

Oblig 3

Hans-Petter Harveg

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Project 1

a.

I have two solutions to this one, so I will include both

1. Using the van der Waals equation and simply solve for P

$$(p + \frac{aN^2}{V^2})(V - Nb) = NkT \rightarrow p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \quad (1)$$

2. Taking the derivative of F_{vdW} , with respect to V

$$\begin{aligned} p &= -\frac{\partial F_{vdW}}{\partial V} = -\frac{\partial}{\partial V} \left[-NkT \left(\ln \left(\frac{n_q(V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V} \right] \\ &= -(-NkT \left(\frac{1}{V - Nb} \right) + \frac{aN^2}{V^2}) \\ &= NkT \left(\frac{1}{V - Nb} \right) - \frac{aN^2}{V^2} \\ p &= NkT \left(\frac{1}{V - Nb} \right) - \frac{aN^2}{V^2} \end{aligned} \quad (2)$$

b.

Introducing the following sizes

$$p_c = \frac{a}{27b^2} \quad , \quad V_c = 3Nb \quad , \quad kT_c = \frac{8a}{27b}$$

$$\hat{p} = \frac{p}{p_c} \quad , \quad \hat{V} = \frac{V}{V_c} \quad , \quad \hat{T} = \frac{T}{T_c}$$

We can write (eq.2) as

$$\begin{aligned}
\hat{p}p_c &= \frac{Nk\hat{T}T_c}{\hat{V}V_c - Nb} - \frac{aN^2}{(\hat{V}V_c)^2} \\
\hat{p}\left(\frac{a}{27b^2}\right) &= \frac{Nk\hat{T}\left(\frac{8a}{27b}\right)}{\hat{V}(3Nb) - Nb} - \frac{aN^2}{(\hat{V}(3Nb))^2} \\
\rightarrow \hat{p} &= \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}
\end{aligned} \tag{3}$$

c.

The script can be found [here](#)

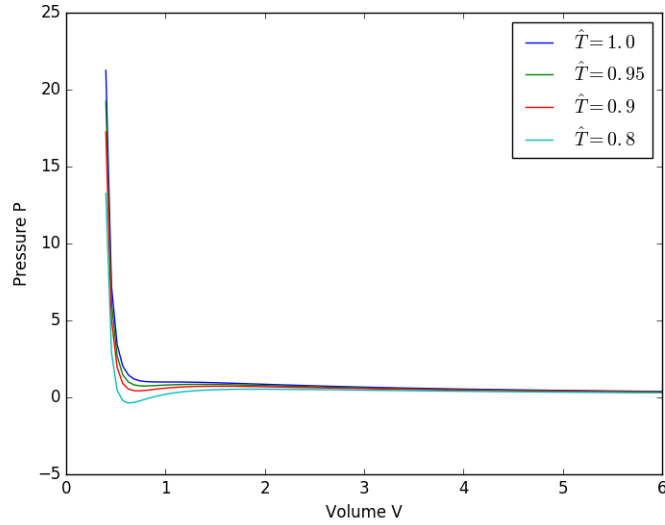


Figure 1: The pressure \hat{P} as a function of \hat{V} for $\hat{V} = [0.4 : 6.0]$ for $\hat{T} = [1.0, 0.95, 0.9, 0.08]$

d.

Introducing the following sizes

$$\hat{\rho} = \frac{1}{\hat{V}} = \frac{\rho}{\rho_c} \quad , \quad \rho_c = \frac{1}{3b} \rightarrow \hat{V} = \frac{\rho_c}{\rho} = \frac{1}{\rho 3b} \tag{4}$$

Using (eq.2), we can write the dimensionless equation

$$\begin{aligned}
\hat{\rho} &= \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2} \\
&= \frac{8\hat{T}}{3\left(\frac{1}{\rho 3b}\right) - 1} - \frac{3}{\left(\frac{1}{\rho 3b}\right)^2} \\
&= \frac{8\hat{T}}{3\left(\frac{1}{\rho 3b} - 1\right)} - \frac{3}{\left(\frac{1}{\rho}\right)^2} \\
&= \frac{8\hat{T}}{\frac{3-\hat{\rho}}{\hat{\rho}}} - 3\hat{\rho}^2 \\
&\rightarrow \frac{8\hat{T}\hat{\rho}}{3-\hat{\rho}} - 3\hat{\rho}^2
\end{aligned} \tag{5}$$

e.

The script can be found [here](#)

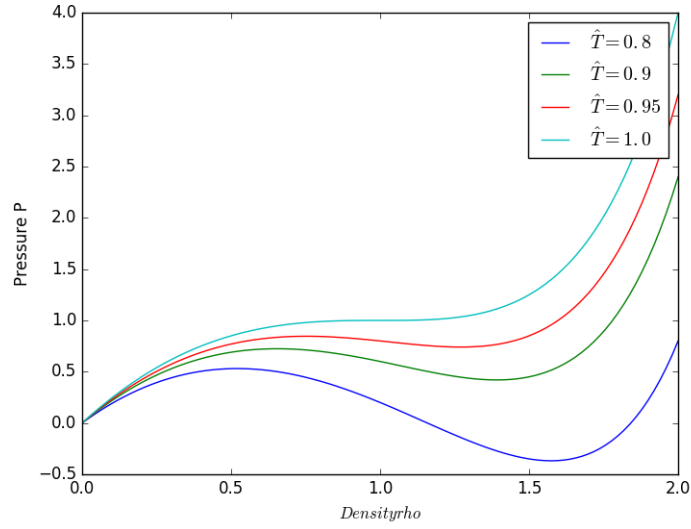


Figure 2: The pressure \hat{P} as a function of $\hat{\rho}$ for $\hat{\rho} = [0.0 : 2.0]$ for $\hat{T} = [0.8, 0.9, 0.95, 1.0]$

f.

We can see from the plot that for the temperature $T = 1.0$, the density is an unique function, while for temperatures $T < 1.0$, the density become non-unique.

Meaning we can observe several similar densities for a given temperature for temperatures below 1.0.

g.

We want to see where the isothermal compressibility is negative. The isothermal compressibility is defined as

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right) \quad (6)$$

We can see from the plot that for $T = 1.0$, the isothermal compressibility stay positive. It seems to flatten out around $\rho \approx 0.8$, then, around $\rho \approx 1.2$, it increases again.

For temperatures $T < 1.0$, we can see that the isothermal compressibility becomes negative around $\rho = 0.5 \approx 0.8$, depending on the temperature, and return to positive around $\rho = 1.2 \approx 1.7$, depending on the temperature.

TODO: WHY IS NEGATIVE COMPRESSIBILITY A NON-PHYSICAL CONDITION?

h.

We will now look at the PV isotherms of N_2 . Using (??), we can write the equation as

$$P = P_c \left[\frac{8T\hat{T}/T_c}{3\hat{V}/V_c - 1} - \frac{3V_c^2}{\hat{V}^2} \right] \quad (7)$$

Where

$$P_c = 33.6 \text{ atm}, \quad V_c = 0.089 \text{ l/mol}, \quad T_c = 126 \text{ K} \quad (8)$$

The script can be found [here](#)

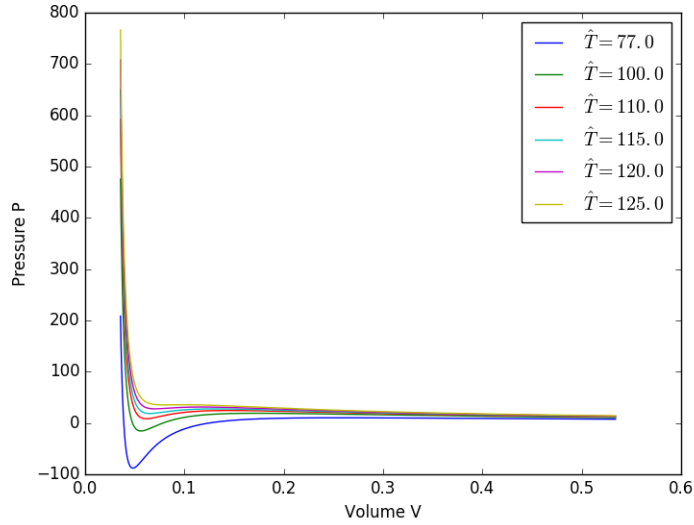


Figure 3: To relate the van der Waals fluid to nitrogen (N_2) gas, we have used the numerical values for the sizes from problem **b.**; $p_c = 33.6 \text{ atm}$, $V_c = 0.0891/\text{mol}$ and $T_c = 126 \text{ K}$ to plot, using the van der Waals equation of state the PV isotherms of N_2 for $\hat{T} = [77 \text{ K}, 100 \text{ K}, 110 \text{ K}, 115 \text{ K}, 125 \text{ K}]$

i.

We can find the equal area by drawing a straight line using "by eye" approximation.

The script can be found [here](#)

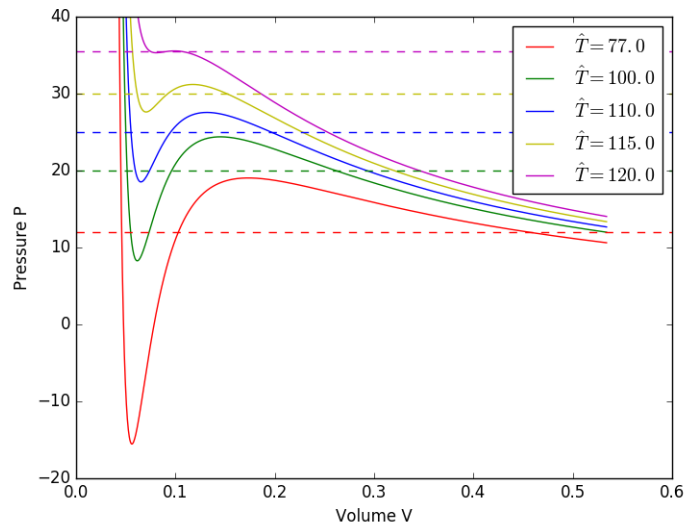


Figure 4: TODO:

j.

This problem was formulated as an extra challenge. I sadly did not have time to solve this problem.

k.

TODO:

l.

TODO:

Project 2

a.

We start by expanding dS and dV

$$ds = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (9)$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \quad (10)$$

If we insert (??) into (??), we get

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \right] \quad (11)$$

A little bit of algebra:

$$dS = \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right] dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP \quad (12)$$

Because the pressure is constant, we have that $dP = 0$

$$dS = \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right] dT \Leftrightarrow \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (13)$$

We can now use the identities for the heat capacities:

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T}\right)_P \quad (14)$$

and

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (15)$$

Which gives us the relation

$$\frac{C_V}{T} = \frac{C_P}{T} + V\alpha \left(\frac{\partial S}{\partial V}\right)_T \quad (16)$$

We now need an expression for the last partial differentiation. We start with a constant volume $dV = 0$, which gives from (??)

$$0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (17)$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (18)$$

we now use that

$$\beta_T = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (19)$$

and get that

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta_T} \quad (20)$$

Inserting this into (??) we get the relation for the heat capacities:

$$C_V = C_P + VT \frac{\alpha^2}{\beta_T} \quad (21)$$

b.

From (??) we have

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V} \quad (22)$$

We now need to look at these expressions. We start with $\left(\frac{\partial S}{\partial T}\right)_P$. We know from this that $dP = 0$. Since the expression involves S and T we are going to look at $dP(S, T) = 0$

$$dP = 0 = \left(\frac{\partial P}{\partial T}\right)_S dT + \left(\frac{\partial P}{\partial S}\right)_T dS \quad (23)$$

From this we get

$$\left(\frac{\partial S}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T} \quad (24)$$

We use the same logic with $\left(\frac{\partial S}{\partial T}\right)_V$:

$$dV(S, T) = 0 = \left(\frac{\partial V}{\partial T}\right)_S dT + \left(\frac{\partial V}{\partial S}\right)_T dS \quad (25)$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial S}\right)_T} \quad (26)$$

We can now insert this into (??)

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial P}{\partial S}\right)_T} = \left(\frac{\partial P}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_T \quad (27)$$

We can then use that

$$\beta_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S, \quad \beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (28)$$

And we then get

$$\frac{C_P}{C_V} = \left(\frac{\partial P}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_T = \frac{\beta_T}{\beta_S} \quad (29)$$

c.

We start with the first law for pressure-volume work

$$dU = dQ - dW = dQ - PdV \quad (30)$$

We then, as the exercise hinted, expand dH . We do this for $H(T, P)$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad (31)$$

But in this system $dP = 0$, so this reduces to

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT \quad (32)$$

We also know that for this pressure-volume system the change enthalpy is given as

$$dH = dU + PdV \quad (33)$$

Inserting this for dU in (??) we get

$$dQ = \left(\frac{\partial H}{\partial T} \right)_P dT \quad (34)$$

and since we have constant pressure, we get

$$\left(\frac{\partial Q}{\partial T} \right)_P = C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (35)$$

d.

Running the lammmps script we get the following data:

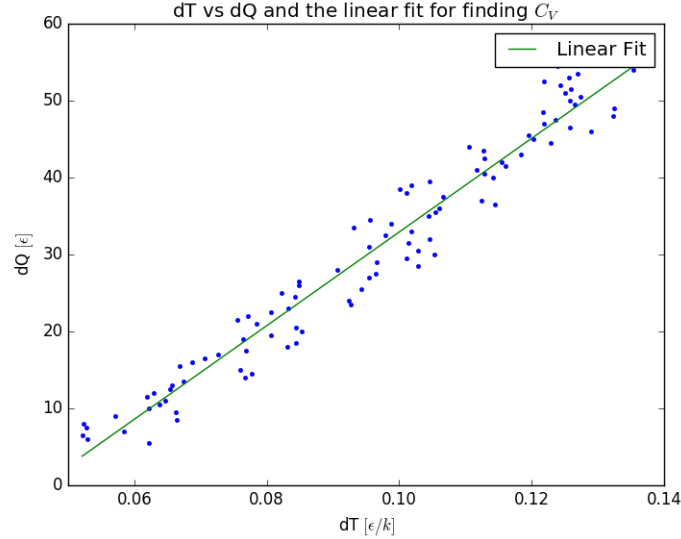


Figure 5: dQ versus dT for a Lennard-Jones system with constant volume. A linear fit used to find the slope, which corresponds to the heat capacity C_V

We know that

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V \Rightarrow dQ = C_V dT \quad (36)$$

So the fitted slope is the C_V . So we get the result

$$C_V = (611.34 \pm 13.38)k \quad (37)$$

e.

For an ideal gas the heat capacity is given as

$$C_V = \frac{1}{2}NR \quad (38)$$

Where R is the gas constant, f the degree of freedom and N the number of particles. In LJ-units $R = 1$. All the particles are point particles and therefore have $f = 3$. And there are $N = 540$ particles. We thus get

$$C_V = 750k \quad (39)$$

This is a bit above the heat capacity we got. This may both due to an error due to a low number of particles. It may also be due to the Lennard-Jones potential not being a perfect model for an ideal gas.

f.

The density was so kept at $\rho = 0.01$ and the temperature was varied from the triple point temperature to 10 times the critical temperature¹ in 6 steps. The resulting heat capacities was calculated for each temperature.

We can see that the heat capacity seems to decrease somewhat as temperature increases. A more constant C_V may have been expected², so the reason for this behaviour is not clear.

g.

We can now do something similar to what we did above, but we instead let the temperature be constant at $T = 2$, and vary the density from a diluted gas density of $\rho = 0.01$ to the triple point density of $\rho = 0.84$ (in practice I ended it at $\rho = 0.8$). We then get

Again we see a decrease in C_V as ρ increases. And again I am not sure why this is the case.

¹I used $T_{tp} = 0.694$ and $T_c = 1.32$ as these was the one I found at http://www.sklogwiki.org/SklogWiki/index.php/Lennard-Jones_model

²We already saw that it should be constant at 750 k

h.

If we now hold the pressure constant we can find C_P . This was done with a constant temperature $T = 2$ and at a diluted gas density $\rho = 0.01$ and at the triple point density.

We can see that both C_P and C_V have decreased alot from the diluted gas density to the triple point density. More important, C_P should not be negative! This seems to be a problem with lammmps (for me at least). At the triple point density the simulation goes its own way. Even though I use $T = 2$, the simulation insist on using $T = 0.92$ in the log file. The log file also gives a negative heat capacity, so it is not my calculation. Why this is, I simply don't know.

Since we need β_T to find the theoretical value of $C_P - C_V$, which I'm not sure who to find from our simulations, since it depends on a constant temperature – the temperature in the simulation varies. So I have nothing to compare the numerical data with, unfortunately.

i.

Running the lammmps script and fitting for dQ vs dT , we get a numerical value for the heat capacity for N_2

$$C_V = 3.188 \quad (40)$$

We expect that the units for C_V should be $[Q]/[T]$. In real unit this becomes $(Kcal/mole)/K = Kcal/(mole \cdot K)$. So

$$C_V = 3.188 \text{ Kcal/mole/K} \quad (41)$$

Appendix

Source code from project 1

Code from problem c.

```
1
2 import numpy as np
3 import matplotlib.pyplot as plt
4
5 # Setup lists
6 T_values = [1.0, 0.95, 0.9, 0.8]
7 V = np.linspace(0.4, 6.0, 100)
8
9 # Calculate pressure for a given T:
10 for T in T_values:
11     p = 8*T/(3*V - 1) - 3/(V**2)
12     plt.plot(V, p)
13
14
15 # Plot:
16 plt.legend([' $\hat{T} = 1.0$ ', ' $\hat{T} = 0.95$ ', ' $\hat{T} = 0.9$ ', ' $\hat{T} = 0.8$ '])
```

```

17 plt.xlabel('Volume V')
18 plt.ylabel('Pressure P')
19 plt.show()

```

Code from problem e.

```

1
2 import numpy as np
3 import matplotlib.pyplot as plt
4
5 # Setup lists
6 T_values = [0.8, 0.9, 0.95, 1.0]
7 rho = np.linspace(0.0, 2.0, 100)
8
9 # Calculate pressure for a given T:
10 for T in T_values:
11     p = (8*rho*T)/(3 - rho) - 3*rho**2
12     plt.plot(rho, p)
13
14
15 # Plot:
16 plt.legend([' $\hat{T} = 0.8$ ', ' $\hat{T} = 0.9$ ', ' $\hat{T} = 0.95$ ', ' $\hat{T} = 1.0$ '])
17 plt.xlabel('Density rho')
18 plt.ylabel('Pressure P')
19 plt.show()

```

Code from problem h.

```

1
2 import numpy as np
3 import matplotlib.pyplot as plt
4
5 # Setup lists
6 T_values = [77.0, 100.0, 110.0, 115.0, 120.0, 125.0] # [K]
7
8 T_c = 126.0
9 P_c = 36.6 # [atm]
10 V_c = 0.089 # [l/mol]
11
12 V = np.linspace(0.4*V_c, 6.0*V_c, 1000)
13
14 # Calculate pressure for a given T:
15 for T in T_values:
16     p = (P_c)*((8*T/T_c)/(3*(V/V_c) - 1) - 3/((V/V_c)**2))
17     plt.plot(V, p)
18
19
20 # Plot:
21 plt.legend([' $\hat{T} = 77.0$ ', ' $\hat{T} = 100.0$ ', ' $\hat{T} = 110.0$ ', ' $\hat{T} = 115.0$ ', ' $\hat{T} = 120.0$ ', ' $\hat{T} = 125.0$ '])
22 plt.xlabel('Volume V')
23 plt.ylabel('Pressure P')
24 plt.show()

```

Code from problem i.

```

1
2 import numpy as np
3 import matplotlib.pyplot as plt
4
5 # Setup lists
6 T_values = [100.0, 110.0, 115.0, 120.0, 125.0] # [K]
7 col = ['r', 'g', 'b', 'y', 'm']
8 P_values = [12.0, 20.0, 25.0, 30.0, 35.5] # [K]
9
10 #
11 T_c = 126.0
12 P_c = 36.6 # [atm]
13 V_c = 0.089 # [l/mol]
14
15 V = np.linspace(0.4*V_c, 6.0*V_c, 1000)
16
17 # Calculate pressure for a given T:
18 i = 0
19 for T in T_values:
20     p = (P_c)*((8.0*T/T_c)/(3.0*(V/V_c) - 1) - 3/((V/V_c)**2))
21     plt.plot(V, p, col[i])
22     i += 1
23
24 # Plot:
25 plt.legend([' $\hat{T} = 77.0$ ', ' $\hat{T} = 100.0$ ', ' $\hat{T} = 110.0$ ', ' $\hat{T} = 115.0$ ', ' $\hat{T} = 120.0$ ', ' $\hat{T} = 125.0$ '])
26 plt.xlabel('Volume V')
27 plt.ylabel('Pressure P')
28 plt.ylim(-20,40)
29
30 # Add lines to separeate the plot into "two sections"
31 for i in range(len(col)):
32     plt.plot([0.0,0.6],[P_values[i],P_values[i]], '%s—'%(col[i]),
33             lw='1', label="_not in legend")
34
35 plt.show()

```

Source code from project 2

Code from problem d.

```

1 #
2 import numpy as np
3 import matplotlib.pyplot as plt
4 from scipy import stats
5
6 #
7 d_data = (np.loadtxt("problem_d_lammps.dat", skiprows=1).T)
8 dT = d_data[3]
9 dQ = d_data[2]
10
11 #
12 slope, intercept, r_value, p_value, std_err = stats.linregress(dT,
13     dQ)
14
15 dT_cont = np.linspace(np.min(dT), np.max(dT), 1000)

```

```

16 # Plot
17 plt.plot(dT,dQ,".")
18 plt.plot(dT_cont,slope*dT_cont + intercept,label="Linear Fit")
19 plt.title("dT vs dQ and the linear fit for finding  $C_V$ ")
20 plt.xlabel(r"dT [ $\epsilon/k$ "] )
21 plt.ylabel(r"dQ [ $\epsilon$ "] )
22 plt.legend()
23 plt.show()
24
25 print("C-V = {} +/- {}".format(slope,std_err))

```

Bazzinga!