2.8: Maxwell Relations

Maxwell relations are conditions equating certain derivatives of state variables which follow from the exactness of the differentials of the various state functions.

Relations deriving from $E(S,V,N)$

The energy $E(S,V,N)$ is a state function, with

$$dE = T\,dS - p\,dV + \mu\,dN\ , \tag{2.8.1}$$

and therefore

$$T = \bigg(\frac{\partial E}{\partial S}\bigg)_{V,N} \qquad , \qquad -p = \bigg(\frac{\partial E}{\partial V}\bigg)_{S,N} \qquad , \qquad \mu = \bigg(\frac{\partial E}{\partial N}\bigg)_{S,V} . \tag{2.8.2}$$

Taking the mixed second derivatives, we find

$$\begin{aligned}
\frac{\partial^2 E}{\partial S\,\partial V} &= \bigg(\frac{\partial T}{\partial V}\bigg)_{S,N} = -\bigg(\frac{\partial p}{\partial S}\bigg)_{V,N} \\
\frac{\partial^2 E}{\partial S\,\partial N} &= \bigg(\frac{\partial T}{\partial N}\bigg)_{S,V} = \bigg(\frac{\partial \mu}{\partial S}\bigg)_{V,N} \\
\frac{\partial^2 E}{\partial V\,\partial N} &= -\bigg(\frac{\partial p}{\partial N}\bigg)_{S,V} = \bigg(\frac{\partial \mu}{\partial V}\bigg)_{S,N} .
\end{aligned}$$

Relations deriving from $F(T,V,N)$

The energy $F(T,V,N)$ is a state function, with

$$dF = -S\,dT - p\,dV + \mu\,dN\ , \tag{2.8.3}$$

and therefore

$$-S = \bigg(\frac{\partial F}{\partial T}\bigg)_{V,N} \qquad , \qquad -p = \bigg(\frac{\partial F}{\partial V}\bigg)_{T,N} \qquad , \qquad \mu = \bigg(\frac{\partial F}{\partial N}\bigg)_{T,V} . \tag{2.8.4}$$

Taking the mixed second derivatives, we find

$$\begin{aligned}
\frac{\partial^2 F}{\partial T\,\partial V} &= -\bigg(\frac{\partial S}{\partial V}\bigg)_{T,N} = -\bigg(\frac{\partial p}{\partial T}\bigg)_{V,N} \\
\frac{\partial^2 F}{\partial T\,\partial N} &= -\bigg(\frac{\partial S}{\partial N}\bigg)_{T,V} = \bigg(\frac{\partial \mu}{\partial T}\bigg)_{V,N} \\
\frac{\partial^2 F}{\partial V\,\partial N} &= -\bigg(\frac{\partial p}{\partial N}\bigg)_{T,V} = \bigg(\frac{\partial \mu}{\partial V}\bigg)_{T,N} .
\end{aligned}$$

Relations deriving from $\mathcal{H}(S,p,N)$

The enthalpy $\mathcal{H}(S,p,N)$ satisfies

$$d\mathcal{H} = T\,dS + V\,dp + \mu\,dN\ , \tag{2.8.5}$$

which says $\mathcal{H} = \mathcal{H}(S,p,N)$, with

$$T = \bigg(\frac{\partial \mathcal{H}}{\partial S}\bigg)_{p,N} \qquad , \qquad V = \bigg(\frac{\partial \mathcal{H}}{\partial p}\bigg)_{S,N} \qquad , \qquad \mu = \bigg(\frac{\partial \mathcal{H}}{\partial N}\bigg)_{S,p} . \tag{2.8.6}$$

Taking the mixed second derivatives, we find

$$
\begin{aligned}
\frac{\partial^2\mathcal{H}}{\partial S\,\partial p} &= \left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \\
\frac{\partial^2\mathcal{H}}{\partial S\,\partial N} &= \left(\frac{\partial T}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \\
\frac{\partial^2\mathcal{H}}{\partial p\,\partial N} &= \left(\frac{\partial V}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial p}\right)_{S,N} .
\end{aligned}
$$

Relations deriving from $G(T,p,N)$

The Gibbs free energy $G(T,p,N)$ satisfies

$$
dG = -S\,dT + V\,dp + \mu\,dN\ , \tag{2.8.7}
$$

therefore $G = G(T,p,N)$, with

$$
-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad , \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} . \tag{2.8.8}
$$

Taking the mixed second derivatives, we find

$$
\begin{aligned}
\frac{\partial^2 G}{\partial T\,\partial p} &= -\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} \\
\frac{\partial^2 G}{\partial T\,\partial N} &= -\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} \\
\frac{\partial^2 G}{\partial p\,\partial N} &= \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} .
\end{aligned}
$$

Relations deriving from $\Omega(T,V,\mu)$

The grand potential $\Omega(T,V,\mu)$ satisfied

$$
d\Omega = -S\,dT - p\,dV - N\,d\mu\ , \tag{2.8.9}
$$

hence

$$
-S = \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \quad , \quad -p = \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \quad , \quad -N = \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} . \tag{2.8.10}
$$

Taking the mixed second derivatives, we find

$$
\begin{aligned}
\frac{\partial^2\Omega}{\partial T\,\partial V} &= -\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial p}{\partial T}\right)_{V,\mu} \\
\frac{\partial^2\Omega}{\partial T\,\partial \mu} &= -\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial T}\right)_{V,\mu} \\
\frac{\partial^2\Omega}{\partial V\,\partial \mu} &= -\left(\frac{\partial p}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial V}\right)_{T,\mu} .
\end{aligned}
$$

Relations deriving from $S(E,V,N)$

We can also derive Maxwell relations based on the entropy $S(E,V,N)$ itself. For example, we have

$$
dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN\ . \tag{2.8.11}
$$

Therefore $S = S(E,V,N)$ and

$$\frac{\partial^2 S}{\partial E\, \partial V = \left(\frac{\partial(T^{-1})}{\partial V}\right)_{E,N} = \left(\frac{\partial(pT^{-1})}{\partial E}\right)_{V,N}}\ , \tag{2.8.12}$$

et cetera.

Generalized thermodynamic potentials

We have up until now assumed a generalized force-displacement pair $(y, X) = (-p, V)$. But the above results also generalize to magnetic systems, where $(y, X) = (H, M)$. In general, we have

$$\begin{aligned}
&\backslash\text{tt THIS}\backslash\text{tt}\backslash\ \text{SPACE AVAILABLE} && dE = T\, dS + y\, dX + \mu\, dN \\
&F = E - TS && dF = -S\, dT + y\, dX + \mu\, dN \\
&\mathcal{H} = E - yX && d\mathcal{H} = T\, dS - X\, dy + \mu\, dN \\
&G = E - TS - yX && dG = -S\, dT - X\, dy + \mu\, dN \\
&\Omega = E - TS - \mu N && d\Omega = -S\, dT + y\, dX - N\, d\mu\ .
\end{aligned}$$

Generalizing $(-p, V) \rightarrow (y, X)$, we also obtain, *mutatis mutandis*, the following Maxwell relations:

$$\begin{aligned}
&\left(\frac{\partial T}{\partial X}\right)_{S,N} = \left(\frac{\partial y}{\partial S}\right)_{X,N} && \left(\frac{\partial T}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial S}\right)_{X,N} && \left(\frac{\partial y}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial X}\right)_{S,N} \\
&\left(\frac{\partial T}{\partial y}\right)_{S,N} = -\left(\frac{\partial X}{\partial S}\right)_{y,N} && \left(\frac{\partial T}{\partial N}\right)_{S,y} = \left(\frac{\partial \mu}{\partial S}\right)_{y,N} && \left(\frac{\partial X}{\partial N}\right)_{S,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{S,N} \\
&\left(\frac{\partial S}{\partial X}\right)_{T,N} = -\left(\frac{\partial y}{\partial T}\right)_{X,N} && \left(\frac{\partial S}{\partial N}\right)_{T,X} = -\left(\frac{\partial \mu}{\partial T}\right)_{X,N} && \left(\frac{\partial y}{\partial N}\right)_{T,X} = \left(\frac{\partial \mu}{\partial X}\right)_{T,N} \\
&\left(\frac{\partial S}{\partial y}\right)_{T,N} = \left(\frac{\partial X}{\partial T}\right)_{y,N} && \left(\frac{\partial S}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial T}\right)_{y,N} && \left(\frac{\partial X}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{T,N} \\
&\left(\frac{\partial S}{\partial X}\right)_{T,\mu} = -\left(\frac{\partial y}{\partial T}\right)_{X,\mu} && \left(\frac{\partial S}{\partial \mu}\right)_{T,X} = \left(\frac{\partial N}{\partial T}\right)_{X,\mu} && \left(\frac{\partial y}{\partial \mu}\right)_{T,X} = -\left(\frac{\partial N}{\partial X}\right)_{T,\mu}\ .
\end{aligned}$$