

Mandatory assignment 2

FYS2160

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1 Elastic rubber band

In this task we will use the following equations.

$$g(L) = \left(\frac{\partial P}{\partial T} \right)_L = \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \quad (1)$$

$$f(T, L) = \left(\frac{\partial P}{\partial L} \right)_T = \frac{aT}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] \quad (2)$$

Where L is the length of the elastic rubber band, at a temperature T , and under a tension P . L_0 is the length of the unstretched rubber band, and $a > 0$ is an empirical constant with the SI-units of pascal per kelvin, or kilo gram per meter, seconds squared kelvin.

1.1)

We want to verify that (1) and (2) are well defined functions by checking the Maxwell relation

$$\left[\frac{\partial f}{\partial T} \right]_L = \left[\frac{\partial g}{\partial L} \right]_T, \quad (3)$$

so let's start derivating. We start with f .

$$\begin{aligned} \left[\frac{\partial f}{\partial T} \right]_L &= \frac{\partial}{\partial T} \left(\frac{aT}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] \right) \\ &= \frac{a}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] \end{aligned}$$

And do the same for g , by using the product rule

$$\begin{aligned}\left[\frac{\partial g}{\partial L}\right]_T &= \frac{\partial}{\partial L} \left(\frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \right) \\ &= \frac{a}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] + \frac{aL}{L_0} \left[\frac{3L_0^3}{L^4} \right] \\ &= \frac{a}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right]\end{aligned}$$

The two expressions are equal, they satisfy (3) the Maxwell relation, which is what we wanted to show.

1.2

We now want to show that

$$f(T, L) = T \frac{dg}{dL} \quad (4)$$

In the previous task we have already calculated dg/dL , so we can use this answer to find that

$$T \frac{dg}{dL} = \frac{aT}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] \quad (5)$$

Which is equal to $f(T, L)$, as we wanted to show.

1.3)

We want to derive an equation of state $P(T, L)$, which relates the tension, temperature and length of the rubber band. To do this we integrate (1) and (2), with regard to T and L respectively, and solve for P . We use the definition of $\frac{\partial P}{\partial T}$ (1) and find

$$\begin{aligned}\frac{\partial P}{\partial T} &= \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \\ \int \frac{\partial P}{\partial T} dT &= \int \frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] dT \\ P(T, L) &= \frac{aLT}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] + C\end{aligned}$$

Where C is the integration constant. We do the same for $\frac{\partial P}{\partial L}$ (2) and find

$$\begin{aligned}
\frac{\partial P}{\partial L} &= \frac{aT}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] \\
\int \frac{\partial P}{\partial L} dL &= \int \frac{aT}{L_0} \left[1 + 2 \left(\frac{L_0}{L} \right)^3 \right] dL \\
P(T, L) &= \frac{aT}{L_0} \left(\int 1 dL + 2L_0^3 \int L^{-3} dL \right) \\
&= \frac{aT}{L_0} \left(L + 2L_0^3 \left[\frac{-L^{-2}}{2} \right] \right) + C \\
&= \frac{aT}{L_0} \left(L - \frac{L_0^3}{L^2} \right) + C \\
P(T, L) &= \frac{aTL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] + C
\end{aligned}$$

By using the two different methods we find the same equation of state, as we should, with an undetermined integration constant C . The tension when $L = L_0$ is equal to C . When $L = L_0$ the system is at equilibrium, which means that the tension should be zero. Therefore the integration constant C should be equal to zero for the results to make physical sense. We could also argue that the integration constant from the first integral is a function of T , while the other is a function of L . Both have to be zero, since they don't appear when we differentiate with respect to the other variable. We therefore have that the equation of state is

$$P(T, L) = \frac{aTL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right]. \quad (6)$$

1.4

The rubber band follows the relations that are analogous to those of a gas. The work done to increase the length of the rubber band by dL is $\delta W = P dL$. Because of this we have to first law of thermodynamics

$$\Delta U = T dS + P dL \quad (7)$$

The Helmholtz free energy $F(T, L)$ is the appropriate thermodynamic potential for this problem, since we are looking at a system in a thermal bath with a constant temperature T . And in a thermal bath the Helmholtz free energy will be minimized. We know that the surroundings does not keep the system at a constant pressure. And we know that there is no particle exchange from the rubber band with the surroundings. It is therefore best to use the Helmholtz free energy, since this will be minimized in the type of system we are working on.

We can find an expression for the Helmholtz free energy using (7) and the definition of Helmholtz

free energy

$$\begin{aligned}
F(T, L) &= U - TS \\
dF &= dU - T dS - S dT \\
&= T dS + P dL - T dS - S dT \\
&= P dL - S dT
\end{aligned}$$

We have now found the expression for a small change in the Helmholtz free energy

$$dF = P dL - S dT \quad (8)$$

1.5

We know that (2) is a well behaved function from task one. We therefore know that

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial L} \right)_T \right)_L = \left(\frac{\partial}{\partial L} \left(\frac{\partial F}{\partial T} \right)_L \right)_T \quad (9)$$

By using the expression we found for the change in the Helmholtz free energy (8) we can derive the Maxwell relation for our system. Let's begin

$$\begin{aligned}
\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial L} \right)_T \right)_L &= \left(\frac{\partial}{\partial T} \frac{\partial}{\partial L} \left(P dL - S \underbrace{dT}_{=0} \right)_T \right)_L \\
&= \left(\frac{\partial}{\partial T} \cancel{\frac{\partial}{\partial L}} P dL \right)_L \\
&= \left(\frac{\partial P}{\partial T} \right)_L
\end{aligned}$$

We do the same for right hand side of (9)

$$\begin{aligned}
\left(\frac{\partial}{\partial L} \left(\frac{\partial F}{\partial T} \right)_L \right)_T &= \frac{\partial}{\partial L} \left(\frac{\partial}{\partial T} \left(P \underbrace{dL}_{=0} - S dT \right)_L \right)_T \\
&= - \frac{\partial}{\partial L} \left(\cancel{\frac{\partial}{\partial T}} S dT \right)_T \\
&= - \left(\frac{\partial S}{\partial L} \right)_T
\end{aligned}$$

We now have an expression for both sides of (9). By multiplying each side by -1 we end up with

$$\left(\frac{\partial S}{\partial L} \right)_T = \left(- \frac{\partial P}{\partial T} \right)_L \quad (10)$$

1.6

From the equation of state it follows that

$$P(T, L) = Tg(L). \quad (11)$$

From this it follows that

$$\left(\frac{\partial P}{\partial T}\right)_L = \frac{P}{T} \quad (12)$$

From this and (10) we can show that the internal energy U only depends on T

$$\begin{aligned} \left(\frac{\partial S}{\partial L}\right)_T &= \left(-\frac{\partial P}{\partial T}\right)_L \\ \left(\frac{\partial S}{\partial L}\right)_T &= -\frac{P}{T} \\ \left(\frac{\partial}{\partial L} \left(\frac{dU}{T} - \frac{P dL}{T}\right)\right)_T &= -\frac{P}{T} \\ \frac{1}{T} \frac{\partial}{\partial L} (dU) - \frac{1}{T} \frac{\partial}{\partial L} (P dL) &= -\frac{P}{T} \\ \frac{1}{T} \frac{\partial U}{\partial L} - \frac{P}{T} &= -\frac{P}{T} \\ \frac{1}{T} \frac{\partial U}{\partial L} &= 0 \\ \frac{\partial U}{\partial L} &= 0 \end{aligned}$$

Since the derivative with respect to L is zero, the internal energy of the system does not change by changing the length of the rubber band. Since the internal energy is not a function of L , it is only a function of T .

1.7

The heat capacity at a constant length L is related to the change in the internal energy at fixed L as

$$dU = C_L dT. \quad (13)$$

We assume that the heat capacity is constant, and that the rubber band is stretched adiabatically and reversibly ($Q_{rev} = 0, dS = 0$) from L_0 at an initial temperature T_i to a final temperature T_f with a length L_f . From this we are interested in finding the final temperature T_f . We start with (13)

$$\begin{aligned}
dU &= C_L dT \\
T dS + P dL &= C_L dT \\
P dL &= C_L dT \\
\left(\frac{aTL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \right) dL &= C_L dT \\
\left(\frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \right) dL &= C_L \frac{1}{T} dT \\
\int_{L_0}^{L_f} \left(\frac{aL}{L_0} \left[1 - \left(\frac{L_0}{L} \right)^3 \right] \right) dL &= \int_{T_i}^{T_f} C_L \frac{1}{T} dT \\
\frac{a}{L_0} \left[\int_{L_0}^{L_f} L dL - L_0^3 \int_{L_0}^{L_f} L^{-3} dL \right] &= C_L \int_{T_i}^{T_f} \frac{1}{T} dT \\
\frac{a}{L_0} \left(\frac{1}{2} (L_f^2 - L_i^2) + L_0^3 \left(\frac{1}{L_f} - \frac{1}{L_i} \right) \right) &= C_L \ln \left(\frac{T_f}{T_i} \right) \\
\frac{a}{L_0 C_L} \left(\frac{1}{2} (L_f^2 - L_i^2) + L_0^3 \left(\frac{1}{L_f} - \frac{1}{L_i} \right) \right) &= \ln \left(\frac{T_f}{T_i} \right)
\end{aligned}$$

Raising e to the power of each side of the equation, and multiplying by T_i we get

$$T_f = T_i \exp \left\{ \frac{a}{L_0 C_L} \left(\frac{1}{2} (L_f^2 - L_i^2) + L_0^3 \left(\frac{1}{L_f} - \frac{1}{L_i} \right) \right) \right\} \quad (14)$$

Which is the expression for the change in temperature as a function of the length of the rubber band. As we see, since $L_f > L_i$ the temperature increases as we pull the rubber band.

1.8

As the rubber band is contracting we assume that there is no heat flow from the environment, and no work done by the outside, $\delta Q = \delta W = 0$. From these assumptions we can calculate the change in entropy and the change in temperature from the final state L_f to the equilibrium state L_0 .

Since there is no work or heat exchange with the environment we know that the internal energy is constant. Since we go from an equilibrium state with a temperature of T_i and a length of L_0 , to a state where we have stretched the rubber band to L_f with a temperature T_f . Since there is no interaction with the environment the system has to reach its original temperature when it is finished contracting. Therefore the temperature change is equal to temperature change when we stretched out the rubber band (14), but negative. The relative temperature change is therefore

$$\frac{T_f - T_i}{T_i} = \exp \left\{ \frac{a}{L_0 C_L} \left(\frac{1}{2} (L_f^2 - L_i^2) + L_0^3 \left(\frac{1}{L_f} - \frac{1}{L_i} \right) \right) \right\} - 1 \quad (15)$$

The rubber band will therefore cool down when contracting.

We start by using the definition of the change in internal energy ΔU (7), and since there is no heat exchange or work exchange with the environment, this has to be equal to zero. We therefore get

$$\begin{aligned}
dU &= T dS + P dL = 0 \\
T dS &= -P dL \\
dS &= -\frac{P}{T} dL \\
&= -\frac{aL}{L_0} \left(1 - \frac{L_0^3}{L^3}\right) dL \\
\int dS &= -\int \frac{aL}{L_0} \left(1 - \frac{L_0^3}{L^3}\right) dL \\
\Delta S &= -\frac{a}{L_0} \int \left(L - L_0^3 L^{-2}\right) dL \\
&= -\frac{a}{L_0} \left[\frac{1}{2} L^2 + \frac{L_0^3}{L} \right]_{L_f}^{L_0} \\
&= -\frac{a}{L_0} \left[\frac{1}{2} L_0^2 - \frac{1}{2} L_f^2 + \frac{L_0^3}{L_0} - \frac{L_0^3}{L_f} \right] \\
&= \frac{a}{L_0} \left[\frac{1}{2} (L_f^2 - L_0^2) + L_0^3 \left(\frac{1}{L_f} - \frac{1}{L_0} \right) \right]
\end{aligned}$$

Here we have an expression for the change in entropy, and as we see this quantity is always larger than zero when $L_f > L_0$, which it always is when we stretch the rubber band.

When we let the rubber band contract to its equilibrium state the temperature decreases and the entropy increases. This is equivalent to a gas expanding into vacuum, except that the rubber band will not contract indefinitely, but will reach an equilibrium state.

2 Maxwell relations and response functions

In this task we will use the following definitions

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (16)$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (17)$$

2.1

We will start with the expression for the change in entropy with a constant pressure

$$(dS)_P = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (18)$$

We will now use the definition of a change in the volume dV

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \quad (19)$$

We put this in for dV in (18)

$$(dS)_P = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T \left(\left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \right) \quad (20)$$

Since we are looking at the case where we have constant pressure, the dP is equal to zero, and we can remove the term.

$$(dS)_P = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P dT \quad (21)$$

To simplify the equation we divide by dT

$$\left(\frac{dS}{dT} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (22)$$

We will now substitute for the maxwell relation

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (23)$$

to remove one of the entropy terms in our equation

$$\left(\frac{dS}{dT} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (24)$$

We will now use the definition of the heat capacity as a function of entropy

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (25)$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P \quad (26)$$

To use these definitions in our equation we first multiply by T

$$T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (27)$$

We substitute in the definitions, and we end up with

$$C_P = C_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (28)$$

2.2

We can use equation (28) for an ideal gas, where we have a know relationship

$$\begin{aligned} P &= \frac{NkT}{V} \\ V &= \frac{NkT}{P} \\ \left(\frac{\partial P}{\partial T}\right)_V &= \frac{Nk}{V} \\ \left(\frac{\partial P}{\partial V}\right)_V &= \frac{Nk}{T} \end{aligned}$$

By inserting this in (28) we find

$$\begin{aligned} C_P &= C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \\ &= C_V + T \frac{Nk}{V} \frac{Nk}{T} \\ &= C_V + \frac{N^2 k^2 T}{PV} \\ &= C_V + \frac{N^2 k^2 T}{NkT} \\ &= C_V + Nk \end{aligned}$$

Which is the same expression as we found in chapter 1 of the book.

2.3

We will now use the identity

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial V}{\partial T}\right)_P \quad (29)$$

From this we have that

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (30)$$

We can insert this into (28) to find

$$\begin{aligned} C_P &= C_V - T \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \left(\frac{\partial V}{\partial T}\right)_P \\ C_P - C_V &= TV \underbrace{\frac{1}{-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T}}_{=\kappa_T} \underbrace{\left[\left(\frac{1}{V} \frac{\partial V}{\partial T}\right)_P\right]^2}_{=\beta^2} \\ &= \frac{TV\beta^2}{\kappa_T} \end{aligned}$$

In the transition between line 2 and 3 we multiplied by V^2/V^2 , and moved them around so that we could use the definition of κ_T and β .

2.4

The definition of κ_T (16) and β (17) can be calculated if we know the relationship of V to both P and T . For an ideal gas we know this, and can therefore calculate the expression for these two functions.

$$\begin{aligned}
 \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \\
 &= -\frac{1}{V} \frac{\partial}{\partial P} \left(\frac{NkT}{P} \right)_T \\
 &= -\frac{NkT}{V} \frac{\partial}{\partial P} (P^{-1}) \\
 &= \frac{NkT}{VP^2} \\
 &= \frac{PV}{P^2V} \\
 &= \frac{1}{P}
 \end{aligned}$$

We do the same for β

$$\begin{aligned}
 \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \\
 &= \frac{1}{V} \frac{\partial}{\partial T} \left(\frac{NkT}{P} \right)_P \\
 &= \frac{Nk}{VP} \frac{\partial}{\partial T} (T) \\
 &= \frac{Nk}{VP} \\
 &= \frac{Nk}{NkT} \\
 &= \frac{1}{T}
 \end{aligned}$$

From this we can check the result we found for the difference in heat capacities for an ideal gas is task 2.3

$$\begin{aligned}
C_P - C_V &= \frac{TV\beta^2}{\kappa_T} \\
&= \frac{TV\beta}{T^2} \\
&= \frac{VP}{T} \\
&= \frac{NkT}{T} \\
&= Nk
\end{aligned}$$

Which is consistent with what we found in task 2.2