Maxwell's Relations

Each extensive degree of freedom in the energy equation has a conjugate force:

$-P \longleftrightarrow V$

$T \longleftrightarrow S$

$\mu_i \longleftrightarrow N_i$

μ_i ← chemical potential for species i

$$dU = TdS - pdV + \sum_k \mu_k dN_k$$

There are also other forms of work:

$f \longleftrightarrow L$		force – length
$\gamma \longleftrightarrow A$		surface tension — area
$\phi \longleftrightarrow Q$		electric potential — charge
$B \longleftrightarrow I$		magnetic field — magnetic moment

In general

$$\mathcal{F}_j = \left(\frac{\partial U}{\partial x_j}\right)_{S,V,\vec{N},x_{i\neq j}}$$

$\mathcal{F}$ = generalized force

X = generalized extensive variable

$$dU = TdS - pdV + \sum_k \mu_k dN_k + f dL + \gamma dA + \phi dQ + B dI + \sum_j \mathcal{F}_j dX_j$$

← Fundamental energy equation

What is the appropriate free energy when $T, P, N,$ & A are held constant?

$$dU = TdS - pdV + \mu dN + \gamma dA$$

This also defines: $\gamma = \left(\frac{\partial U}{\partial A}\right)_{S,N,V}$

The natural variables for U in this case are

S, V, N, A

but we've specified that T & P are independent, so we have to transform to a free energy which makes this so:

$$U - TS + PV = G$$

$$dU - TdS - SdT + pdV + Vdp = dG$$

$$\cancel{TdS} - \cancel{pdV} + \mu dN + \gamma dA - \cancel{TdS} - SdT + \cancel{pdV} + Vdp = dG$$

$$dG = -SdT + Vdp + \mu dN + \gamma dA$$

(Natural variables are T, P, N, A)

and this also defines:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,N}$$

The Maxwell relations interrelate partial derivatives

$$dF = -SdT - pdV + \mu dN$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$ ← cross derivatives are equal for the state functions

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_T$$

$\left(\frac{\partial F}{\partial V}\right)_T = -p$ ← we get these from looking at the dF expression

$\left(\frac{\partial F}{\partial T}\right)_V = -S$

$$\therefore \quad -\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$\downarrow$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$ ← one of the Maxwell relations

A recipe for finding Maxwell's relations

Suppose you want to know how the entropy of a material changes when it is squeezed: $\left(\frac{\partial S}{\partial P}\right)_{T,N}$
(maybe we also have a fixed quantity N & temperature T)

- The independent variables are: T, P, N

- What free energy is a natural function of these variables? $G(T,P,N)$

- What's the differential form of the free energy expression?

$$dG = -SdT + VdP + \mu dN$$

- Identify the partial you want:

$$-S = \frac{\partial G}{\partial T}$$

$$\frac{-\partial S}{\partial P} = \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)$$

$$= \frac{\partial V}{\partial T}$$

$\therefore$

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$$

↑ this is much easier to measure than the quantity we're interested in!

Perhaps table 9.1 in Dill & Bromberg is useful...

Susceptibilities are useful

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

α has intensive units $[K^{-1}]$

α = the thermal expansion coefficient

The Maxwell relation tells us:

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

if $\alpha > 0$, then increasing the pressure orders the material

if $\alpha < 0$, then increasing the pressure disorders the material.

Most materials have $\alpha > 0$

ideal gas:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \qquad V = \frac{NkT}{P}$$

$$\frac{\partial V}{\partial T} = \frac{Nk}{P}$$

$$\alpha = \frac{P}{NkT}\,\frac{Nk}{P} = \frac{1}{T}$$ which is always > 0

Cold water is anomalous – it has $\alpha < 0$ so applying pressure disorders it. (cold H_2O is cage-like, and applying pressure distorts & disorders the cages)

We can use α to find $S(P)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_{T,N} dP$$

$$= \left(-\frac{\partial V}{\partial T}\right)_{P,N} dP = -\alpha V\, dP$$

So:

$$\Delta S = -\int_{P_1}^{P_2} \alpha(P) V(P)\, dP$$

Another easily-measured susceptibility is

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \text{isothermal compressibility}$$

for an ideal gas, $\frac{\partial V}{\partial P} = \frac{\partial}{\partial P}\left(\frac{NkT}{P}\right) = \frac{-NkT}{P^2}$

$$\therefore \quad \kappa = \frac{-P}{NkT}\left(\frac{-NkT}{P^2}\right) = \frac{1}{P}$$

Water also has an anomalous $\kappa(T)$: it is less compressible between $0°$ and $46°C$

An example: How does U change with volume?
This will tell us about cohesive forces in the materials.
How could we get this information from experiments?

Start with $U(T,V)$ & $S(T,V)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

Fundamental Energy equation

$$dU = T\,dS - p\,dV$$

$$\left(\frac{\partial u}{\partial v}\right)_T dV + \left(\frac{\partial u}{\partial T}\right)_V dT = T\left[\left(\frac{\partial s}{\partial v}\right)_T dV + \left(\frac{\partial s}{\partial T}\right)_V dT\right] - p dV$$

When T is constant,

$$\left(\frac{\partial u}{\partial v}\right)_T \cancel{dV} = \left(T\left(\frac{\partial s}{\partial v}\right)_T - p\right)\cancel{dV}$$

Use a Maxwell relation for $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$\left(\frac{\partial p}{\partial T}\right)_V$ ≀ thermal pressure coefficient

$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk}{V}$ for an ideal gas,

$$\therefore \left(\frac{\partial u}{\partial v}\right)_T = \frac{NkT}{V} - p = 0$$

For typical liquids however $T\left(\frac{\partial p}{\partial T}\right)_V - p < 0$
at high densities & > 0 at high densities!

high ρ	low ρ
$V\downarrow$ $u\uparrow$	$V\uparrow$ $u\uparrow$
Pushing against repulsive forces	Pulling apart attractive forces

Fundamental Function	Variables to Relate	Maxwell's Relation
$U(S,V,N)$	S,V	$(\partial T/\partial V)_{S,N} = -(\partial p/\partial S)_{V,N}$
$dU = T\,dS - p\,dV + \mu\,dN$	S,N	$(\partial T/\partial N)_{S,V} = (\partial \mu/\partial S)_{V,N}$
	V,N	$-(\partial p/\partial N)_{S,V} = (\partial \mu/\partial V)_{S,N}$
$F(T,V,N)$	T,V	$(\partial S/\partial V)_{T,N} = (\partial p/\partial T)_{V,N}$
$dF = -S\,dT - p\,dV + \mu\,dN$	T,N	$-(\partial S/\partial N)_{T,V} = (\partial \mu/\partial T)_{V,N}$
	V,N	$-(\partial p/\partial N)_{T,V} = (\partial \mu/\partial V)_{T,N}$
$H(S,p,N)$	S,p	$(\partial T/\partial p)_{S,N} = (\partial V/\partial S)_{p,N}$
$dH = T\,dS + V\,dp + \mu\,dN$	S,N	$(\partial T/\partial N)_{S,p} = (\partial \mu/\partial S)_{p,N}$
	p,N	$(\partial V/\partial N)_{S,p} = (\partial \mu/\partial p)_{S,N}$
(S,V,μ)	S,V	$(\partial T/\partial V)_{S,\mu} = -(\partial p/\partial S)_{V,\mu}$
$T\,dS - p\,dV - N\,d\mu$	S,μ	$(\partial T/\partial \mu)_{S,V} = -(\partial N/\partial S)_{V,\mu}$
	V,μ	$(\partial p/\partial \mu)_{S,V} = (\partial N/\partial V)_{S,\mu}$
$G(T,p,N)$	T,p	$-(\partial S/\partial p)_{T,N} = (\partial V/\partial T)_{p,N}$
$dG = -S\,dT + V\,dp + \mu\,dN$	T,N	$-(\partial S/\partial N)_{T,p} = (\partial \mu/\partial T)_{p,N}$
	p,N	$(\partial V/\partial N)_{T,p} = (\partial \mu/\partial p)_{T,N}$
(T,V,μ)	T,V	$(\partial S/\partial V)_{T,\mu} = (\partial p/\partial T)_{V,\mu}$
$-S\,dT - p\,dV - N\,d\mu$	T,μ	$(\partial S/\partial \mu)_{T,V} = (\partial N/\partial T)_{V,\mu}$
	V,μ	$(\partial p/\partial \mu)_{T,V} = (\partial N/\partial V)_{T,\mu}$
(S,p,μ)	S,p	$(\partial T/\partial p)_{S,\mu} = (\partial V/\partial S)_{p,\mu}$
$T\,dS + V\,dp - N\,d\mu$	S,μ	$(\partial T/\partial \mu)_{S,p} = -(\partial N/\partial S)_{p,\mu}$
	p,μ	$(\partial V/\partial \mu)_{S,p} = -(\partial N/\partial p)_{S,\mu}$
(T,p,μ)	S,p	$-(\partial S/\partial p)_{T,\mu} = (\partial V/\partial T)_{p,\mu}$
$-S\,dT + V\,dp - N\,d\mu$	T,μ	$(\partial S/\partial \mu)_{T,p} = (\partial N/\partial T)_{p,\mu}$
	p,μ	$(\partial V/\partial \mu)_{T,p} = -(\partial N/\partial p)_{T,\mu}$

Source: HB Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition. Wiley, New York, 1985.

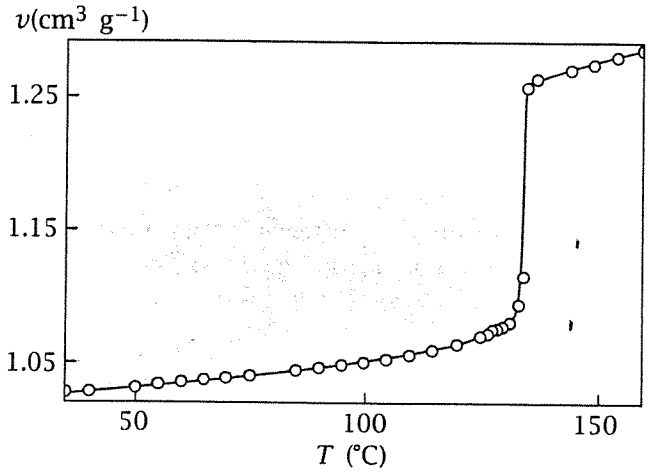

Figure 9.2 The specific volume v (volume per unit mass) of polyethylene versus temperature T. According to Equation (9.13), the thermal expansion coefficient α is proportional to the slope dv/dT. At low temperature, polyethylene is a hard crystalline plastic material. On melting at around 130°C, the specific volume v increases sharply and α is large. Source: JE Mark, A Eisenberg, WW Graessley, L Mandelkern, and JL Koenig, *Physical Properties of Polymers*, 2nd edition, American Chemical Society, Washington, DC, 1993. Data are from FA Quinn Jr and L Mandelkern, *J Am Chem Soc* **83**, 2857 (1961).

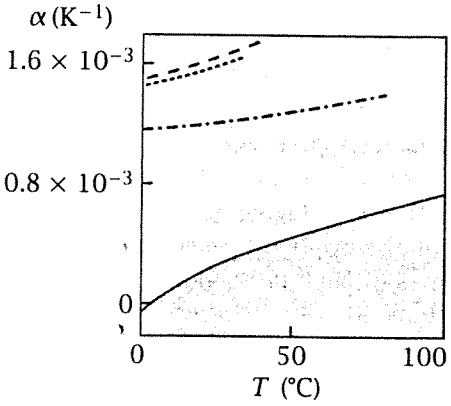

Figure 9.3 Thermal expansion coefficients α measured at atmospheric pressure for water (——), benzene (–·–·–), n-pentane (·····), and diethyl ether (– – –). Source: A Hvidt, *Acta Chemica Scand A* **32**, 675–680 (1978). Data for water are from GS Kell, *J Chem Eng Data* **20**, 97 (1975). Data for benzene, n-pentane, and diethyl ether are from Landolt–Börnstein, *Physikalisch–Chemisch Tabellen II*, 5. Auflage, 1232 (1923).

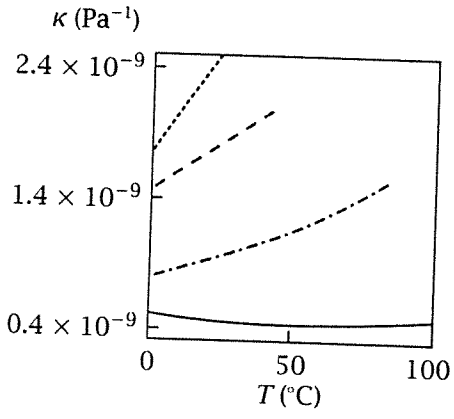

Figure 9.5 Compressibilities κ measured at atmospheric pressure for water (——), benzene (–·–·–), n-pentane (·····), and diethyl ether (– – –). Source: A Hvidt, *Acta Chemica Scand A* **32**, 675–680 (1978). Data for water are from GS Kell, *J Chem Eng Data* **20**, 97 (1975). Data for benzene are from *CRC Handbook of Chemistry and Physics*, 55th edition, CRC Press, Boca Raton, FL, 1974–1975, F-16. Data for pentane and diethyl ether are from Landolt–Börnstein, *Physikalisch–Chemisch Tabellen I*, 5. Auflage, 97–100 (1923).