K} \tag{10}$$

# 2 Harden Problem 2

Consider a system of particles where the internal energy is a function only of temperature.

## 2.1 Problem 2.a

### 2.1.1 Volume - bonus

Consider the Gibbs free energy of this gas of particles:

$$G = E - ST + PV.$$

Since we wish to demonstrate $V$ is a function only $P/T$, let's divide through by temperature to get

$$\mathcal{M} = -\frac{G}{T} = S - \frac{E}{T} + V\frac{P}{T}. \tag{11}$$

Although we haven't gained any new insights, traditionally this function $\mathcal{M}$ is called a Massieu function (it's still just the Gibbs free energy). The variation of the Massieu function is

$$\begin{aligned} d\mathcal{M} &= dS - d\left(\frac{E}{T}\right) + d\left(V\frac{P}{T}\right) \\ &= dS - \frac{1}{T}dE - Ed\left(\frac{1}{T}\right) + \frac{P}{T}dV + Vd\left(\frac{P}{T}\right) \\ &= dS - \frac{1}{T}\left[TdS - PdV\right] - Ed\left(\frac{1}{T}\right) + \frac{P}{T}dV + Vd\left(\frac{P}{T}\right) \\ &= -Ed\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right). \end{aligned} \tag{12}$$

We can even make a Maxwell equation for $\mathcal{M}$

$$d\mathcal{M} = -Ed\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right).$$

$$\left.\frac{\partial\mathcal{M}}{\partial\left(1/T\right)}\right|_{(P/T)} = -E \quad \text{and} \quad \left.\frac{\partial\mathcal{M}}{\partial\left(P/T\right)}\right|_{(1/T)} = V$$

$$\left.\frac{\partial E}{\partial\left(P/T\right)}\right|_{(1/T)} = -\left.\frac{\partial V}{\partial\left(1/T\right)}\right|_{(P/T)} \tag{13}$$

BUT $E$ is a function of $T$ only therefore

$$\left.\frac{\partial E}{\partial\,(P/T)}\right|_{(1/T)} = 0$$

which means from Eq. (13)

$$\boxed{\left.\frac{\partial V}{\partial\,(1/T)}\right|_{(P/T)} = 0}. \tag{14a}$$

Why did I call this the solution? Because the thermodynamic function varies only with $1/T$ and $P/T$ and by Eq. (14a) the volume doesn't vary with temperature **only** $P/T$ *i.e.*

$$\boxed{V = V\left(\frac{P}{T}\right)} \tag{14b}$$

### 2.1.2 Derivative

Independent from this (as far as I can tell), we can write

$$\begin{aligned} dE &= TdS - PdV \\ \left.\frac{\partial E}{\partial V}\right|_T &= T\left.\frac{\partial S}{\partial V}\right|_T - P \\ &= 0 \\ \left.\frac{\partial S}{\partial T}\right|_V &= \frac{P}{T} \end{aligned}$$

where we said the derivative of energy was zero since $E$ is only a function of $T$. Through the Helmholtz free energy, $F$, we can develop an appropriate Maxwell equation (which is exactly the same one as we did in § 1.1 , Eq. (3) ). Applying it, we have

$$\boxed{\left.\frac{\partial P}{\partial T}\right|_V = \frac{P}{T}}. \tag{15}$$

## 2.2 Problem 2.b

We know (see Kadar Eq. (1.14)) that for a gas whose energy depends only on temperature that

$$\begin{aligned} C_P - C_V &= \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P - \left.\frac{\partial E}{\partial T}\right|_V = \frac{dE}{dT} + P\left.\frac{\partial V}{\partial T}\right|_P - \frac{dE}{dT} \\ &= P\left.\frac{\partial V}{\partial T}\right|_P \\ &= P\left[\frac{\partial}{\partial T}V\,(P/T)\right]_P = P\left[-\frac{P}{T^2}V'\right] \end{aligned}$$

$$\boxed{C_P - C_V = -\left(\frac{P}{T}\right)^2 V'} \tag{16}$$

## 3 Harden Problem 3

Relate the ratio of the heat capacities at constant $V$ and $P$ to the isothermic and adiabatic compressibilities.

By definition we know all four response functions are

$$\begin{cases} \kappa_S &= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_S \\ \kappa_T &= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T \end{cases} \tag{17}$$

$$\begin{cases} C_V &= T\left.\frac{\partial S}{\partial T}\right|_V \\ C_P &= T\left.\frac{\partial S}{\partial T}\right|_P \end{cases} \tag{18}$$

Let's start from the heat capacities. We simply utilize the chain rule for the derivatives of $S$ to get

$$\begin{cases} C_V &= T\left.\frac{\partial S}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial P}\right|_V\left.\frac{\partial P}{\partial T}\right|_V \\ C_P &= T\left.\frac{\partial S}{\partial T}\right|_P = T\left.\frac{\partial S}{\partial V}\right|_P\left.\frac{\partial V}{\partial T}\right|_P \end{cases}$$

Then the ratio is

$$\frac{C_V}{C_P} = \frac{T\left.\frac{\partial S}{\partial P}\right|_V\left.\frac{\partial P}{\partial T}\right|_V}{T\left.\frac{\partial S}{\partial V}\right|_P\left.\frac{\partial V}{\partial T}\right|_P} = \left[\left.\frac{\partial S}{\partial P}\right|_V\left(\left.\frac{\partial S}{\partial V}\right|_P\right)^{-1}\right]\left[\left(\left.\frac{\partial V}{\partial T}\right|_P\right)^{-1}\left.\frac{\partial P}{\partial T}\right|_V\right]. \tag{19}$$

where we've put focus on the pairs derivatives by bracketting them. What we want is a triple derivative rule that collapses both terms in each pair into a single term. The triple derivative rule is in general

$$\left.\frac{\partial x}{\partial y}\right|_z\left.\frac{\partial z}{\partial x}\right|_y\left.\frac{\partial y}{\partial z}\right|_x = -1 \tag{20a}$$

which is the easiest form to remember but for our current purposes is convenient to write as

$$\left.\frac{\partial x}{\partial y}\right|_z\left.\frac{\partial z}{\partial x}\right|_y = -\left.\frac{\partial z}{\partial y}\right|_x \tag{20b}$$

Applying Eq. (20b) to the $S$-terms in Eq. (19) , we see

$$\left.\frac{\partial S}{\partial P}\right|_V\left(\left.\frac{\partial S}{\partial V}\right|_P\right)^{-1} = \left.\frac{\partial S}{\partial P}\right|_V\left.\frac{\partial V}{\partial S}\right|_P = -\left.\frac{\partial V}{\partial P}\right|_S.$$

Now applying it to the $T$-terms in Eq. (19) , we get

$$\left(\left.\frac{\partial V}{\partial T}\right|_P\right)^{-1}\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial T}{\partial V}\right|_P\left.\frac{\partial P}{\partial T}\right|_V = -\left.\frac{\partial P}{\partial V}\right|_T$$

Putting these back into the ratio (Eq. (19) ) gives the much cleaner

$$\frac{C_V}{C_P} = \left.\frac{\partial V}{\partial P}\right|_S\left.\frac{\partial P}{\partial V}\right|_T$$

But wait a minute! Just just flip the second term into the denominator then compare to Eq. (18) and we see

$$\frac{C_V}{C_P} = \left.\frac{\partial V}{\partial P}\right|_S \left.\frac{\partial P}{\partial V}\right|_T = \frac{\left.\frac{\partial V}{\partial P}\right|_S}{\left.\frac{\partial V}{\partial P}\right|_T} = \frac{-1/V \left.\frac{\partial V}{\partial P}\right|_S}{-1/V \left.\frac{\partial V}{\partial P}\right|_T}$$

$$\boxed{\frac{C_V}{C_P} = \frac{\kappa_s}{\kappa_T}} \tag{21}$$

# 4 Harden Problem 4

Consider an elastic rod with a relaxed length $L_0$. We stretch the rod by applying tension

$$\tau = aT^2\left(L - L_0\right) \tag{22}$$

and state that the heat capacity at the equalibrium length some linear function of temperature.

## 4.1 Problem 4.a

What is the form of the heat capacity at an arbitrary length? We know

$$C_L(T, L_0) = bT \tag{23}$$

from the question. We also know the general definition of heat capacity is

$$C_L(T, L) = T \left.\frac{\partial S}{\partial T}\right|_L \tag{24}$$

We could integrate over length to get

$$C_L(T, L) = C_L(T, L_0) + \int_{L_0}^{L} \left.\frac{\partial C_L}{\partial L}\right|_T dL \tag{25}$$

but then we'd need to know how $C_L$ changes with $L$ at a constant temperature. Can we do this?

Yes. First substitute Eq. (24) into the integral

$$\begin{aligned} C_L(T, L) &= C_L(T, L_0) + \int_{L_0}^{L} \frac{\partial}{\partial L}\left[T \left.\frac{\partial S}{\partial T}\right|_L\right]_T dL \\ &= C_L(T, L_0) + T \int_{L_0}^{L} \frac{\partial}{\partial T}\left[\left.\frac{\partial S}{\partial L}\right|_T\right]_L dL \end{aligned} \tag{26}$$

Next develop a Maxwell equation for $\partial S/\partial L|_T$ from the Helmholtz free energy ($F$):

$$\begin{gathered} dF = -SdT + \tau dL \\ \left.\frac{\partial F}{\partial T}\right|_L = -S \quad \text{and} \quad \left.\frac{\partial F}{\partial L}\right|_T = \tau \\ \left.\frac{\partial S}{\partial L}\right|_T = -\left.\frac{\partial \tau}{\partial T}\right|_L . \end{gathered} \tag{27}$$

Eq. (27) will be important for the rest of this problem and we can use it right now in Eq. (26) to get

$$\begin{aligned}
C_L(T,L) &= C_L(T,L_0) + T\int_{L_0}^{L}\frac{\partial}{\partial T}\left[-\left.\frac{\partial\tau}{\partial T}\right|_L\right]_L dL\\
&= C_L(T,L_0) - T\int_{L_0}^{L}\left.\frac{\partial^2\tau}{\partial T^2}\right|_L dL\\
&= bT - T\int_{L_0}^{L}\left[\frac{\partial^2}{\partial T^2}aT^2\left(L-L_0\right)\right]_L dL\\
&= bT - a2T\int_{L_0}^{L}\left(L-L_0\right)dL\\
&= bT - a2T\left[\frac{1}{2}L^2 - L_0L\right]_{L_0}^{L} = bT - a2T\left[\frac{1}{2}L^2 - L_0L - \frac{1}{2}L_0^2 + L_0^2\right]
\end{aligned}$$

$$\boxed{C_L(T,L) = bT - aT\left[L-L_0\right]^2} \tag{28}$$

## 4.2 Problem 4.b

The entropy is

$$\begin{aligned}
S &= \int dS\\
&= S_0 + \left.\int_{L_0}^{L} dS\right|_T + \left.\int_{T_0}^{T} dS\right|_L\\
&= S_0 + \int_{L_0}^{L}\left.\frac{\partial S}{\partial L}\right|_{T=T_0} dL + \int_{T_0}^{T}\left.\frac{\partial S}{\partial T}\right|_L dT
\end{aligned}$$

Notice that some prudence is needed here: $S_0$ signifies $S(L_0, T_0)$ then we want to consider the effect of varying the length from $L_0$ to $L$ **BUT** $T$ is still at $T_0$. Then we bring the temperature from $T_0$ to $T$. Of course, it doesn't matter if we raise the length from $L_0$ to $L$ at $T_0$ then $T_0$ to $T$ or if we raise the temperature from $T_0$ to $T$ at $L_0$ then $L_0$ to $L$. Either way we get the same result but the key (and perhaps subtle point) is that we must keep one of the variables fixed at it's initial value for the first integral.

Anyway, the first integrand is that Maxwell equation (Eq. (27) ) and the second is just the definition of the heat capacity. So then the entropy is

$$\begin{aligned}
S &= S_0 + \int_{L_0}^{L} \left.\frac{\partial S}{\partial L}\right|_{T=T_0} dL + \int_{T_0}^{T} \left.\frac{\partial S}{\partial T}\right|_{L} dT \\
&= S_0 - \int_{L_0}^{L} \left[\left.\frac{\partial \tau}{\partial T}\right|_{L}\right]_{T=T_0} dL + \int_{T_0}^{T} \frac{C_L}{T} dT \\
&= S_0 - \int_{L_0}^{L} \left[2aT_0\left(L-L_0\right)\right] dL + \int_{T_0}^{T} \left[b - a\left[L-L_0\right]^2\right] dT \\
&= S_0 - 2aT_0\left[\frac{L^2}{2} - LL_0\right]_{L_0}^{L} + \left[b - a\left[L-L_0\right]^2\right]\left[T-T_0\right] \\
&= S_0 - 2aT_0\left[\frac{L^2}{2} - LL_0 - \frac{L_0^2}{2} + L_0^2\right] + \left[b - a\left[L-L_0\right]^2\right]\left[T-T_0\right] \\
&= S_0 - aT_0\left[L-L_0\right]^2 - aT\left[L-L_0\right]^2 + aT_0\left[L-L_0\right]^2 + b\left[T-T_0\right]
\end{aligned}$$

$$\boxed{S = S_0 - aT\left(L-L_0\right)^2 + b\left(T-T_0\right)} \tag{29}$$

## 4.3 Problem 4.c

We know $S$ from Eq. (29) and we have the definition of $C_\tau$:

$$C_\tau = T \left.\frac{\partial S}{\partial T}\right|_{\tau}.$$

The problem is $S$ isn't stated as a function of $\tau$. So either we can restate $S$ as a function of $\tau$ or we can restate the derivative. We choose the latter such that

$$\begin{aligned}
C_\tau = T \left.\frac{\partial S}{\partial T}\right|_{\tau} &= T \left.\frac{\partial S}{\partial T}\right|_{L} \left.\frac{\partial T}{\partial T}\right|_{\tau} + T \left.\frac{\partial S}{\partial L}\right|_{T} \left.\frac{\partial L}{\partial T}\right|_{\tau} \\
&= T \left.\frac{\partial S}{\partial T}\right|_{L} + T \left.\frac{\partial S}{\partial L}\right|_{T} \left.\frac{\partial L}{\partial T}\right|_{\tau} \\
&= C_L + T \left.\frac{\partial S}{\partial L}\right|_{T} \left.\frac{\partial L}{\partial T}\right|_{\tau}
\end{aligned}$$

where we'll get $L$ by rearranging Eq. (22) which is explicitly

$$L = L_0 + \frac{\tau}{aT^2}$$

then the heat capacity is

$$\begin{aligned}
C_\tau &= C_L + T\,\left.\frac{\partial L}{\partial T}\right|_\tau \left.\frac{\partial S}{\partial L}\right|_T \\
&= C_L + T\,\left.\frac{\partial L}{\partial T}\right|_\tau \left.\frac{\partial S}{\partial L}\right|_T \\
&= \left[bT - aT\left(L-L_0\right)^2\right] + T\left[-\frac{2\tau}{aT^3}\right]\left[-2aT\left(L-L_0\right)\right] \\
&= bT - aT\left(L-L_0\right)^2 + \frac{4}{T}\left(L-L_0\right)\tau \\
&= bT - aT\left(L-L_0\right)^2 + \frac{4}{T}\left(L-L_0\right)\left[aT^2\left(L-L_0\right)\right] \\
&= bT - aT\left(L-L_0\right)^2 + 4aT\left(L-L_0\right)^2
\end{aligned}$$

$$\boxed{C_\tau = bT + 3aT\left(L-L_0\right)^2} \tag{30a}$$

or

$$\boxed{C_\tau = bT + 3\frac{\tau^2}{aT^3}} \tag{30b}$$