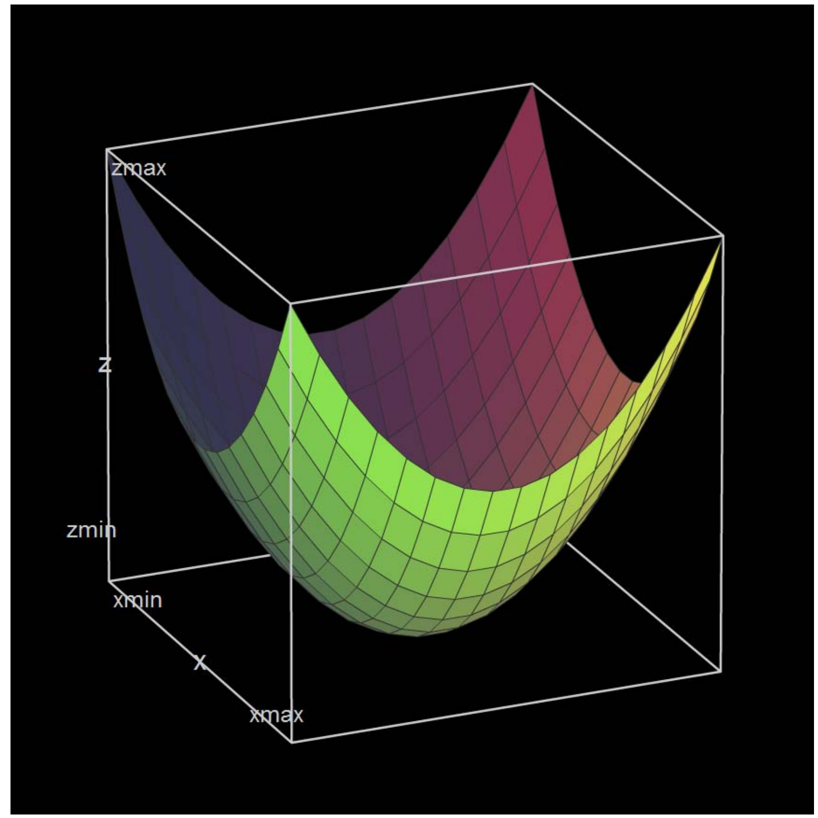
Multidimensional Functions

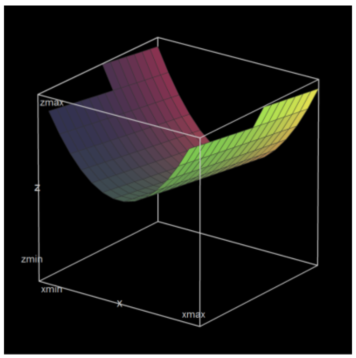
- Simple "3D" Function:
  $z = f(x, y) = x^2 + y^2$
- What's "the derivative?"
- Does our 2D definition even make sense?



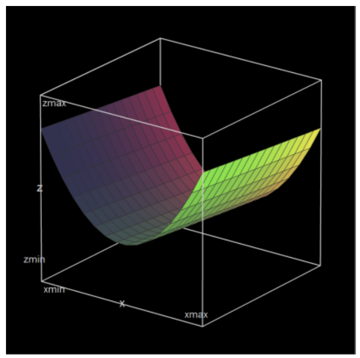
http://www.math.uri.edu/~bkaskosz/flashmo/graph3d/

Partial Derivative Example #1

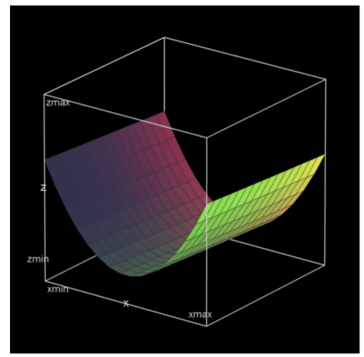
$$z = f(x, y) = x^2 + y^2,\ \left(\frac{\partial f}{\partial x}\right)_y = 2x$$



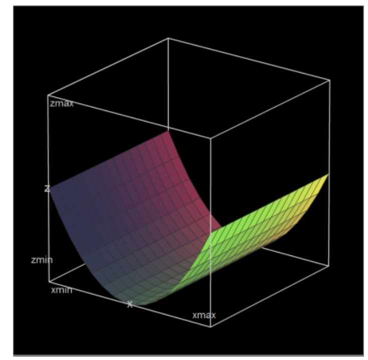
y = -1.05 to -0.95
x = -1 to 1



y = -0.8 to -0.7
x = -1 to 1



y = -0.55 to -0.45
x = -1 to 1



y = -0.05 to 0.05
x = -1 to 1

- Looking at small slices along y, the slope in the x-z plane is the same
- **Key result:** Partial derivatives tell us the slope in a specified plane!

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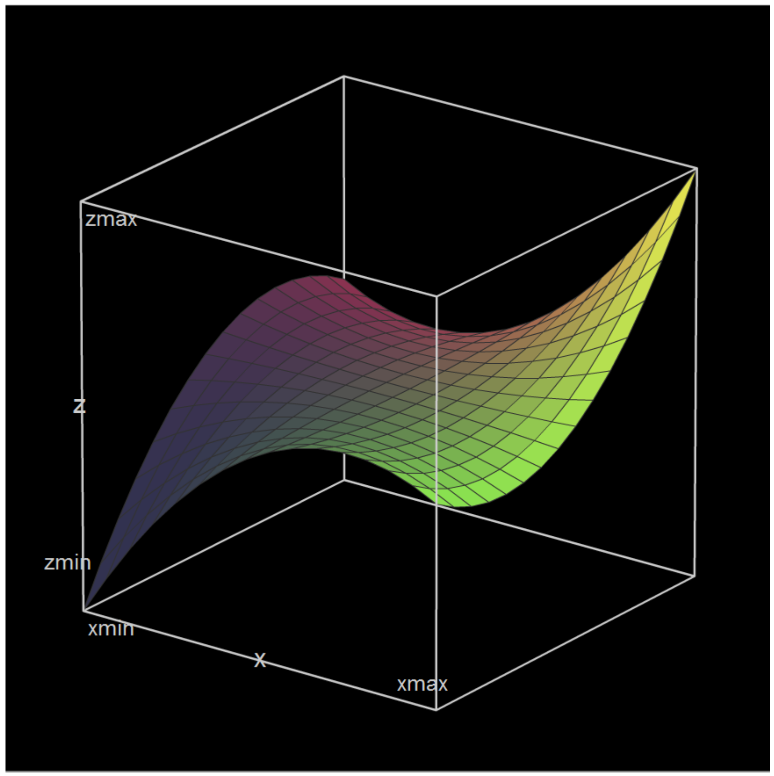
Partial Derivative Example #2

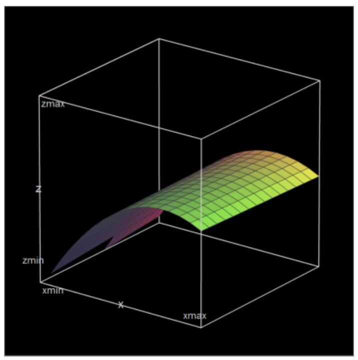
$$z = f(x, y) = x^2y + xy^2$$



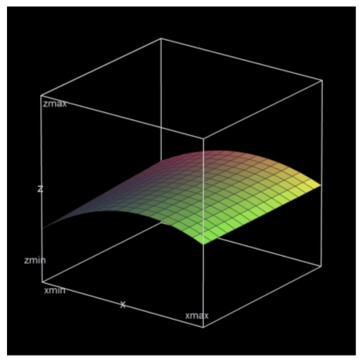
http://www.math.uri.edu/~bkaskosz/flashmo/graph3d/

Partial Derivative Example #2

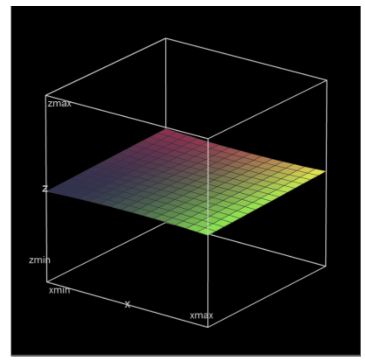
$$z = f(x, y) = x^2y + xy^2,\ \left(\frac{\partial f}{\partial x}\right)_y = 2xy + y^2$$



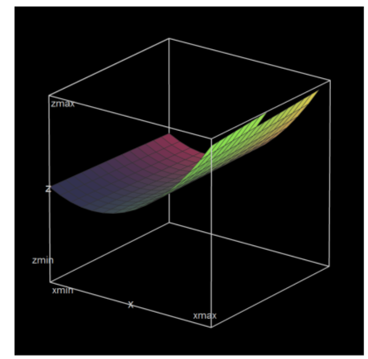
y = -1.05 to -0.95
x = -1 to 1



y = -0.55 to -0.45
x = -1 to 1



y = -0.05 to 0.05
x = -1 to 1



y = 0.95 to 1.05
x = -1 to 1

- Partial derivative depends on y, so slope in x-z plane will depend on *which* x-z plane
- **Just because y was constant *while* taking the derivative, doesn't mean it has to be constant afterward!**

http://www.math.uri.edu/~bkaskosz/flashmo/graph3d/

Partial Derivative Example #2

- First partial derivative with respect to x (y constant):

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy + y^2$$

- First partial derivative with respect to y (x constant):

$$\left(\frac{\partial f}{\partial y}\right)_x = x^2 + 2xy$$

- Second partial derivative with respect to y (x constant):

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = 2x + 2y$$

- Second partial derivative with respect to x (y constant):

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = 2x + 2y$$

Partial Derivative Example #2

- First partial derivative with … co…
- First partial derivative …

- Se… wi… co…

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = 2x + 2y$$

- …ative

$$\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y = 2x + 2y$$

- It’s true in general that:

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right]_y$$

Self Test: Ideal Gas Law

- Consider the ideal gas law:

$$V(P,T,n) = \frac{nRT}{P} = nRTP^{-1}$$

- Calculate the following:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} \text{ and } \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

Differentials

- If we know $y_0 = f(x_0)$ what's the change in y_0 if x_0 is changed a little (dx)?

$$y_0 + dy \approx f(x_0) + \left(\frac{dy}{dx}\right) dx = f(x_0) + \left(\frac{df}{dx}\right) dx$$

- Therefore:

$$dy = \left(\frac{df}{dx}\right) dx$$

Differentials relate a small change in one variable (dy) to a small change in other variable(s) (dx)

- What's the corresponding result for N-dimensions?

Differentials Example

- If h(x) = f(x)g(x), can we find dh?

$$\frac{dh}{dx} = \frac{d}{dx}[f(x)g(x)]$$

$$dh = \left[\left(\frac{df}{dx}\right)dx\right]g(x) + f(x)\left[\left(\frac{dg}{dx}\right)dx\right]$$

- Thus, it's true that:

$$dh = df \cdot g(x) + f(x) \cdot dg = f(x)dg + g(x)df$$

- Remember your homework?

$$d(PV) = PdV + VdP$$

Multidimensional Differentials

- If f = f(x, y, z), we can write the *exact differential* of f as:

$$df = \left(\frac{\partial f}{f x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

- This is a mathematical fact, not a thermodynamic one (shown without proof), but it ***must*** apply to all functions in thermodynamics

But I Don't Like Calculus…

- Last class, we determined that (for reversible processes, only PV work):

$$\Delta E = T\Delta S - P\Delta V$$

- For smaller changes:

$$dE = TdS - PdV$$

In other words, E is a "natural function" of S and V.

- Combine the math with the science: **Presto!**

$$T = \left(\frac{\partial E}{\partial S}\right)_V \text{ and } P = -\left(\frac{\partial E}{\partial V}\right)_S$$

Summary: Gibbs Energy Changes

- To calculate changes in Gibbs energy at constant P use: $\Delta G = \Delta H - T\Delta S$
  - All our tricks for entropy, enthalpy apply
  - Useful for calculating standard state reactions

- As a last resort use

$$\int d(\Delta G) = \int_{P_1}^{P_2} \Delta V dP - \int_{T_1}^{T_2} \Delta S dT$$

  - Where $\Delta X = X_{products} - X_{reactants}$

Summary: Gibbs Energy Changes

- If ΔS, ΔH constant vs. T:

$$\Delta G(T_2) - \Delta G(T_1) = \Delta S(T_2 - T_1)$$

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- Phase transitions: $\Delta G_{tr} = 0$
- Chemical reactions behave like enthalpy, entropy (why?)
- Pressure changes
  - Solids, liquids: $\Delta G(P_2) - \Delta G(P_1) = \Delta V(P_2 - P_1)$
  - Ideal gasses: $\Delta G(P_2) - \Delta G(P_1) = \Delta nRT \ln\left(\frac{P_2}{P_1}\right)$