Suggested Volterra Exercise ?

$\boxed{8.2-19b}$

$$x_1 \left(\frac{\partial \bar{\theta}_1}{\partial X_1} \right)_{T,P} + X_2 \left(\frac{\partial \bar{\theta}_2}{\partial X_1} \right)_{T,P} = 0$$

I'll work with 8.2-19b since that is the more general and delicious form

recalling the definition of the volterra derivative

$$\frac{\delta \bar{\theta}_i}{\delta X_i} = \frac{\partial \bar{\theta}_i}{\partial X_i} - \frac{1}{c} \sum_{j=1}^{c} \frac{\partial \bar{\theta}_i}{\partial x_j}$$

lets now apply the definition of the volterra derivative to appease lord Beris and ascend into greek heaven

$$x_1 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} + \frac{1}{2} \left(\frac{\partial \bar{\theta}_1}{\partial x_1} + \frac{\partial \bar{\theta}_1}{\partial x_2} \right) \right) + x_2 \left(\frac{\delta \bar{\theta}_2}{\delta X_1} + \frac{1}{2} \left(\frac{\partial \bar{\theta}_2}{\partial x_1} + \frac{\partial \bar{\theta}_2}{\partial x_2} \right) \right) = 0$$

$$X_1 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + X_2 \left(\frac{\delta \bar{\theta}_2}{\delta X_1} \right) + \frac{1}{2} x_1 \left(\frac{\partial \bar{\theta}_1}{\partial x_1} + \frac{\partial \bar{\theta}_1}{\partial x_2} \right) + \frac{1}{2} X_2 \left(\frac{\partial \bar{\theta}_2}{\partial x_1} + \frac{\partial \bar{\theta}_2}{\partial x_2} \right) = 0$$

$$X_1 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + X_2 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + \frac{1}{2} \left[\sum_{i=1}^{2} X_i \left(\frac{\partial \bar{\theta}_i}{\partial X_1} \right) + \sum_{i=1}^{2} X_i \left(\frac{\partial \bar{\theta}_i}{\partial X_2} \right) \right] = 0$$

$$X_1 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + X_2 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + \frac{1}{2} \left[\sum_{j=1}^{2} \sum_{i=1}^{2} x_i \frac{\partial \theta_i}{\partial X_j} \right] = 0$$

the double sum is zero by gibbs - duhem, so,

$$X_1 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) + X_2 \left(\frac{\delta \bar{\theta}_1}{\delta X_1} \right) = 0$$

for $\bar{G}$ result would be the same. imagine i wrote these all as
const T, P

Part b

(b) now replacing the Volterra derivatives with their partial derivative counterparts

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1} - \frac{1}{2}\left(\frac{\partial\bar{\theta}_1}{\partial x_1} + \frac{\partial\bar{\theta}_1}{\partial x_2}\right)\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1} - \frac{1}{2}\left(\frac{\partial\bar{\theta}_2}{\partial x_1} + \frac{\partial\bar{\theta}_2}{\partial x_2}\right)\right) = 0$$

$$\frac{1}{2}x_1\left(\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) - \left(\frac{\partial\bar{\theta}_1}{\partial x_2}\right)\right) + \frac{1}{2}x_2\left(\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) - \left(\frac{\partial\bar{\theta}_2}{\partial x_2}\right)\right) = 0$$

$$x_1\left(\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) - \left(\frac{\partial\bar{\theta}_1}{\partial x_2}\right)\right) + x_2\left(\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) - \left(\frac{\partial\bar{\theta}_2}{\partial x_2}\right)\right) = 0$$

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) - x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_2}\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) - x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_2}\right) = 0$$

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) - \left[x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_2}\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_2}\right)\right] = 0$$

now, thanks to the dark magic of volterra we can kinda choose whichever of these to be zero that we'd like

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) - \sum_{j=1}^{2} x_i\left(\frac{\partial\bar{\theta}_i}{\partial x_2}\right) = 0$$

applying Gibbs-Duhem one last time

$$x_1\left(\frac{\partial\bar{\theta}_1}{\partial x_1}\right) + x_2\left(\frac{\partial\bar{\theta}_2}{\partial x_1}\right) = 0$$

praise be to lord beris.

Volterra Problem # 2

the gradient of g or f

$$\nabla g = \langle 2x_1 , 2x_2 \rangle$$

$$\nabla f = \langle 2(x_1 - 1) , 2(x_2 - 1) \rangle$$

in the molar plane

now projecting these into the physical plane

$$\tilde{\nabla} g = \langle 2x_1 , 2x_2 \rangle - \frac{1}{2}\left(\langle 2x_1 , 2x_2 \rangle \cdot \langle 1, 1 \rangle\right)\langle 1, 1 \rangle$$

$$= \langle 2x_1 , 2x_2 \rangle - \langle x_1 + x_2 , x_1 + x_2 \rangle$$

$$= \langle x_1 - x_2 , x_2 - x_1 \rangle$$

$$\hat{\nabla} f = \langle 2x_1 - 2 , 2x_2 - 2 \rangle - \frac{1}{2}\left(\langle 2x_1 - 2 , 2x_2 - 2 \rangle \cdot \langle 1, 1 \rangle\right)\langle 1, 1 \rangle$$

$$= \langle 2x_1 - 2 , 2x_2 - 2 \rangle - \langle x_1 + x_2 - 2 , x_1 + x_2 - 2 \rangle$$

$$= \langle x_1 - x_2 , x_2 - x_1 \rangle$$

See code below to make graphical representation

cheg325 homework1 volterra coding

AUTHOR
k.wodehouse

PUBLISHED
February 14, 2025

Graphing

$$\tilde{\nabla} g(x_1, x_2) =< x_1 - x_2,\ x_2 - x_1 >$$

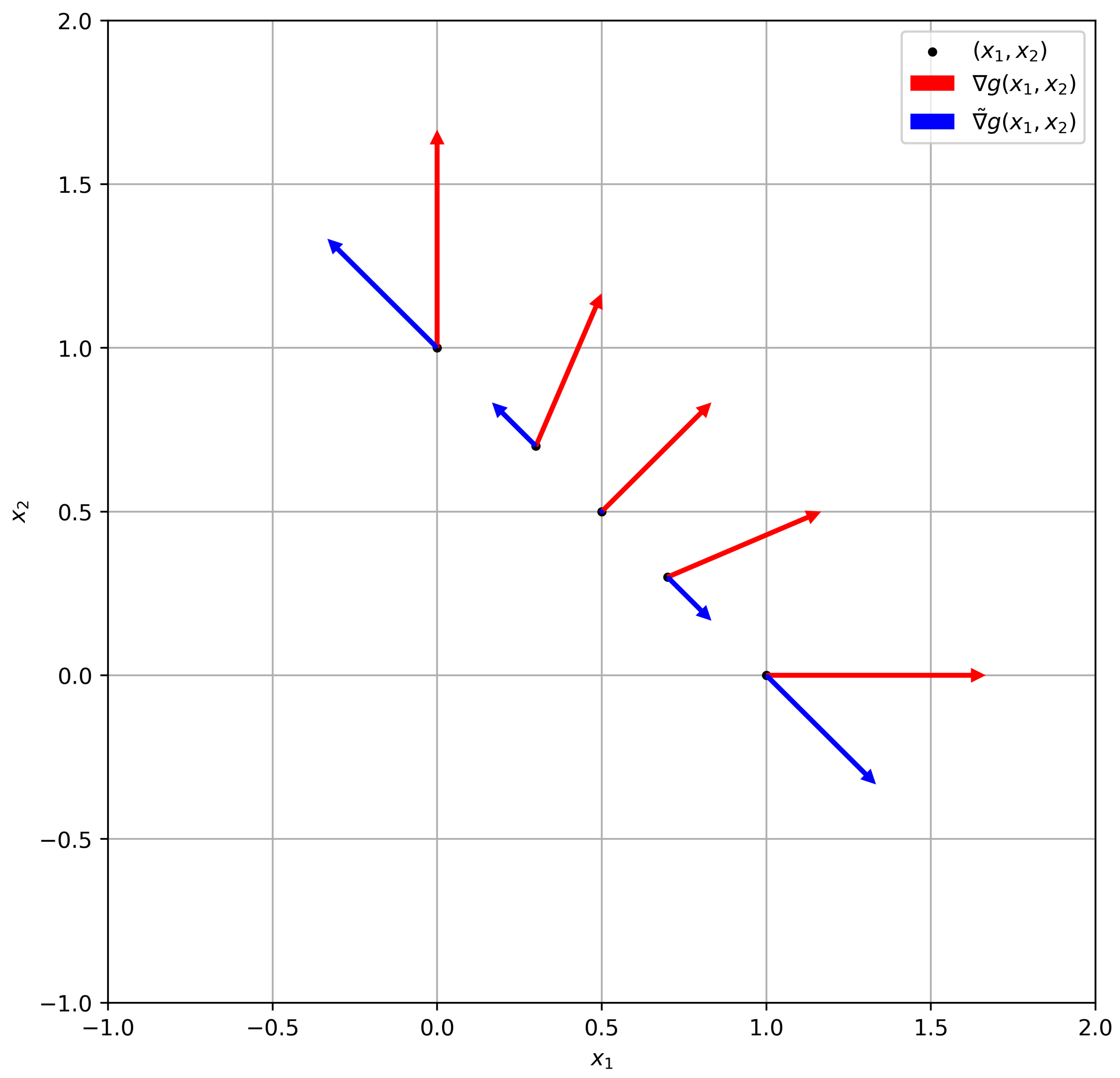
```
import numpy as np
import matplotlib.pyplot as plt

def molar_grad_g(x1, x2):
    return x1 - x2, x2 - x1

def grad_g(x1, x2):
    return 2*x1, 2*x2

x1 = np.array([1.0, 0.3, 0.5, 0.7, 0.0])
x2 = 1 - x1
xcomp, ycomp = molar_grad_g(x1, x2)
xcomp_grad, ycomp_grad = grad_g(x1, x2)


fig, ax = plt.subplots(figsize=(8,8), dpi=500, subplot_kw={'xlim':(-1,2), 'ylim':(-1,2),
ax.scatter(x1, x2, zorder=3, s=10, c='black')
ax.quiver(x1, x2, xcomp_grad, ycomp_grad, angles='xy', scale_units='xy', scale=3, width=0
ax.quiver(x1, x2, xcomp, ycomp, angles='xy', scale_units='xy', scale=3, width=0.005, zord
ax.grid(zorder=0)
ax.legend(['$(x_1, x_2)$', r'${\nabla}g(x_1, x_2)$' , r'$\tilde{\nabla}g(x_1, x_2)$']);
```



and now

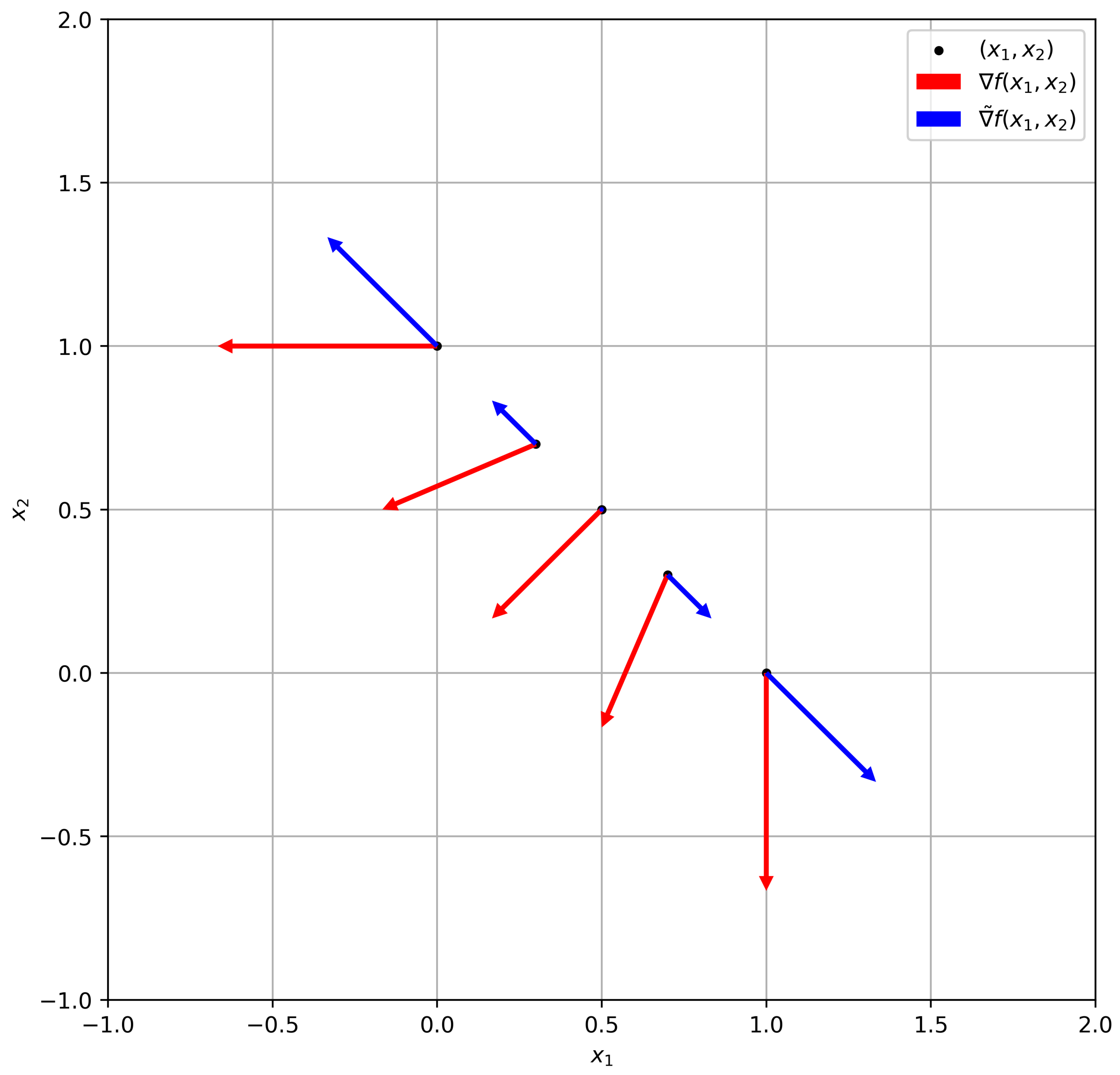
$$\tilde{\nabla} f(x_1, x_2) =< x_1 - x_2,\ x_2 - x_1 >$$

```
def molar_grad_f(x1, x2):
    return x1 - x2, x2 - x1

def grad_f(x1, x2):
    return 2*(x1 - 1), 2*(x2 - 1)

x1 = np.array([1.0, 0.3, 0.5, 0.7, 0.0])
x2 = 1 - x1
xcomp, ycomp = molar_grad_f(x1, x2)
xcomp_grad, ycomp_grad = grad_f(x1, x2)

fig, ax = plt.subplots(figsize=(8,8), dpi=500, subplot_kw={'xlim':(-1,2), 'ylim':(-1,2),
ax.scatter(x1, x2, zorder=3, s=10, c='black')
ax.quiver(x1, x2, xcomp_grad, ycomp_grad, angles='xy', scale_units='xy', scale=3, width=0
ax.quiver(x1, x2, xcomp, ycomp, angles='xy', scale_units='xy', scale=3, width=0.005, zord
ax.grid(zorder=0)
ax.legend(['$(x_1, x_2)$', r'${\nabla} f(x_1, x_2)$', r'$\tilde{\nabla} f(x_1, x_2)$']) ;
```




```
# this is filler text -- ignore.
```