

# Intersection between two surfaces - updated version 4

## 1 Background

In this problem we will have two Gibbs free energy surfaces, corresponding to two different solids. In order to calculate the Gibbs free energy, first of all we have to calculate the electronic energy. It is possible to distort the volume of the cell, and hence, the electronic energy varies accordingly. Thus, there is a dependence on the electronic energy and the volume of the solid. This dependence can be fitted to an analytical expression, such as the Birch-Murnaghan isothermal equation of state:

$$U(V) = U_0 + \frac{9V_0B_0}{16} \left\{ \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}, \quad (1)$$

where  $U_0$  and  $V_0$  represent the minimum value of energy and pressure, and  $B_0$  is the bulk moduli of the solid at that volume. Because the pressure  $P$  may be written as a function of the volume  $V$  as:

$$P(V) = - \left( \frac{\partial U(V)}{\partial V} \right)_s, \quad (2)$$

it is then possible to obtain an expression for  $P(V)$ :

$$P(V) = \frac{3B_0}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (3)$$

This is how we take into account the effect of the pressure on materials. Up to now, no temperature has been considered. We can then say that Eq. 3 is at 0 Kelvin. It is possible to account for the temperature by computing the frequencies of vibration in a solid. These frequencies are denoted as  $\nu_{i,\mathbf{k}}$ . Each atomic position is considered to be an independent harmonic oscillator; when summing over all the vibrational levels, it is possible to derive a vibrational partition function,  $Z$ :

$$Z_{i,\mathbf{k}} = \frac{\exp \left( -\frac{h\nu_{i,\mathbf{k}}}{2k_B T} \right)}{1 - \exp \left( -\frac{h\nu_{i,\mathbf{k}}}{k_B T} \right)} \quad (4)$$

and obtain an expression for the Helmholtz free energy ( $F$ ) knowing that  $F = -k_B T \ln Z$ . However, the frequencies depend on  $P(V)$ :  $\nu_i(P(V))$ . Thus,

$$F(P(V), T) = \frac{1}{2} h \nu_{i,\mathbf{k}}(P(V)) + k_B T \ln \left[ 1 - \exp \left( \frac{-h \nu_{i,\mathbf{k}}(P(V))}{k_B T} \right) \right] \quad (5)$$

According to these two maxwell relations:

$$P(V, T) = \left( \frac{\partial F(P(V), T)}{\partial V} \right)_T \quad S(P(V), T) = - \left( \frac{\partial F(P(V), T)}{\partial T} \right)_V \quad (6)$$

we can obtain expressions for the pressure at finite temperature, entropy and Gibbs free energy, respectively:

$$P(V, T) = \underbrace{-\frac{\partial U(V)}{\partial V}}_{\substack{\text{Birch-Murnaghan} \\ P(V, T=0\text{K}) \\ \text{analytic expression}}} - \sum_{i,\mathbf{k}} \left[ \frac{1}{2} + \frac{1}{\exp \left( \frac{h \nu_{i,\mathbf{k}}(P(V))}{k_B T} \right) - 1} + h \frac{\partial \nu_{i,\mathbf{k}}(P(V))}{\partial V} \right] \quad (7)$$

(A quadratic fit of the frequencies with respect to volume will be considered,  $\nu_{i,\mathbf{k}}(P(V)) \equiv \nu_{i,\mathbf{k}}(V) = c \cdot V^2 + d \cdot V + f$ , so that  $\frac{\partial \nu_{i,\mathbf{k}}(P(V))}{\partial V} \equiv \frac{\partial \nu_{i,\mathbf{k}}(V)}{\partial V} = 2c \cdot V + d$ ).

$$S(P(V), T) = -k_B \sum_{i,\mathbf{k}} \ln \left[ 1 - \exp \left( \frac{-h \nu_{i,\mathbf{k}}(P(V))}{k_B T} \right) \right] + \frac{h}{T} \sum_{i,\mathbf{k}} \frac{\nu_{i,\mathbf{k}}(P(V))}{\exp \left( \frac{h \nu_{i,\mathbf{k}}(P(V))}{k_B T} \right) - 1} \quad (8)$$

$$G(P(V), T) = \underbrace{U(V)}_{=\text{EL}} + \underbrace{\frac{1}{2} \sum_{i,\mathbf{k}} h \nu_{i,\mathbf{k}}(P(V))}_{=\text{E0}} + \underbrace{h \sum_{i,\mathbf{k}} \frac{\nu_{i,\mathbf{k}}(P(V))}{\exp \left( \frac{h \nu_{i,\mathbf{k}}(P(V))}{k_B T} \right) - 1}}_{=\text{ET}} + \underbrace{P(V, T) \cdot V}_{=\text{PV}} - \underbrace{T \cdot S(P(V), T)}_{=\text{TS}} \quad (9)$$

**Notation:**  $U(V)$  (or EL) is the electronic energy, and has been obtained from a simulation for each volume  $V$ . There is a summation over all the  $i, \mathbf{k}$  frequencies. These frequencies have also been obtained from a simulation for that solid.  $h$  is the plank constant,  $k_B$  is the Boltzmann constant. The second and third term of Eq. 9 are also called E0 and ET.  $T$  is the temperature,  $P$  is the pressure,  $S$  is the entropy and  $G$  the Gibbs free energy.

For a given solid 1, all the frequencies  $\nu_{i,\mathbf{k}}$  and the electronic energy  $U$  are calculated by a simulation program and printed in an output file for a given volume. There are several output files, one for each different volume. For a given solid 2, there are also several output files, one for each volume. The simulation also prints out the entropy  $S$  for an array of temperatures that goes from 10K to 2000K with a step of 20.1K.

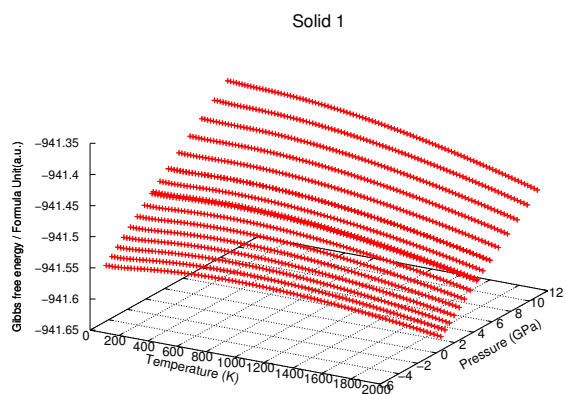
I have written a python program that:

- a) Extracts from the outputs the value of all the frequencies  $\nu_{i,\mathbf{k}}$  for each volume and for each solid.

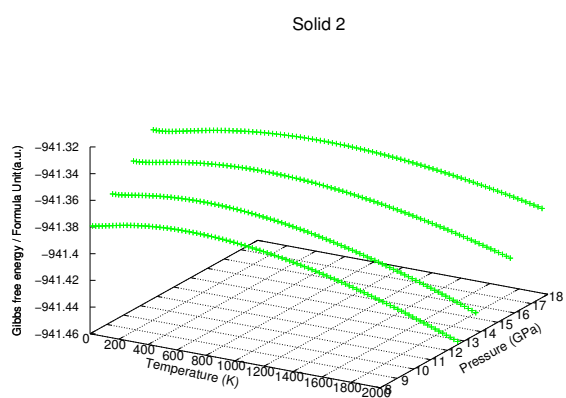
- b)* Extracts the value of entropy  $S$  for each temperature  $T$ , for each volume and for each solid.
- c)* Extracts the value of the different volumes  $V$ .
- d)* Performs the  $U$  vs  $V$  fit (Eq. 1).
- e)* Fits the quadratically frequencies as a function of the volume.
- f)* Calculates the pressure according to Eq. 7
- g)* Calculates the Gibbs free energy according to Eq. 9

## 2 Statement of the problem

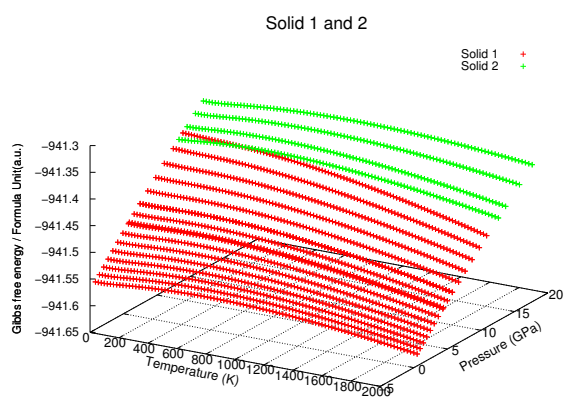
If we represent each solid separately, we get figs. 1a, 1b and 1c.



(a) G.Solid1.scatter.eps



(b) G.Solid2.scatter.eps



(c) G.Solid1.and.2.scatter.eps

**Figure 1:** Solid 1 and 2. Scatter plots. Scripts and data on the attached folder.

If you look at the file `solid_1__sorted_as_P_wise.dat` and `solid_2__sorted_as_P_wise.dat` there is overlapping data: solid 1 goes from a pressure of -4.41 GPa to 10.85 GPa, and solid 2 goes from 8.06 GPa to 17.64 GPa. The array of pressures is different on both solids. However, the array of temperatures is the same: from 10K to 2000K with a step of 20.1K.

The crossing between the surface of Solid 1 with the surface of Solid 2 will define a line / curve, that plotted in 2D in a Temperature-pressure diagram, will give me the phase boundary between these two compounds.

I would like to plot in a 2D temperature-pressure diagram this line / curve that arises from the crossing of both Gibbs free energy surfaces.

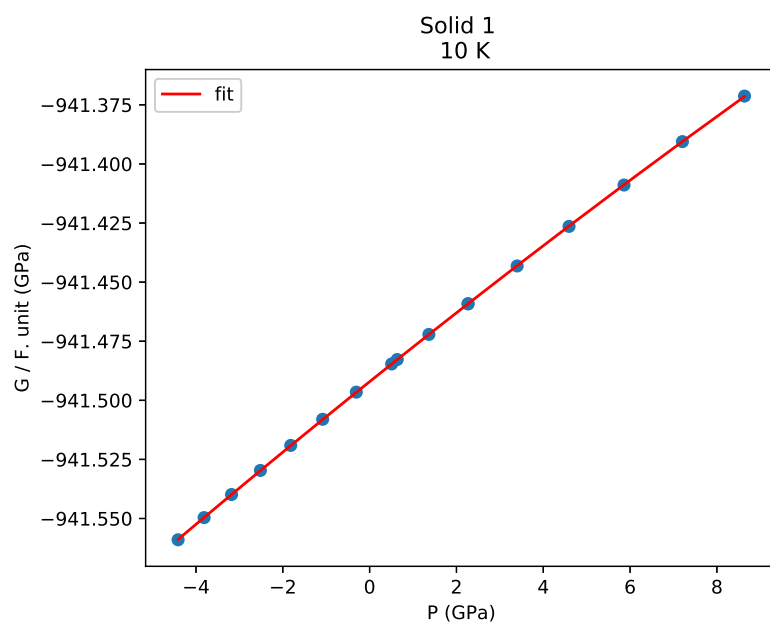
### 3 The way thought on how to attack this problem

Obtaining an analytical expression for  $G(T, P)$  can be quite complicated. For a given temperature, if we just assume a quadratic behaviour:

$$G(P) = a_0 + a_1P + a_2P^2 \quad (10)$$

and we plot it for 10.0 Kelvin for example, we get Fig. 2 (script: `y_variable__curve_fit.py`).

```
def func(y, a0, a1, a2):  
    return a0 + a1 * y + a2*y**2  
  
y_data, z_data, x_data = np.loadtxt('./10K.dat').T  
  
popt, pcov = curve_fit(func, y_data, z_data)
```

**Figure 2**

So, we could fit  $G(T, P)$  to:

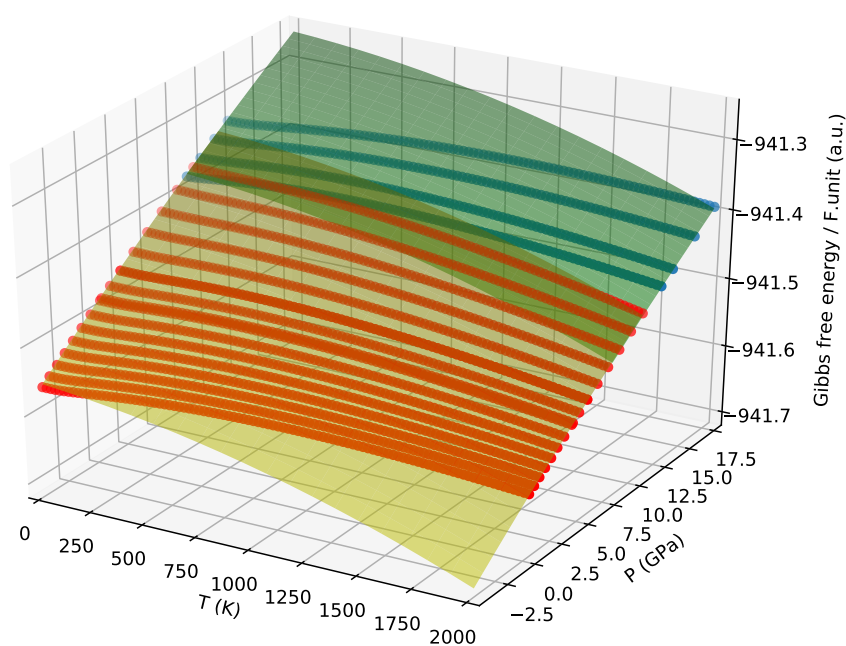
$$G(T, P) = a_0 + a_1P + a_2T + a_3P^2 + a_4T^2 + a_5TP \quad (11)$$

And we get the result on Fig. 3 (script: `x_and_y_variable_curve_fit.py`).

```
# Function to fit:
def func(X, a0, a1, a2, a3, a4, a5):
    x, y = X
    return a0 + a1*y + a2*x + a3*y**2 + a4*x**2 + a5*x*y

# Load data:
y_data, z_data, x_data = np.loadtxt('./1__scatter_xyz_sort_y_wise.dat').T
y_data_2, z_data_2, x_data_2 = np.loadtxt('./2__scatter_xyz_sort_y_wise.dat').T

# Calling non linear curve_fit
popt, pcov = curve_fit(func, (x_data, y_data), z_data)
popt_2, pcov_2 = curve_fit(func, (x_data_2, y_data_2), z_data_2)
```



**Figure 3**



Now, the intersection between these two surfaces is satisfied when:  $G^I(T, P) = G^{II}(T, P)$

```
# Setting "x" and "y" to be symbolic:
x, y = sym.symbols('x y', real=True)

z_I = a0 + a1*y + a2*x + a3*y**2 + a4*x**2 + a5*x*y
z_II = a0_s2 + a1_s2*y + a2_s2*x + a3_s2*y**2 + a4_s2*x**2 + a5_s2*x*y

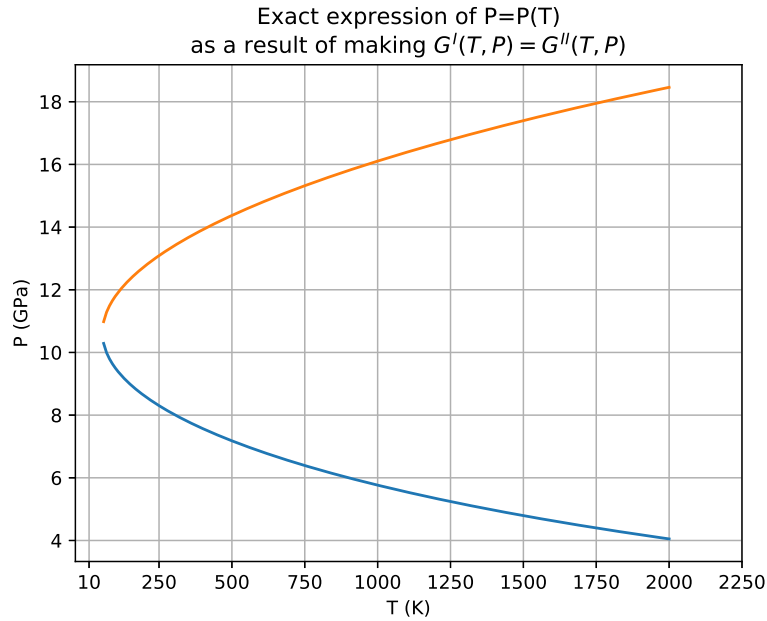
sol = sym.solve(z_I-z_II, y)

print 'sol =', sol
```

$G^I(T, P) = G^{II}(T, P)$  produces a function  $P = P(T)$ : But in this case, two solutions are found:

$$P = 0.000319T - 1.2223 \cdot 10^{-15} \sqrt{-1.07919 \cdot 10^{24}T^2 + 2.00910 \cdot 10^{28}T - 1.12101 \cdot 10^{30}} + 10.61 \quad (12)$$

$$P = 0.000319T + 1.2223 \cdot 10^{-15} \sqrt{-1.07919 \cdot 10^{24}T^2 + 2.00910 \cdot 10^{28}T - 1.12101 \cdot 10^{30}} + 10.61 \quad (13)$$



**Figure 4**

For  $T = 10.0$  both Eq. 12 and 13 are not defined (nan), because you get  $\sqrt{\text{neg. number}}$ . We can also try to plot the difference  $G^I(T, P) - G^{II}(T, P)$ , as a function of  $P$ , for a given temperature. We see that for a given temperature of 10.0K, the difference is not zero, and this explains why at 10.0K we did not observe solution in Fig. 4!

```
def G1(x,y):
    a0 = -941.487789748
    a1 = 0.014688246093
    a2 = -2.53546607894e-05
    a3 = -9.6435353414e-05
    a4 = -2.47408356408e-08
    a5 = 3.77057147803e-07
    return a0 + a1*y + a2*x + a3*y**2 + a4*x**2 + a5*x*y

def G2(x,y):
    a0_s2 = -941.483110904
    a1_s2 = 0.01381970471
    a2_s2 = -2.63051565187e-05
    a3_s2 = -5.5529184524e-05
    a4_s2 = -2.46707082089e-08
    a5_s2 = 3.50929634874e-07
    return a0_s2 + a1_s2*y + a2_s2*x + a3_s2*y**2 + a4_s2*x**2 + a5_s2*x*y

# NUMERIC:
def difference(x,y):
    return G1(x,y)-G2(x,y)

diff = []
press = np.linspace(8,15,1000)
fixed_T = 100
for p in press:
    diff.append(difference(fixed_T,p))
```

However, at 100K, the difference is positive and negative depending on which  $P$  (Fig. 6)

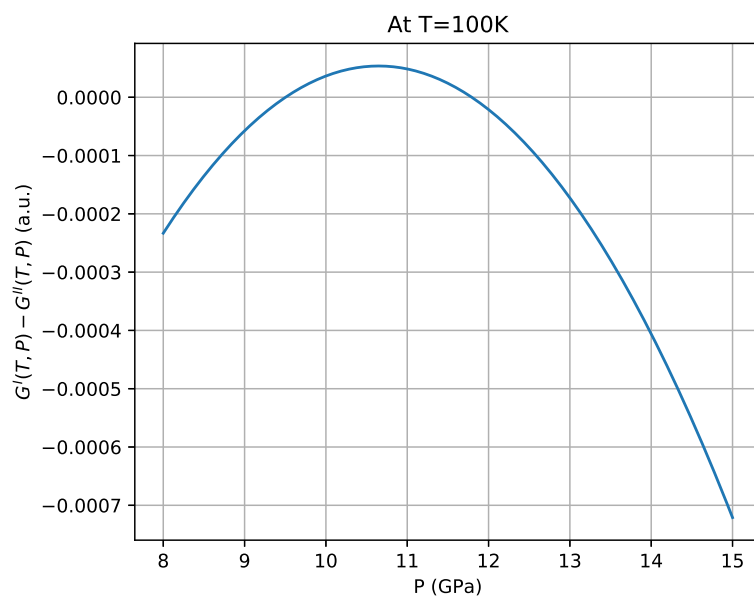


Figure 5

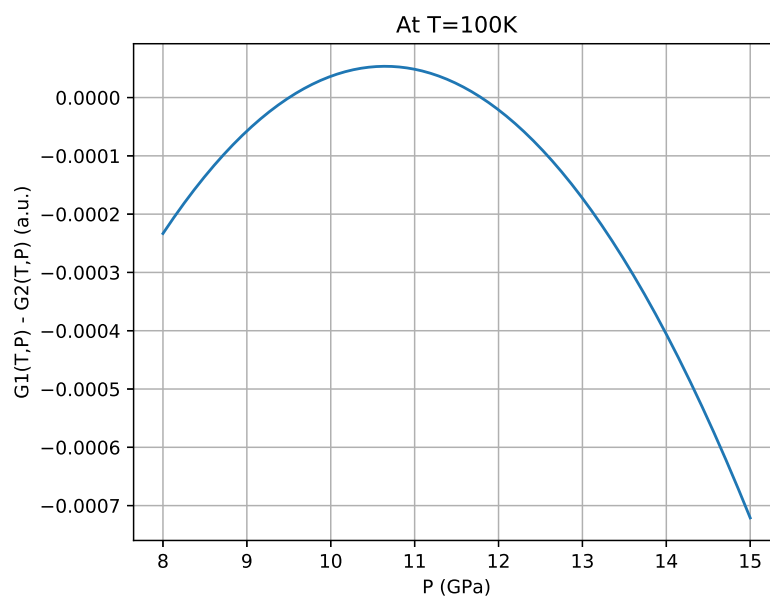
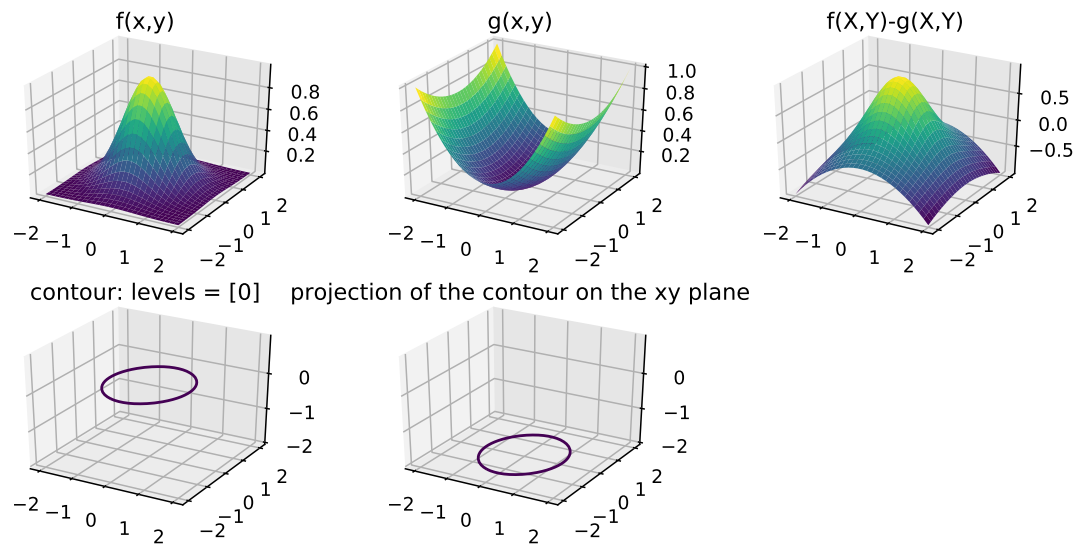


Figure 6

If we try to plot the contour of two intersected functions  $f(x, y)$  and  $g(x, y)$ :



**Figure 7**

If we apply this to our system,

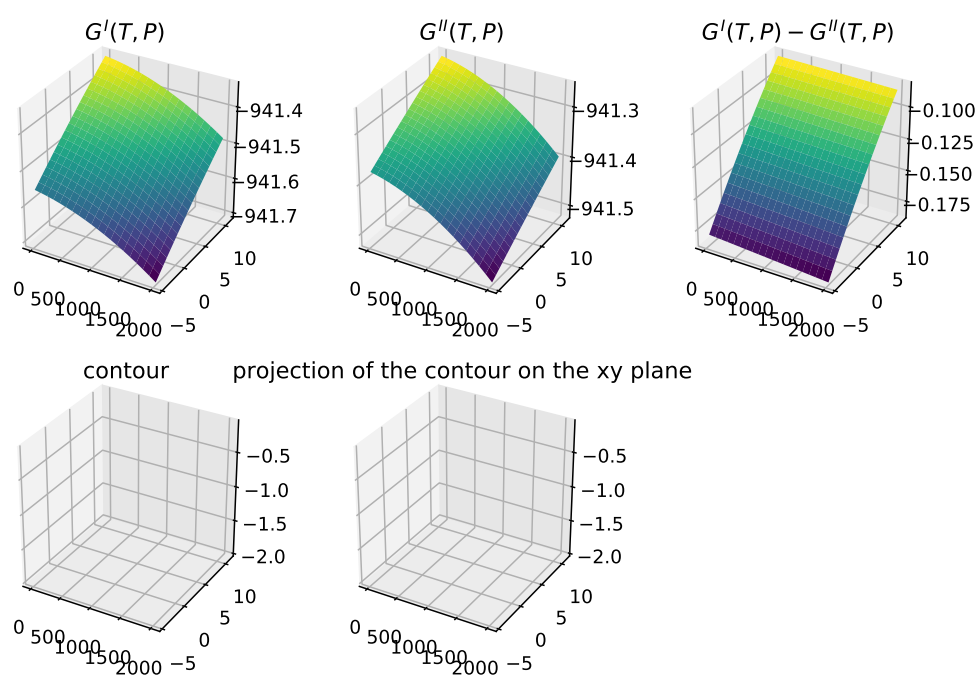
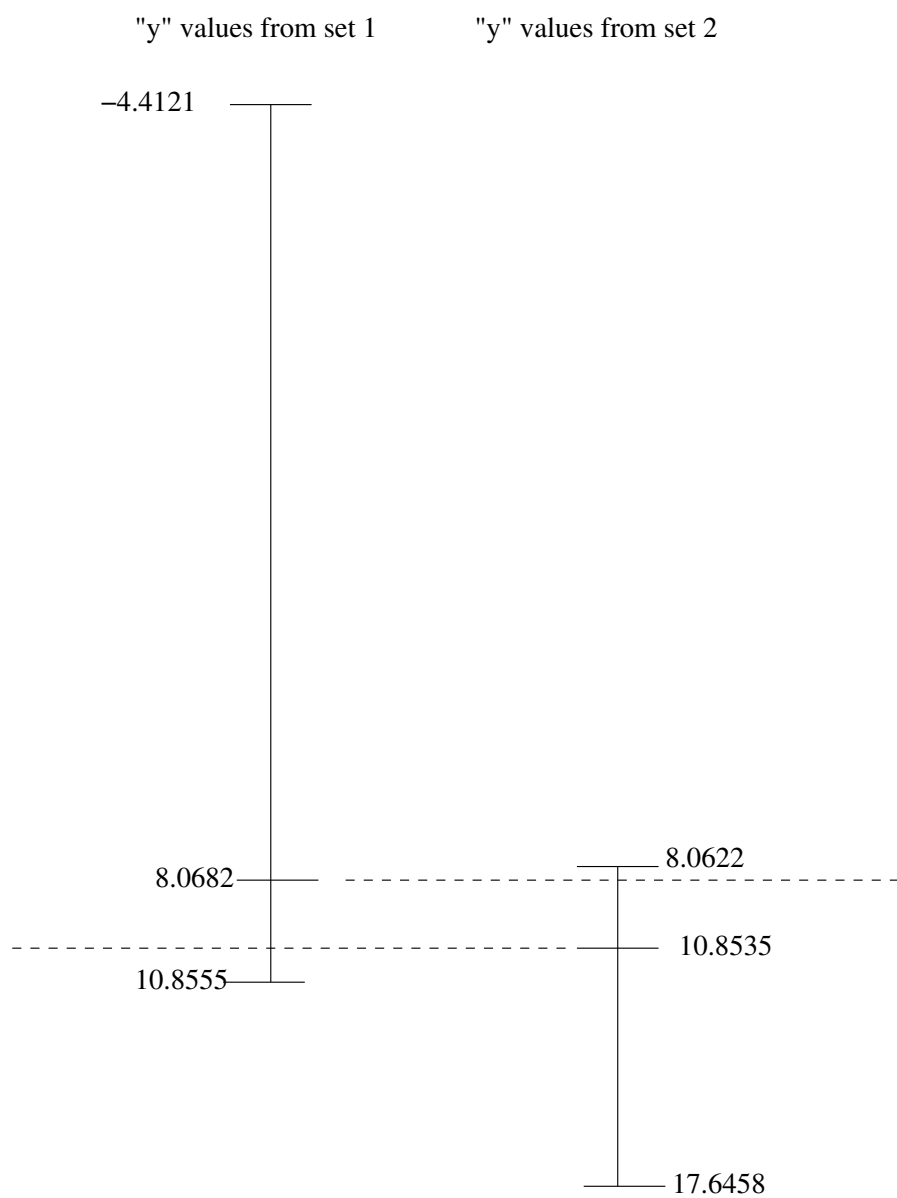


Figure 8

**Figure 9**