

Show that $\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x \left(\frac{\partial f}{\partial x}\right)_y = -1$

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$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy$$

$$dy = \left(\frac{\partial y}{\partial f}\right)_x df + \left(\frac{\partial y}{\partial x}\right)_f dx$$

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f \left[\left(\frac{\partial y}{\partial f}\right)_x df + \left(\frac{\partial y}{\partial x}\right)_f dx \right]$$

$$dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x \right] df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial x}\right)_f dx$$

matching the coefficients for dx and df

$$0 = \left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x \quad ; \quad 1 = \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial x}\right)_f$$

and final results

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1 \quad ; \quad \frac{1}{\left(\frac{\partial x}{\partial y}\right)_f} = \left(\frac{\partial y}{\partial x}\right)_f$$

Description of the state of a system

Energy: U

Entropy and temperature: S, T

Generalized forces and displacements:

pressure, volume: p, V

tension, length: τ, L

chemical potential, particle number: μ, N

magnetic field, magnetization: B, M

Response functions: $\kappa_x = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_x$; $x = \{T, S\}$
 $C_x = T \left(\frac{\partial S}{\partial T} \right)_x$; $x = \{V, p\}$

What constitutes a complete description of a system?

How many variables can be independent chosen?

How many EOSs do we need to know everything?

Are some EOSs more complete than others?

Internal energy as a function of S, V, N

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

First order (partial) derivatives:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T; \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p; \quad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

The thermodynamic relations involving first order derivatives of the energy are sometimes called equations of state in a strict sense because they are experimentally determined. $U(S,V,N)$ can be calculated from them by integration up to a (irrelevant) constant.

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Second order derivatives: $\left(\frac{\partial^2 U}{\partial S^2}\right)_{N,V}$

$$\left(\frac{\partial^2 U}{\partial S^2}\right), \quad \left(\frac{\partial^2 U}{\partial V^2}\right), \quad \left(\frac{\partial^2 U}{\partial N^2}\right)$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right), \quad \left(\frac{\partial^2 U}{\partial V \partial S}\right), \quad \left(\frac{\partial^2 U}{\partial S \partial N}\right), \quad \left(\frac{\partial^2 U}{\partial N \partial S}\right) \text{ etc. (9 total)}$$

They are not all independent: because a state function must be a conservative function, the order of the partial derivatives in the second order partial derivatives can be switched without changing the value:

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right), \quad \left(\frac{\partial^2 U}{\partial S \partial N}\right) = \left(\frac{\partial^2 U}{\partial N \partial S}\right), \quad \left(\frac{\partial^2 U}{\partial V \partial N}\right) = \left(\frac{\partial^2 U}{\partial N \partial V}\right)$$

Maxwell relations

$$\left(\frac{\partial^2 U}{\partial S \partial V} \right) = \left(\frac{\partial^2 U}{\partial V \partial S} \right)$$
$$\left(\frac{\partial T}{\partial V} \right)_{S,N} = - \left(\frac{\partial p}{\partial S} \right)_{V,N}$$

For 3 independent state functions, there are 3 Maxwell relations for the internal energy U .

**Response functions are second order partial derivatives.
How many should there be?**

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The ones we have defined so far all are for constant N :

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p,N} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} \quad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,N}$$

$$c_p = \frac{1}{N} T \left(\frac{\partial S}{\partial T} \right)_{p,N} \quad c_V = \frac{1}{N} T \left(\frac{\partial S}{\partial T} \right)_{V,N}$$

For constant N : $U(S, V, N) = U(S, V)$

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there are 3 independent second order partial derivatives:

$$\left(\frac{\partial^2 U}{\partial S^2}\right), \quad \left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right), \quad \left(\frac{\partial^2 U}{\partial V^2}\right)$$

and hence there can only be 3 independent response functions.

Out 5 standard response functions we only need to know 3 and can calculate the other 2. This explains the existence of the well known thermodynamic identities:

$$c_p = c_V + \frac{\alpha^2 TV}{N \kappa_T}$$
$$\kappa_T = \kappa_S + \frac{\alpha^2 TV}{N c_p}$$

What about the well known relation $\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}$?

Internal energy as a function of T, V, N

Common: we want to control the temperature: $U = U(T, V, N)$

First order (partial) derivatives:

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = ? \quad ; \quad \left(\frac{\partial U}{\partial V}\right)_{T,N} = ? \quad ; \quad \left(\frac{\partial U}{\partial N}\right)_{T,V} = ?$$

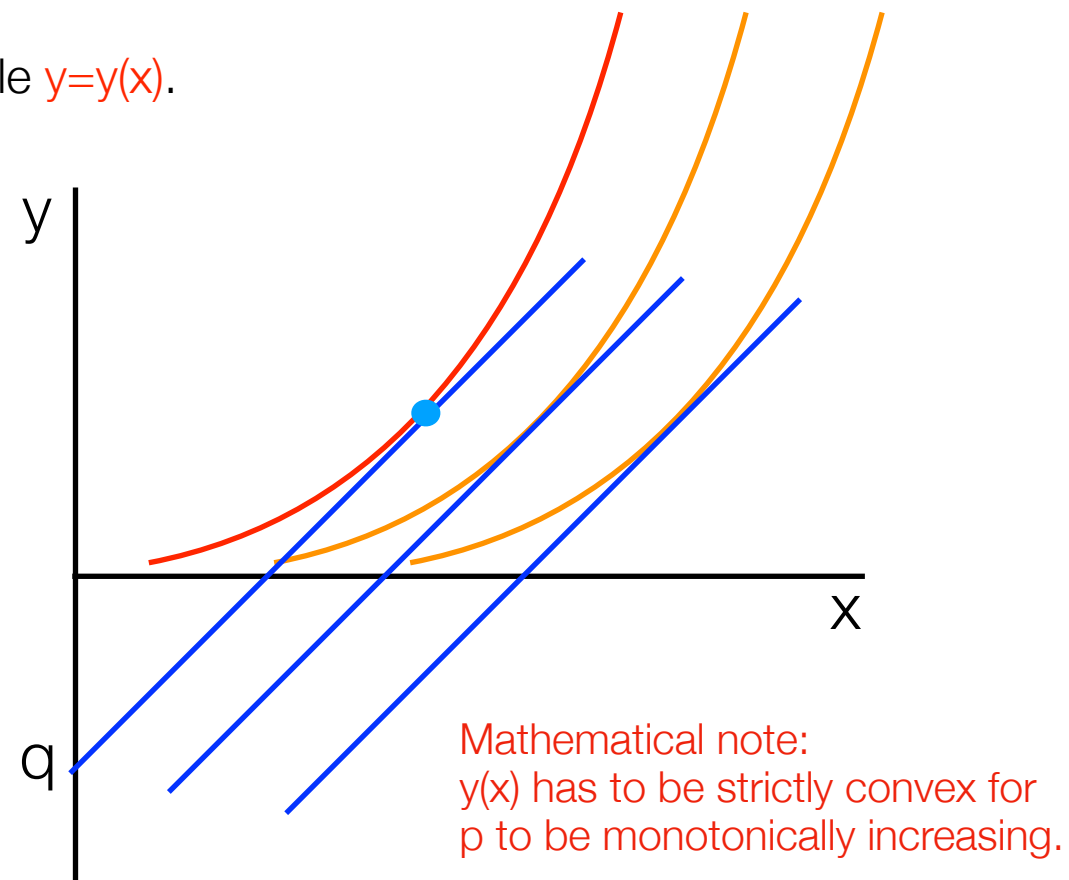
Loss of information!

Simple example: Consider a function of one variable $y=y(x)$.

Any point $(x,y=y(x))$ defines a state.

The derivative is $p=dy/dx = p(x)$ and inverting this relationship $x = x(p)$ we find $y=y(x(p)) = y(p)$.

Unfortunately any function $y(x-a)$ gives the same $y(p)$ and we have lost all information about a . To describe a state given by points (x,y) with the slope p we need to replace y with y -intercept of the slope q $(x,y) \rightarrow (p,q)$:



$y = px + q$ or $q = y - px$ which defines the Legendre transform $y[p]$ of $y(x)$.

Helmholtz Free Energy

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

$$F(T, V, N) \equiv U[T] = U - TS$$

Note on notation: Many textbooks use F to denote the Helmholtz Free Energy, but some use A (German for labor (Arbeit), including our textbook. I prefer F .

$$dF = \left(\frac{\partial F}{\partial T} \right)_{V,N} dT + \left(\frac{\partial F}{\partial V} \right)_{T,N} dV + \left(\frac{\partial F}{\partial N} \right)_{T,V} dN$$

To identify the partial derivatives of F start with total differential of F : dF

$$dF = dU - TdS - SdT$$

and use the thermodynamic identity,

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

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$$dF = dU - TdS - SdT$$

and using the thermodynamic identity,

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we arrive at

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

and

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} ; \quad p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} ; \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

Enthalpy

$$H(S, p, N) \equiv U[p] = U + pV$$

Gibbs Free Energy

$$G(T, p, N) \equiv U[T, p] = U - ST + pV$$

Maxwell relations

Fundamental relations