For fixed $N \Rightarrow$ Maxwell Relations.

mixed partial derivatives must be equal.

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

$$\left.\frac{\partial}{\partial S}\right|_V \qquad \left.\frac{\partial}{\partial V}\right|_S$$

$$-\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial^2 U}{\partial V\,\partial S} = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial^2 H}{\partial P\,\partial S} = \frac{\partial^2 H}{\partial S\,\partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial V\,\partial T} = \frac{\partial^2 F}{\partial T\,\partial V} = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T \quad \left.\frac{\partial}{\partial P}\right|_T \left(\frac{\partial G}{\partial T}\right)_P = \frac{\partial^2 G}{\partial P\,\partial T} = \frac{\partial^2 G}{\partial T\,\partial P} = \left.\frac{\partial}{\partial T}\right|_P \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Thermodynamic Square

Gibbs – Duhem

if the system is extensive

$$U(S, V, N)$$

$$\left[U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)\right] \frac{\partial}{\partial \lambda}\Bigg|_{\lambda=1}$$

$$\left(\frac{\partial U}{\partial S}\right)_{VN} S + \left(\frac{\partial U}{\partial V}\right)_{SN} V + \left(\frac{\partial U}{\partial N}\right)_{SV} N = U$$

$$TS + (-P)V + \mu N = U$$

$$dU = T dS + S dT - P dV - V dP + \mu dN + N d\mu$$

$$\boxed{0 = S dT - V dP + N d\mu}$$ Gibbs – Duhem

$$dG = V dP - S dT + \mu dN = N d\mu + \mu dN$$

$$G = \mu N \implies \mu = \frac{G}{N}$$

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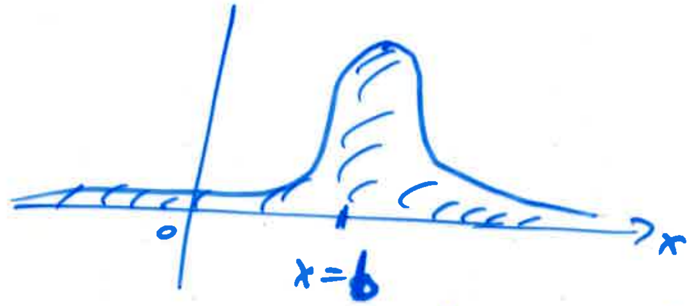
③ Grand Potential = Grand Canonical Potential = ~~= Thermodynamic Potential~~ = Landau Potential

$$\Omega = \Phi = F - \mu N = F - G = -PV$$

Gaussian Integrals

integrand $A e^{-(x-b)^2}$



Bell curve, Normal distribution

$$I = \int_{x=-\infty}^{\infty} e^{-x^2}\,dx = ?$$

$$I^2 = \left(\int_{x=-\infty}^{\infty} e^{-x^2}\,dx\right)\left(\int_{y=-\infty}^{\infty} e^{-y^2}\,dy\right)$$

x and y are dummy variables of integration

$$= \int_{x=-\infty}^{\infty}\int_{y=-\infty}^{\infty} e^{-x^2}\cdot e^{-y^2}\,dx\,dy = \int_{x=-\infty}^{\infty}\int_{y=-\infty}^{\infty} e^{-(x^2+y^2)}\,\underbrace{dx\,dy}_{dA}$$

Reinterpret as an area integral in the x-y plane.
Switch from Cartesian (x,y) coordinates to Polar (r, φ)

$$I^2 = \int_{r=0}^{\infty}\int_{\varphi=0}^{2\pi} e^{-r^2}\, r\,dr\,d\varphi = \underbrace{\left(\int_{\varphi=0}^{2\pi} d\varphi\right)}_{2\pi}\left(\int_{r=0}^{\infty} r e^{-r^2}\,dr\right)$$

Notice $\frac{d}{dr}\left(e^{-r^2}\right) = -2re^{-r^2}$

$$I^2 = 2\pi\left(-\frac{1}{2}\right)\int_{r=0}^{\infty} d\left(e^{-r^2}\right) = -\pi\, e^{-r^2}\Big|_{r=0}^{\infty}$$

$$= -\pi\left[0-1\right] = \pi$$

$$\boxed{I = \sqrt{\pi} = \int_{x=-\infty}^{\infty} e^{-x^2}\,dx}$$

change variables $x = \sqrt{a}\,z$, $dx = \sqrt{a}\,dz$

$x \to \pm\infty \Rightarrow z = \pm\infty$

$$I = \sqrt{\pi} = \int_{z=-\infty}^{\infty} e^{-az^2}\sqrt{a}\,dz$$

$$\int_{z=-\infty}^{+\infty} e^{-az^2}\,dz = \sqrt{\frac{\pi}{a}}$$

differentiate both sides with respect to a.

$$\frac{d}{da}\int_{z=-\infty}^{\infty} e^{-az^2}\,dz = \frac{d}{da}\sqrt{\frac{\pi}{a}}$$

$$= \int_{z=-\infty}^{\infty} (-z^2)\,e^{-az^2}\,dz = \sqrt{\pi}\,\frac{d}{da}a^{-1/2} = \frac{-\sqrt{\pi}}{2a^{3/2}}$$

↑ z is a dummy – rename to x

$$\int_{x=-\infty}^{\infty} x^2 e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$

$$\vdots$$

$$\int_{x=-\infty}^{\infty} x^{2n} e^{-ax^2}\,dx = \,?$$

$n = 0, 1, 2, 3, \ldots$

odd n?

integrand is odd in x
$f(-x) = -f(x)$ e.g. sine

$$\int_{x=-\infty}^{\infty} \underbrace{x^{2n+1} e^{-ax^2}}_{f(x)}\,dx = 0 \quad \forall n$$