Q4001 Thermodynamics of Materials

Homework 5

Osamu Katagiri - A01212611@itesm.mx - CEM

In [8]:

```
#**********************************************************************************#
# Futures
%matplotlib inline
# from __future__ import unicode_literals
# from __future__ import print_function

# Generic/Built-in
import datetime
import argparse

# Other Libs
from IPython.display import display, Image
#
from sympy import *
#
import matplotlib.pyplot as plt
plt.rc('xtick', labelsize=14)
plt.rc('ytick', labelsize=14)
#
import numpy as np
np.seterr(divide='ignore', invalid='ignore')

# Owned
# from nostalgia_util import log_utils
# from nostalgia_util import settings_util
__authors__    = ["Osamu Katagiri - A01212611@itesm.mx"]
__copyright__  = "None"
__credits__    = ["Marcelo Videa - mvidea@itesm.mx"]
__license__    = "None"
__status__     = "Under Work"
#**********************************************************************************#
```

Exercise 1

In [6]:

```
display(Image(filename='./directions/1.jpg'))
```

1. The Helmholtz function of a certain gas is

$$A = -\frac{n^2 a}{V} - nRT\ln(V - nb) + J(T)$$

where J is a function of T only. Derive an expression for the pressure of the gas.

$$A = U - TS$$
$$dA = dU - TdS - SdT$$

$dU = TdS - PdV$

$$dA = TdS - PdV - TdS - SdT$$
$$dA = -PdV - SdT$$
$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

- on the other hand,

$$A = \frac{n^2 a}{V} - nRTln\,(V - nb) + J(T)$$
$$\left(\frac{\partial A}{\partial V}\right)_T = \frac{n^2 a}{V^2} - \frac{nRT}{V - nb}$$

$\left(\frac{\partial J}{\partial V}\right)_T = 0$; as J is a function of T only

- therefore

$$-P = \frac{n^2 a}{V^2} - \frac{nRT}{V - nb}$$

Exercise 2

In [10]:
```
display(Image(filename='./directions/2.jpg'))
```

2. The Gibbs function of a gas is given by

$$G = nRT \ln\left(\frac{P}{P_0}\right) - nBP$$

where B is a function of T. Find the expression for:

(a) the equation of state

(b) the entropy

(c) the Helmholtz function

Exercise 2 - Part A

$$dG = -SdT + VdP$$
$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$
$$S = -\left(\frac{\partial G}{\partial T}\right)_P \text{ -\&- } V = \left(\frac{\partial G}{\partial P}\right)_T$$
$$V = \left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(nRTln\left(\frac{P}{P_0}\right) - nBP\right)$$
$$V = \frac{nRT}{\frac{P}{P_0}}\left(\frac{1}{P_0}\right) - nB$$
$$V = \frac{nRT}{P} - nB$$

$$P(V + nB) = nRT$$

Exercise 2 - Part B

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\frac{\partial}{\partial T}\left(nRTln\left(\frac{P}{P_0}\right) - nBP\right)$$

$$S = -nRln\frac{P}{P_0} + nP\frac{dB}{dT}$$

Exercise 2 - Part C

$$A = U - TS \text{ -\&- } G = U + PV - TS = H - TS$$
$$A = G - PV$$
$$G = nRTln\frac{P}{P_0} - nBP$$
$$V = \frac{nRT}{P} - nB \rightarrow P = \frac{nRT}{V + nB}$$
$$A = nRTln\left(\frac{\frac{nRT}{V+nB}}{P_0}\right) - nB\frac{nRT}{V + nB} - \frac{nRT}{V + nB}V$$
$$A = nRT\left(ln\left(\frac{nRT}{P_0(V + nB)}\right) - \frac{nB}{V + nB} - \frac{V}{V + nB}\right)$$

$$A = nRT\left(ln\left(\frac{nRT}{P_0(V + nB)}\right) - 1\right)$$

Exercise 3 & 4

In [8]:
```
display(Image(filename='./directions/3_4.jpg'))
```

3. Read the article by J. Pellicer et al. "Thermodynamics of Rubber Elasticity".
4. With the information from Pellicer's paper:
   (a) Write an expression for conformation work for a elastic system at constant volume.
   (b) What is the relation between the constant k in this paper and the Young's modulus of the elastic material?
   (c) Derive equations 2, 3, 6, 7, 9 and 10.
   (d) Reproduce Figures 2, 3, 4 and 5. Please, use anything but Excel.
   (e) Why is it that rubberlike elasticity is an entropic effect?

[1] Pellicer, J., Manzanares, J. A., Zúñiga, J., Utrillas, P., & Fernández, J. (2001). Thermodynamics of Rubber Elasticity. Journal of Chemical Education, 78(2), 263. [https://doi.org/10.1021/ed078p263 (https://doi.org/10.1021/ed078p263)](https://doi.org/10.1021/ed078p263)

Exercise 4 - Part A

$$\tau dL = dW = dU - TdS$$
$$\tau = \frac{dW}{dL} = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

- for an ideal rubber, $dU = 0$

$$\frac{dW}{dL} = \tau - T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

- where:

$$S = S_o + \int_{L_0}^{L} \left(\frac{\partial S}{\partial L}\right)_{T,V} dL = S_0 - kL_0 \left[\frac{L^2}{2{L_0}^2} + \frac{L_0}{L} - \frac{3}{2} - \lambda_0 T\left(\frac{L^2}{2{L_0}^2} - \frac{2L_0}{L} + \frac{3}{2}\right)\right]$$
$$S = S_0 + \frac{1}{2}kL^2(T\lambda_0 - 1) + \frac{3}{2}L_0(k + kT\lambda_0) - \frac{{L_0}^2(k + 2kT\lambda_0)}{L}$$
$$\left(\frac{\partial S}{\partial L}\right)_{T,V} = kL(T\lambda_0 - 1) + \frac{{L_0}^2(k + 2kT\lambda_0)}{L^2}$$
$$dW = \left(\tau - kTL(T\lambda_0 - 1) + \frac{T{L_0}^2(k + 2kT\lambda_0)}{L^2}\right) dL$$

$$\Delta W = \tau(L - L_0) + (Tk - T^2k\lambda_0)\left(\frac{L^2}{2} - \frac{{L_0}^2}{2}\right) + (Tk{L_0}^2 + 2T^2k{L_0}^2\lambda_0)\left(\frac{1}{L_0} - \frac{1}{L}\right)$$

$$\boxed{\Delta W = \frac{1}{2L}\left[(L - L_0)(-L(kLT + 2\tau) + k(-4 + L^2)T^2\lambda_0 + kTL_0(-2 - L + LT\lambda_0))\right]}$$

Exercise 4 - Part B

$$\frac{3PC_PT_0}{E_0} = \frac{C_{L,V}}{kL_0}$$
$$E_0 = \frac{3PC_PT_0kL_0}{C_{L,V}}$$

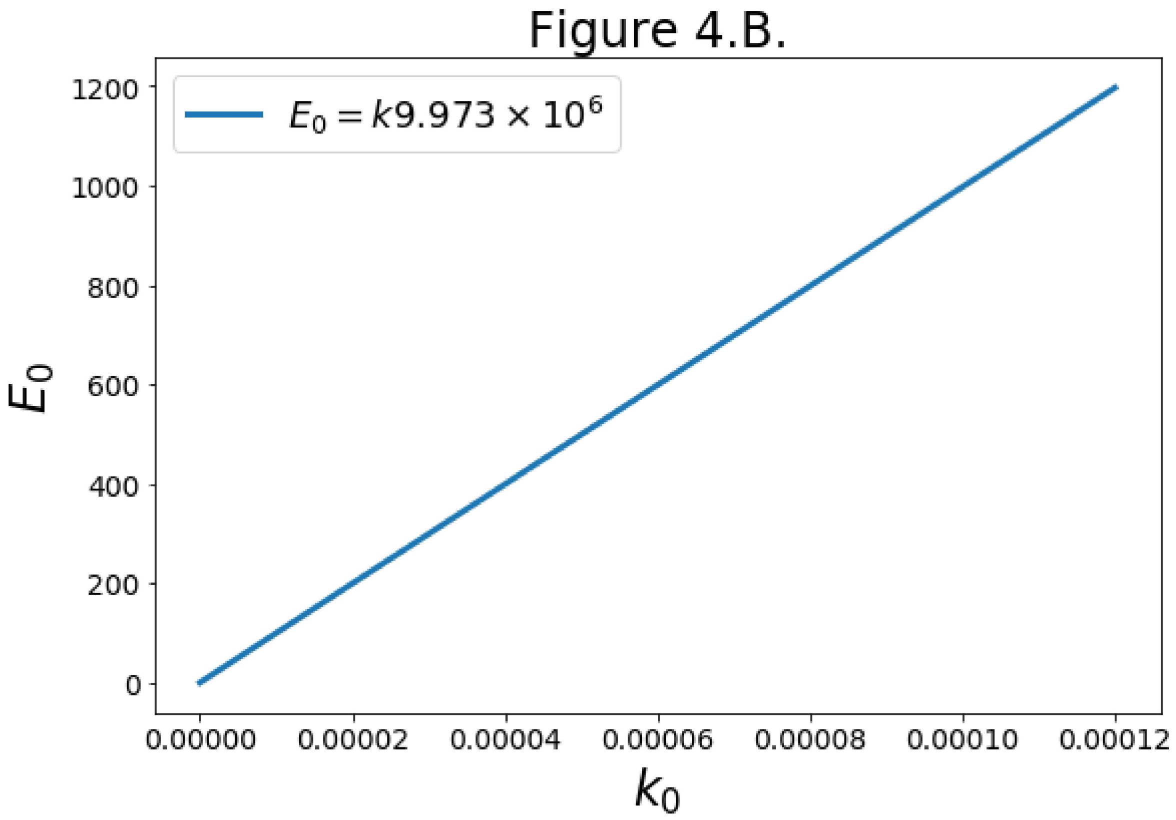
- where:
  $P = 1.01[Kgm^{-3}]$ $\rightarrow$ rubber desnity
  $C_P = 1965[JKg^{-1}K^{-1}]$ $\rightarrow$ specific heat at constant pressure
  $T_0 = 298.15[K]$
  $0.0 < k < 0.00012$
  $L_0 = 1[m]$ $\rightarrow$ length in the absence of applied stress
  $C_{L,V} = 0.178[JKg^{-1}K^{-1}]$ $\rightarrow$ heat capacity at constan length
  $E_0 = 1300[Pa]$ $\rightarrow$ Young's modulus
  for Poly(Butadiene) [2]

As depicted in Figure 4.B, E_0 and k have a direct proportional relationship.

[2] Brandrup, J., Immergut, E. H., Grulke, E. A., Abe, A., & Bloch, D. R. (2005). PHYSICAL CONSTANTS OF SOME IMPORTANT POLYMERS. In Polymer Handbook (4th ed., Vol. 112, pp. 211–212). John Wiley & Sons. Retrieved from https://app.knovel.com/hotlink/toc/id:kpPHE00026/polymer-handbook-4th/polymer-handbook-4th (https://app.knovel.com/hotlink/toc/id:kpPHE00026/polymer-handbook-4th/polymer-handbook-4th)

In [14]:
```
# Function to compute the coefficient of linear expansion of rubber at constant tensi
le stress and volume takes
def E0_(P, Cp, T0, k, L0, Clv):
    return (3*P*Cp*T0*k*L0)/(Clv);

# Draw the plot's workspace
scale = 3;
plt.subplots(figsize=(3*scale, 2*scale));

# Define constants
P = 1.01; #Kg/m3
Cp = 1965; #J/Kg K
T0 = 298.15; #K
k = np.linspace(0.0, 0.00012, 1000);
L0 = 1; #length in the absence of applied stress
Clv = 0.178; #J/K mol

# Plot
E0 = E0_(P, Cp, T0, k, L0, Clv)
plt.plot(k, E0, '-', linewidth=3, label=r'$E_0 = k9.973 \times 10^6$');

# Display plots
plt.xlabel(r'${k}_0$', fontsize=24);
plt.ylabel(r'$E_0$', fontsize=24);
plt.title("Figure 4.B.", size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\m
atplotlib\\pyplot.py'>
```



Exercise 4 - Part C - Eq. 2

$$\tau dL = \frac{dW}{dL} = dU - TdS$$
$$\tau = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau + T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

Exercise 4 - Part C - Eq. 3

$$\left(\frac{\partial S}{\partial L}\right)_{T,V} = -\left(\frac{\partial \tau}{\partial T}\right)_{L,V}$$
$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau + T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$
$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \tau - T\left(\frac{\partial \tau}{\partial T}\right)_{L,V}$$
$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$
$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] - T\frac{\partial}{\partial T}\left(kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]\right)$$
$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = \frac{kT^2}{L_0}\frac{dL_0}{dT}\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right]$$

- if $\lambda_0 = \frac{1}{L_0}\frac{dL_0}{dT}$

$$\left(\frac{\partial U}{\partial L}\right)_{T,V} = kT^2\lambda_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right]$$

Exercise 4 - Part C - Eq. 6

$$\tau = kT\left(\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right)$$
$$\frac{\tau}{kT} = \frac{L^3 - {L_0}^3}{L_0 L^2}$$
$$\tau L_0 L^3 = kTL^3 - kT{L_0}^3$$
$$L^3(L_0 - kT) = -kT{L_0}^3$$
$$L = \left(\frac{-kT{L_0}^3}{L_0 - kT}\right)^{1/3}$$
$$\lambda_{T,V} = \frac{1}{L}\frac{\partial}{\partial T}\left(\frac{-kT{L_0}^3}{L_0 - kT}\right)^{1/3}$$

$$\lambda_{T,V} = -\frac{1}{T}\frac{\left[\frac{L}{L_0}\right]^3 - 1}{\left[\frac{L}{L_0}\right]^3 + 2}$$

Exercise 4 - Part C - Eq. 7

$$\lambda_0 = \frac{L}{L_0}\frac{dL_0}{dT} \rightarrow \frac{1}{L_0}dL_0 = \lambda_0 dT$$

$T = T_0, L_0 = L_0(T_0)$
$T = T, L_0 = L_0(T)$

$$\int_{L_0(T_0)}^{L_0(T)} \frac{1}{L_0}\, dL_0 = \int_{T_0}^{T} \lambda_0\, dT$$
$$ln(L_0(T))|_{T_0}^{T} = \lambda_0 T|_{T_0}^{T}$$
$$ln(L_0(T)) - ln(L_0(T_0)) = \lambda_0(T - T_0)$$
$$ln\left(\frac{L_0(T)}{L_0(T_0)}\right) = \lambda_0(T - T_0)$$
$$\frac{L_0(T)}{L_0(T_0)} = e^{\lambda_0(T-T_0)}$$

$$L_0(T) = L_0(T_0)e^{\lambda_0(T-T_0)}$$

Exercise 4 - Part C - Eq. 9

$$L_0(T) = L_0(T_0)e^{\lambda_0(T-T_0)}$$

$$\lambda_0 = \lambda_{T,V} + \frac{1}{T}\frac{\left[\frac{L}{L_0(T)}\right]^3 - 1}{\left[\frac{L}{L_0(T)}\right]^3 + 2}$$

$$L_0(T) = L_0(T_0)e^{\lambda_{T,V} + \frac{1}{T}\frac{\left[\frac{L}{L_0(T)}\right]^3 - 1}{\left[\frac{L}{L_0(T)}\right]^3 + 2}(T-T_0)}$$

- sustitute $L_0(T)$ in $L_0(T) = L_0(T_0)e^{\lambda_0(T-T_0)}$

$$L_0(T_0)e^{\lambda_{T,V} + \frac{1}{T}\frac{\left[\frac{L}{L_0(T)}\right]^3 - 1}{\left[\frac{L}{L_0(T)}\right]^3 + 2}(T-T_0)} = L_0(T_0)e^{\lambda_0(T-T_0)}$$

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] = kT\left[e^{\lambda(T-T_0)} - \left(\frac{1}{e^{\lambda(T-T_0)}}\right)\right]$$

$$\frac{\partial\tau}{\partial T} = \frac{\partial}{\partial T}kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right] = \frac{\partial}{\partial T}kT\left[e^{\lambda(T-T_0)} - \left(\frac{1}{e^{\lambda(T-T_0)}}\right)\right]$$

$$\frac{\partial\tau}{\partial T}_{L,V} = -k\lambda_{L,V}T\left(e^{-\lambda(T-T_0)} + \frac{2}{\alpha_0}e^{2\lambda(T-T_0)}\right)$$

Exercise 4 - Part C - Eq. 10

$$\left(\frac{\partial S}{\partial L}\right)_{L,V} = \frac{\left(\frac{\partial U}{\partial L}\right)_{L,V} - \tau}{T}$$
$$\left(\frac{\partial S}{\partial L}\right)_{L,V} = \frac{kT^2\lambda_0\left[\frac{L}{L_0}+2\left(\frac{L_0}{L}\right)^2\right]-\tau}{T}$$
$$\left(\frac{\partial S}{\partial L}\right)_{L,V} = -\frac{\tau}{T} + \frac{kT\lambda_0}{L_0}L + 2kT\lambda_0{L_0}^2\frac{1}{L}$$
$$S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{L,V} dL = S_0(T) + \left[-\frac{\tau}{T}\int_{L_0}^{L} dL + \frac{kT\lambda_0}{L_0}\int_{L_0}^{L} L\,dL + 2kT\lambda_0{L_0}^2\int_{L_0}^{L}\frac{1}{L}\,dL\right]$$
$$S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{L,V} dL = S_0(T) + \left[-\frac{\tau(L-L_0)}{T} + \frac{kT\lambda_0\left(\frac{L^2}{2}-\frac{{L_0}^2}{2}\right)}{L_0} + 2kT\lambda_0{L_0}^2\left(\frac{1}{L_0}-\frac{1}{L}\right)\right]$$
$$S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{L,V} dL = S_0(T) + \left[\frac{\tau}{T}(L_0-L) + \frac{kT\lambda_0}{2L_0}(L^2-{L_0}^2) + 2kT\lambda_0{L_0}^2\left(\frac{1}{L_0}-\frac{1}{L}\right)\right]$$

$$\boxed{S_0(T) + \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_{L,V} dL = S_0(T) - kL_0\left[\frac{L^2}{2{L_0}^2} + \frac{L_0}{L} - \frac{3}{2} - \lambda_0 T\left(\frac{L^2}{2{L_0}^2} - \frac{2L_0}{L} + \frac{3}{2}\right)\right]}$$

Exercise 4 - Part D - Figure 2

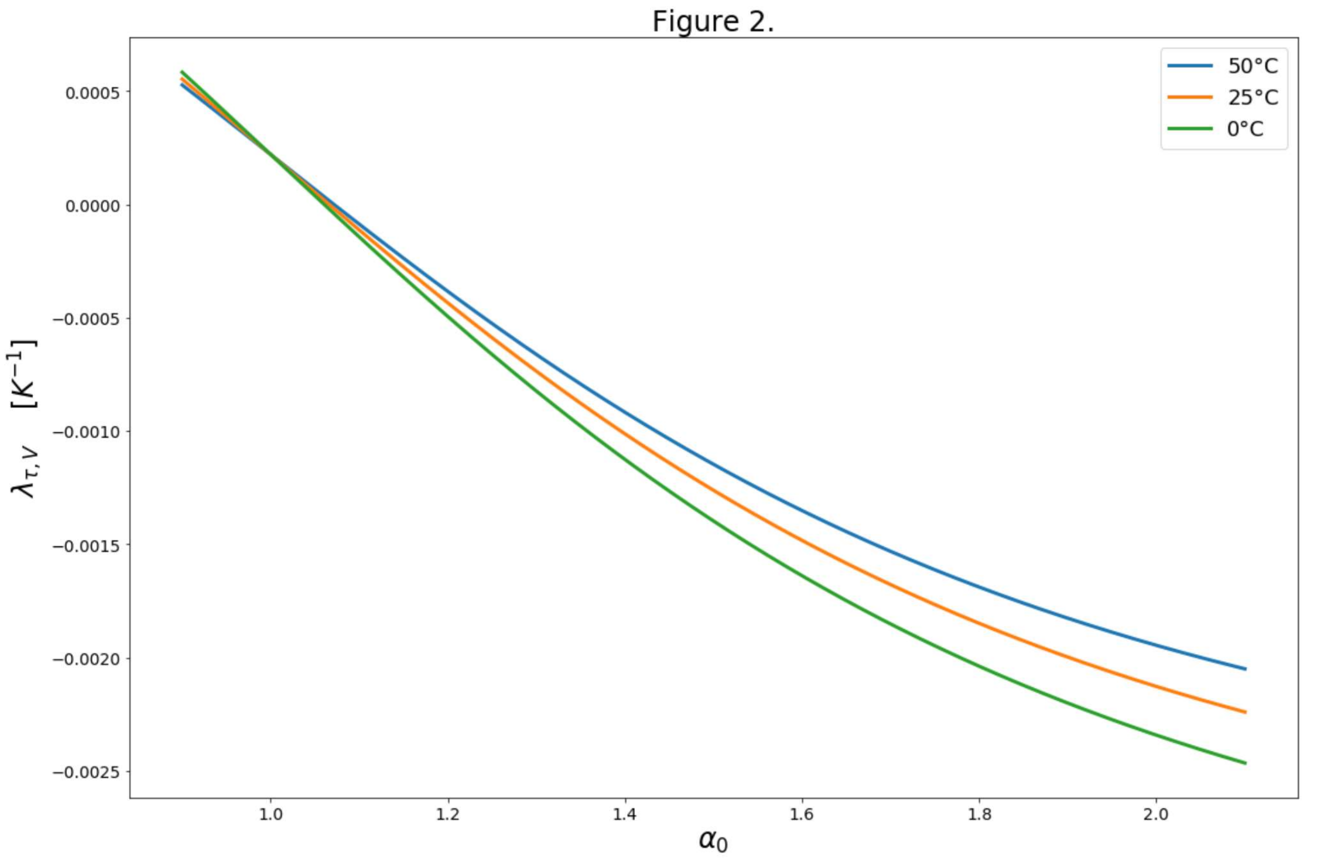
- from eq. (6)

$$\lambda_{\tau,V} = \lambda_0 - \frac{1}{T}\frac{\left[\frac{L}{L_0(T)}\right]^3 - 1}{\left[\frac{L}{L_0(T)}\right]^3 + 2}$$
$$\lambda_{\tau,V} = \lambda_0 - \frac{1}{T}\frac{{\alpha_0}^3 - 1}{{\alpha_0}^3 + 2}$$

- where:
  $T =$ isotropic rubber band temperature $[K]$
  $\lambda = 0.00022K^{-1}$ coefficient of linear expansion
  $\alpha_0 = \frac{L}{L_0(T)}$

In [10]:
```
# Function to compute the coefficient of linear expansion of rubber at constant tensi
le stress and volume takes
def Lambda_(Lambda0, T, alpha0):
    return (Lambda0 - ((((alpha0**3) - 1)/(T*((alpha0**3) + 2)))));

# Draw the plot's workspace
scale = 6;
plt.subplots(figsize=(3*scale, 2*scale));

# Define constants
Lambda0 = 0.00022; #K^(-1)
alpha0 = np.linspace(0.9, 2.1, 1000);

# Plot
T = 323.15; #K
Lambda = Lambda_(Lambda0, T, alpha0);
plt.plot(alpha0, Lambda, '-', linewidth=3, label='50°C');

T = 298.15; #K
Lambda = Lambda_(Lambda0, T, alpha0);
plt.plot(alpha0, Lambda, '-', linewidth=3, label='25°C');

T = 273.15; #K
Lambda = Lambda_(Lambda0, T, alpha0);
plt.plot(alpha0, Lambda, '-', linewidth=3, label='0°C');

# Display plots
plt.xlabel(r'${\alpha}_0$', fontsize=24);
plt.ylabel(r'$\lambda_{\tau , V}$' + '     ' + r'$[K^{-1}]$', fontsize=24);
plt.title("Figure 2.", size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\m
atplotlib\\pyplot.py'>
```



Exercise 4 - Part D - Figure 3

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right]$$

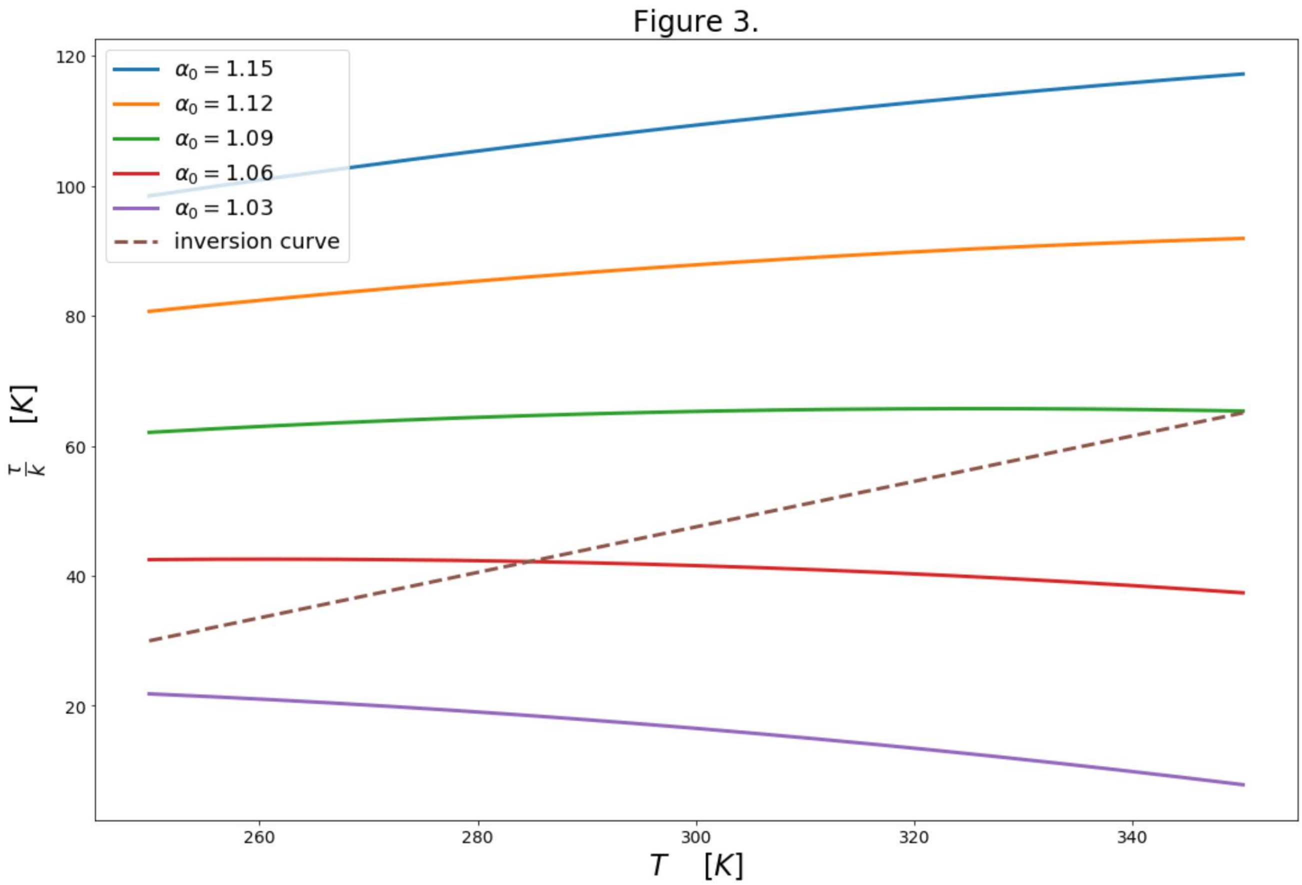
- if $\frac{L}{L_0} = \alpha_0 e^{\lambda_0(T-T_0)}$, then:

$$\tau = kT\left[\alpha_0 e^{\lambda_0(T-T_0)} - \left(\frac{1}{\alpha_0 e^{\lambda_0(T-T_0)}}\right)^2\right]$$

In [11]:

```
# Function to compute the stress $\tau$
def tau_(k, alpha0, Lambda0, T):
    expo = np.exp(Lambda0*(T-T[0]))
    return k*T*((alpha0*expo) - (1/(alpha0*expo))**2);

# Draw the plot's workspace
scale = 6;
plt.subplots(figsize=(3*scale, 2*scale));

# Define constants
k = 0.00486; #NK^(-1)
Lambda0 = -0.00022; #K^(-1)
T = np.linspace(249.9, 350.1, 1000);

# Plot
alpha0 = 1.15;
tau = tau_(k, alpha0, Lambda0, T)
plt.plot(T, tau/k, '-', linewidth=3, label=r'$\alpha_0 = 1.15$');

alpha0 = 1.12;
tau = tau_(k, alpha0, Lambda0, T)
plt.plot(T, tau/k, '-', linewidth=3, label=r'$\alpha_0 = 1.12$');

alpha0 = 1.09;
tau = tau_(k, alpha0, Lambda0, T)
plt.plot(T, tau/k, '-', linewidth=3, label=r'$\alpha_0 = 1.09$');

alpha0 = 1.06;
tau = tau_(k, alpha0, Lambda0, T)
plt.plot(T, tau/k, '-', linewidth=3, label=r'$\alpha_0 = 1.06$');

alpha0 = 1.03;
tau = tau_(k, alpha0, Lambda0, T)
plt.plot(T, tau/k, '-', linewidth=3, label=r'$\alpha_0 = 1.03$');

# inversion curve
dy = np.diff(tau/k);
dy = np.append(dy, dy[len(dy)-1]);
inveCurve = max(dy)+0.35*(T-T[0])+30;
plt.plot(T, inveCurve, '--', linewidth=3, label='inversion curve');

# Display plots
plt.xlabel(r'$T$' + '     ' + r'$[K]$', fontsize=24);
plt.ylabel(r'$\frac{\tau}{k}$' + '     ' + r'$[K]$', fontsize=24);
plt.title("Figure 3.", size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>
```



Exercise 4 - Part D - Figure 4

- from eq. (13)

$$\Delta S = -kL_0 \left[\frac{{\alpha_0}^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0 \left(\frac{{\alpha_0}^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2} \right) \right]$$

- from eq. (11)

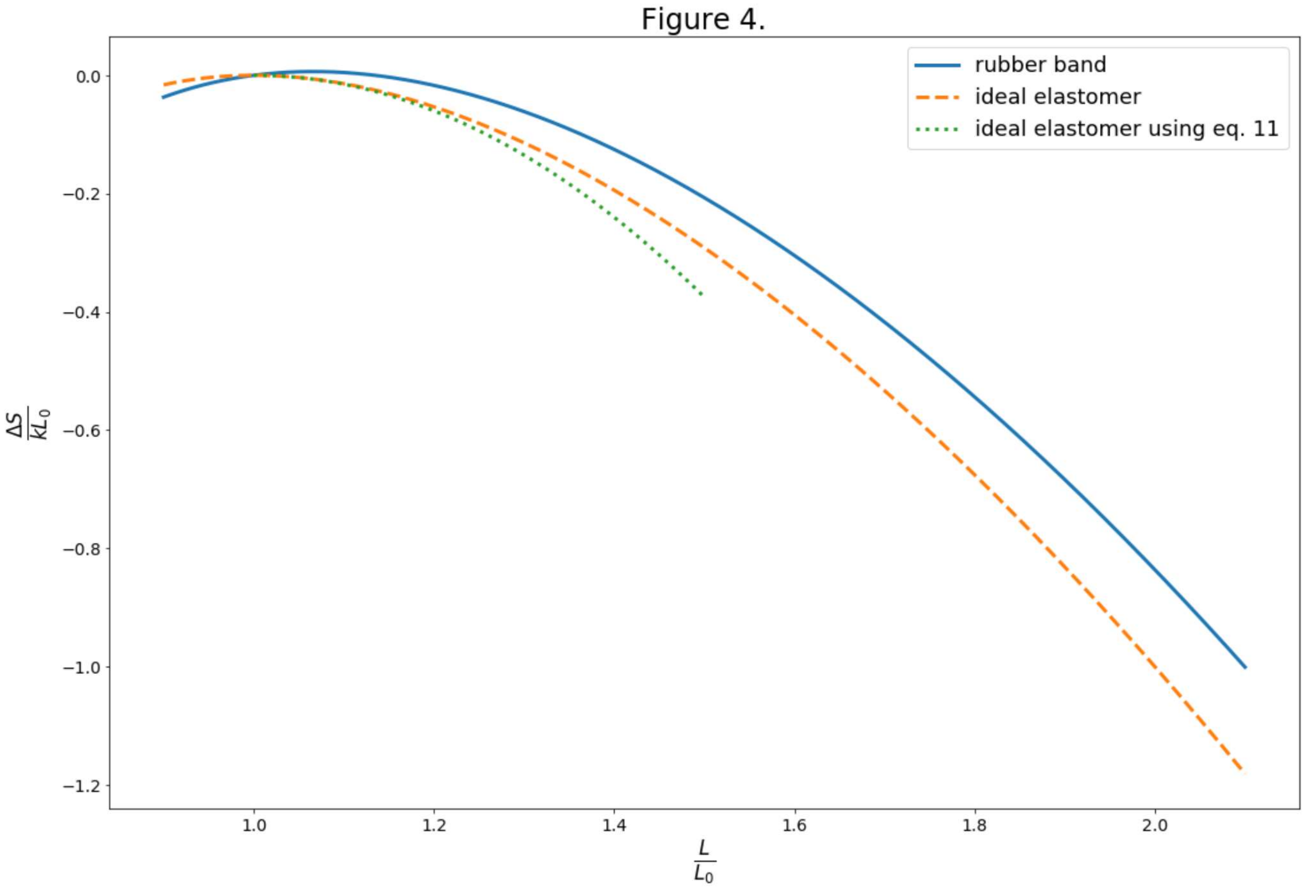
$$S \approx S_0 - \frac{3}{2} k L_0 \left(\frac{L}{L_0} - 1 \right)^2$$
$$\Delta S \approx -\frac{3}{2} k L_0 \left(\frac{L}{L_0} - 1 \right)^2$$

- where:
  $T_0 = 25C = 298.15K$

In [12]:

```
# Function to compute the stress $\tau$
def deltaS_(k, L0, alpha0, Lambda0, T0):
    num = Lambda0*T0*((alpha0**2/2)-(2/alpha0)+(3/2));
    return -k*L0*((alpha0**2/2)+(1/alpha0)-(3/2)-num);

# Function to compute the stress $\tau$
def aproxdeltaS_(k, L0, alpha0):
    return -(3/2)*k*L0*(alpha0 - 1)**2;

# Draw the plot's workspace
scale = 6;
plt.subplots(figsize=(3*scale, 2*scale));

# Define constants
k = 0.00486; #NK^(-1)
L0 = 0.1;
alpha0 = np.linspace(0.9, 2.1, 1000);
T0 = 298.15; #K

# Plot
Lambda0 = 0.00022;
deltaS = deltaS_(k, L0, alpha0, Lambda0, T0);
plt.plot(alpha0, deltaS/(k*L0), '-', linewidth=3, label='rubber band');

Lambda0 = 0.0;
deltaS = deltaS_(k, L0, alpha0, Lambda0, T0);
plt.plot(alpha0, deltaS/(k*L0), '--', linewidth=3, label='ideal elastomer');

alpha0 = np.linspace(1, 1.5, 1000);
Lambda0 = 0.0001;
deltaS = aproxdeltaS_(k, L0, alpha0);
plt.plot(alpha0, deltaS/(k*L0), ':', linewidth=3, label='ideal elastomer using eq. 1
1');

# Display plots
plt.xlabel(r'$\frac{L}{L_0}$', fontsize=24);
plt.ylabel(r'$\frac{\Delta S}{k L_0}$', fontsize=24);
plt.title("Figure 4.", size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\matplotlib\\pyplot.py'>
```



Exercise 4 - Part D - Figure 5

- from eq. (15), solve T:

$$ln\left(\frac{T}{T_0}\right) = \frac{kL_0}{C_{L,V}}\left[\frac{{\alpha_0}^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0\left(\frac{{\alpha_0}^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2}\right)\right]$$

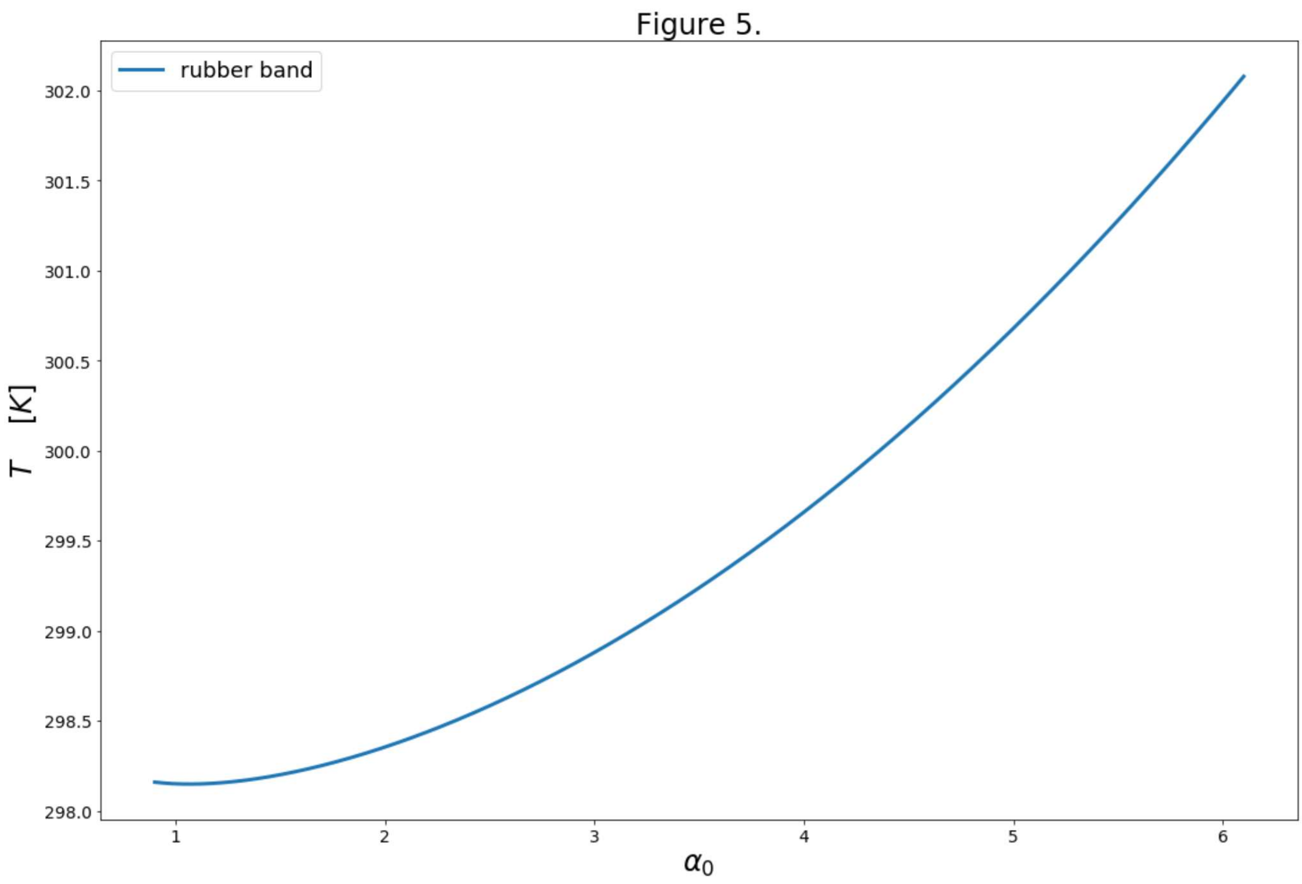
$$ln(T) = \frac{kL_0}{C_{L,V}}\left[\frac{{\alpha_0}^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0\left(\frac{{\alpha_0}^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2}\right)\right] + ln(T_0)$$

$$T = e^{\frac{kL_0}{C_{L,V}}\left[\frac{{\alpha_0}^2}{2} + \frac{1}{\alpha_0} - \frac{3}{2} - \lambda_0 T_0\left(\frac{{\alpha_0}^2}{2} - \frac{2}{\alpha_0} + \frac{3}{2}\right)\right] + ln(T_0)}$$

- where:
  $T_0 = 298.15K$
  $\lambda_0 = 0.00022K^{-1}$
  $\frac{C_{L,V}}{kL_0} = 1220$

In [13]:
```
# Function to compute the stress $\tau$
def T_(alpha0, Lambda0, T0, n):
    num = Lambda0*T0*((alpha0**2/2)-(2/alpha0)+(3/2));
    cons = (1/n)*((alpha0**2/2)+(1/alpha0)-(3/2)-num);
    return np.exp(cons + np.log(T0));

# Draw the plot's workspace
scale = 6;
plt.subplots(figsize=(3*scale, 2*scale));

# Define constants
T0 = 298.15; #K
Lambda0 = 0.00022;
n = 1220; #Clv / K*L0
alpha0 = np.linspace(0.9, 6.1, 1000);

# Plot
T = T_(alpha0, Lambda0, T0, n);
plt.plot(alpha0, T, '-', linewidth=3, label='rubber band');

# Display plots
plt.xlabel(r'$\alpha_0$', fontsize=24);
plt.ylabel(r'$T$' + '     ' + r'$[K]$', fontsize=24);
plt.title("Figure 5.", size=24);
plt.legend(prop={'size': 18});
display(plt);
```

```
<module 'matplotlib.pyplot' from 'C:\\Users\\oskat\\Anaconda3\\lib\\site-packages\\m
atplotlib\\pyplot.py'>
```



Exercise 4 - Part E

Rubber is composed of long polymer chains. Each of the single bonds between two carbon atoms in those chaines can in principle rotate so that the chain is locally either straight or bent. There are many ways to rotate so that the chain bends but there is only one way to rotate so that the chain is straight and maximally extended. Thus entropy favors shorter bent chains. There is much less disorder when chains are straight. So there are more straight chains when the rubber is stretched, so the chains must achieve longer lengths. When the rubber is heated by increasing the temperature, it favors the free energy of structures having more entropy. At equilibrium, shorter chains are favored over longer and the rubber contracts. [3]

[3] Roylance, D. (2000). Atomistic Basis of Elasticity. ACe (Vol. 5). Retrieved from [http://web.mit.edu/course/3/3.11/www/modules/elas_2.pdf (http://web.mit.edu/course/3/3.11/www/modules/elas_2.pdf)](http://web.mit.edu/course/3/3.11/www/modules/elas_2.pdf)

Exercise 5

In [9]:
```
display(Image(filename='./directions/5.jpg'))
```

5. Demonstrate the following thermodynamic relations:

(a) $C_P = C_V + \dfrac{\alpha^2 TV}{\kappa_T}$

(b) $\kappa_T - \kappa_S = \dfrac{\alpha^2 \overline{V} T}{\overline{C}_P}$ where $\kappa_S = -\dfrac{1}{\overline{V}}\left(\dfrac{\partial \overline{V}}{\partial P}\right)_S$

(c) $\dfrac{\kappa_T}{\kappa_S} = \dfrac{\overline{C}_P}{\overline{C}_V}$

(d) $\left(\dfrac{\partial H}{\partial V}\right)_S = -\dfrac{C_P}{\kappa_T C_V}$

(e) $\left(\dfrac{\partial C_P}{\partial P}\right)_T = -TV\left(\alpha^2 + \dfrac{d\alpha}{dT}\right)$

Exercise 5 - Part A

$$H = U + PV$$
$$dH = TdS + VdP$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$G = U + PV - TS$$
$$dG = VdP - SdT$$
$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$dU = TdS - PdV$$
$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = C_V$$

$$H = U + PV$$
$$dH = TdS + VdP$$
$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = C_P$$

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

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

$$\frac{C_V - C_P}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV + \left(\frac{\partial V}{\partial T}\right)_P dP = 0$$
$$(C_P - C_V) dT = T\left(\frac{\partial P}{\partial T}\right)_V dV + T\left(\frac{\partial V}{\partial T}\right)_P dP$$
$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

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

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

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

$$C_P - C_V = -T\frac{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \frac{(-1)\left(\frac{1}{V}\right)\left(\frac{1}{V}\right)}{(-1)\left(\frac{1}{V}\right)\left(\frac{1}{V}\right)}$$
$$C_P - C_V = -T\frac{\alpha^2(-1)}{K_T\left(\frac{1}{V}\right)} = -T\frac{-\alpha^2}{\frac{K_T}{V}}$$

$$\boxed{C_P - C_V = \frac{\alpha^2 V T}{K_T}}$$

Exercise 5 - Part B

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

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

$$\left(\frac{\partial V}{\partial P}\right)_S = V\alpha\left(\frac{\partial T}{\partial P}\right)_S - VK_T$$

$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1$
$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P$
$\left(\frac{\partial T}{\partial P}\right)_S = \frac{-\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\frac{C_P}{T}}$
$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\alpha TV}{C_P}$

$$\left(\frac{\partial V}{\partial P}\right)_S = V\alpha\frac{\alpha TV}{C_P} - VK_T$$
$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\alpha^2 TV^2}{C_P} - VK_T$$

$$K_T - K_S = K_T + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$
$$K_T - K_S = K_T + \frac{1}{V}\left(\frac{\alpha^2 TV^2}{C_P} - VK_T\right)$$

$$K_T - K_S = \frac{\alpha^2 TV}{C_P}$$

Exercise 5 - Part C

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

$$\frac{C_P}{C_V} = \frac{K_T}{K_S}$$

Exercise 5 - Part D

$$dH = TdS + VdP$$
$$\left(\frac{\partial H}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_S + V\left(\frac{\partial P}{\partial V}\right)_S$$
$$\left(\frac{\partial H}{\partial V}\right)_S = V\left(\frac{\partial P}{\partial V}\right)_S$$

$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\alpha^2 TV^2}{C_P} - VK_T$

$$\left(\frac{\partial H}{\partial V}\right)_S = V\left(\frac{1}{\frac{\alpha^2 TV^2}{C_P} - VK_T}\right)$$
$$\left(\frac{\partial H}{\partial V}\right)_S = \frac{C_p}{\alpha^2 TV - K_T C_p}$$

$K_T C_P = \alpha^2 VT + K_T C_V$

$$\left(\frac{\partial H}{\partial V}\right)_S = -\frac{C_p}{C_V K_T}$$

Exercise 5 - Part E

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

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

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

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

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T}\right)_P$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial T}\right)_P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

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

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(V\left(\frac{\partial \alpha}{\partial T}\right)_P + V\alpha^2\right)$$

$$\boxed{\left(\frac{\partial C_P}{\partial P}\right)_T = -TV\left[\alpha^2\left(\frac{\partial \alpha}{\partial T}\right)_P\right]}$$

```
In [ ]:
```