Lecture 16: Second Derivatives of Thermodynamic Potentials

Wednesday, February 19, 2020

Let's examine the derivatives $\frac{\partial^2 U}{\partial S^2}$, $\frac{\partial^2 U}{\partial S \partial V}$, and $\frac{\partial^2 U}{\partial V^2}$. First, let's write out our usual equation and transform it with a product rule:

$$\begin{aligned} \mathrm{d}U &= T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N \\ \mathrm{d}(U + PV) &= T\,\mathrm{d}S + V\,\mathrm{d}P + \mu\,\mathrm{d}N \end{aligned}$$

We can now define some derivatives of this equation:

$$\frac{1}{V}\frac{\partial V}{\partial T}\bigg|_{P,N} = \alpha$$

Here, α is the thermal expansion at a constant pressure (usually written in units related to the volume).

$$K_T = -\frac{1}{V}\,\frac{\partial V}{\partial P}\bigg|_{T,N}$$

K_T is the isothermal compressibility.

$$C_V = \frac{1}{N}\frac{đQ}{\mathrm{d}T}\bigg|_{V,N} = \frac{1}{N}\frac{T\,\mathrm{d}S}{\mathrm{d}T}\bigg|_{V,N} = \frac{T}{N}\,\frac{\partial S}{\partial T}\bigg|_{V,N}$$

is the heat capacity at constant volume and

$$C_P = \frac{T}{N}\,\frac{\partial S}{\partial T}\bigg|_{P,N}$$

is the heat capacity at constant pressure.

We need to relate partial derivatives of various quantities to other quantities which are usually easier to measure. One method is by Maxwell relations:

$$\begin{aligned} U &\longrightarrow \mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N \implies \frac{\partial T}{\partial V}\bigg|_{S,N} = -\frac{\partial P}{\partial S}\bigg|_{V,N} \\ F &\longrightarrow \mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}N \implies \frac{\partial \mu}{\partial T}\bigg|_{N,V} = -\frac{\partial S}{\partial N}\bigg|_{T,V} \\ &\vdots \end{aligned}$$

Suppose we wanted to find a relation for

$$\frac{\partial T}{\partial P}\bigg|_{S,\mu} = \frac{\partial ?}{\partial ?}\bigg|_{?}$$

We need the differentials of P, S, and μ, so we want one of the potentials of the form

$$T\,\mathrm{d}S + V\,\mathrm{d}P - N\,\mathrm{d}\mu$$

Knowing that we can switch the order of second derivatives (take one derivative first),

$$\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial T}{\partial P}\bigg|_{S,\mu} = \frac{\partial V}{\partial S}\bigg|_{P,\mu}$$

Additionally, we can often write

$$\frac{\partial A}{\partial B}\bigg|_{C,D} = \frac{1}{\frac{\partial B}{\partial A}\big|_{C,D}}$$

The Maxwell relations can usually be written in this form. The other method for deriving these relations is using Jacobians. In general,

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial v}{\partial x}\Big|_y & \frac{\partial v}{\partial y}\Big|_x \\ \frac{\partial v}{\partial x}\Big|_y & \frac{\partial v}{\partial y}\Big|_x \end{vmatrix}$$

Using relations with products of determinants, we can prove that

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}$$

Another interesting property is that exchanging rows or columns in the Jacobian introduces minus signs:

$$\frac{\partial(A,B,C)}{\partial(X,Y,Z)} = -\frac{\partial(C,B,A)}{\partial(X,Y,Z)} = -\frac{\partial(A,B,C)}{\partial(Y,X,Z)}$$

Another interesting property is that

$$\frac{\partial(u,y)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x}\Big|_y & \frac{\partial u}{\partial y}\Big|_x \\ \underbrace{\frac{\partial y}{\partial x}\Big|_y}_{0} & \underbrace{\frac{\partial y}{\partial y}\Big|_x}_{1} \end{vmatrix} = \frac{\partial u}{\partial x}\Big|_y$$

Because $\mathrm{d}U$ is an exact derivative,

$$\mathrm{d}(\mathrm{d}U) = 0 = \mathrm{d}T\,\mathrm{d}S - \mathrm{d}P\,\mathrm{d}V + \mathrm{d}\mu\,\mathrm{d}N$$

Suppose we fix N, then

$$\mathrm{d}T\,\mathrm{d}S = \mathrm{d}P\,\mathrm{d}V$$

or

$$\frac{\partial(T,S)}{\partial(P,V)} = 1$$

Additionally, we can use the properties we found above to write

$$\frac{\partial P}{\partial T}\Big|_{V,N} = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(T,V)} = \frac{\partial V}{\partial T}\Big|_P \frac{1}{\frac{\partial(T,V)}{\partial(P,T)}} = \frac{\frac{\partial V}{\partial T}\Big|_P}{-\frac{\partial V}{\partial P}\Big|_T} = \frac{\alpha}{K_T}$$

We have shown that

$$\frac{\partial P}{\partial T}\Big|_{V,N} = \frac{\alpha}{K_T}$$

the right-hand side of which is something that can be measured.

Another relation that can be derived is

$$C_P - C_P = T\frac{V}{N}\frac{\alpha^2}{K_T} > 0$$

We will prove this in a future lecture.