Derivative Crusher Algorithm

by Ratindranath Akhoury

Typed in LaTeX by $\mathbb{E}$van $\mathbb{C}$arpenter

Winter 2022

Idea: A partial derivative with thermodynamically significant variables

$$\left(\frac{\partial x}{\partial y}\right)_z \text{ where } \{x, y, z\} \text{ can be any of } \{S, T, P, V, E, F, G, H\}$$

can be expressed in terms of in terms of first and second derivatives of fundamental relations. This rearranging of expressions is very useful in thermodynamics and statistical mechanics, as it allows us to find simple relations between physical quantities in a thermodynamical system. The Derivative Crusher Algorithm is an algorithm that "crushes" a thermodynamically significant partial derivative into useful and easily measureable quantities. Developed and taught by Professor Ratindranath Akhoury.

Choosing Gibbs Free Energy

Variable	Easy to keep fixed?	Easy to measure change?
S	**Yes**, Adiabatic processes	**No**, change in S depends on change in Q, which is hard to measure
T	**Yes**, with a heat bath or feedback system	**Yes**, by using a thermometer
V	**No**, not easily, thermal expansion of the container is a byproduct of the container being thermally conductive, the volume changes with heat	**Yes**
P	**Yes**, keeping equilibrium with atmosphere	**Yes**, barometer

Table 1: T, P are the easiest quantities to measure and control, making $G(T, P)$ the easiest fundamental relationship to work with.

$$E(S,V) \longrightarrow dE = TdS - PdV$$

$$F(T,V) = E - TS \longrightarrow dF = -SdT - PdV$$

$$G(T,P) = E - TS + pV \longrightarrow dG = -SdT + VdP$$

$$H(S,P) = E + pV \longrightarrow dH = TdS + VdP$$

Operations

The Derivative Crusher Algorithm is made of three operations and six relations. Looking at the derivatives of $G(T,P) = E - TS - PV$ more closely, certain constants can be defined:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = \boxed{-\left(\frac{\partial S}{\partial T}\right)_P \equiv \frac{C_p}{T}} \tag{C1}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = \boxed{\left(\frac{\partial V}{\partial P}\right)_T \equiv \kappa V} \tag{C2}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \boxed{\left(\frac{\partial V}{\partial T}\right)_P \equiv \alpha V} \tag{C3}$$

C_p is specific heat at constant pressure.
κ is isothermal compressibility.
α is volume coefficient of expansion.
The derivative crusher algorithm is made of three partial derivative operations:

1. Bringing y to the numerator:

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}} \tag{D1}$$

2. Bringing z to the numerator:

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}} \tag{D2}$$

3. Introduce new variable w:

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial w}\right)_z}{\left(\frac{\partial y}{\partial w}\right)_z}} \tag{D3}$$

The last crucial component are the Maxwell Relations between S, V, T, P:

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \tag{M1}$$

$$\boxed{\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S} \tag{M2}$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \tag{M3}$$

Steps of the Algorithm

1. Bring potentials E, F, G, H to the numerator (D1 or D2) and eliminate them using:

$$dE = TdS - PdV \qquad dF = -SdT - PdV$$

$$dG = -SdT + VdP \qquad dH = TdS + VdP$$

2. Bring S to numerator using Maxwell Relations depending on what z is in $\left(\frac{\partial x}{\partial y}\right)_z$

$$z = T \qquad \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad , \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

$$z = P, V \quad \boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad , \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}}$$

3. Bring V to numerator in order to get α or κ.
4. Eliminate C_v in favor of C_p, α, κ