Derivative Crusher Algorithm

by Ratindranath Akhoury

Typed in LaTeX by Evan Carpenter

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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 first and second derivatives of fundamental relations. This re-arranging 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.

$$\begin{aligned}
E(S,V) &\longrightarrow dE = TdS - PdV\\
F(T,V) = E - TS &\longrightarrow dF = -SdT - PdV\\
G(T,P) = E - TS + pV &\longrightarrow dG = -SdT + VdP\\
H(S,P) = E + pV &\longrightarrow dH = TdS + VdP
\end{aligned}$$

Operations

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

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \equiv \frac{C_p}{T} = \frac{1}{T}\left(\frac{\partial Q}{\partial T}\right)_P \tag{C1}$$

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

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

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:

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

2. Bringing z to the numerator:

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

3. Introduce new variable w:

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

The last crucial component are the Maxwell Relations between S, V, T, P: [1]

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

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

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

$$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S \tag{M4}$$

[1] Note that in the one dimensional case, pressure is force (negative by convention): $P \to -F$ and $V \to X$

Steps of the Algorithm

1. Bring potentials (E, F, G, H) to the numerator (using 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.

$$\boxed{\frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa}}$$

4. Eliminate C_V in favor of C_p, α, κ A trick for going from $C_V \to C_P$ uses another useful derivative trick:

$$\left(\frac{\partial x}{\partial y}\right)_w = \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_w$$

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_P + \left(\frac{\partial Q}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_P + T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$C_V = C_P + T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{C_P - C_V = VT\frac{\alpha^2}{\kappa}} = R$$