Kapitel 8

Maxwell-Beziehungen & Antwortkoeffizienten

8.2 Ableitungen in einkomp. Systemen

c) Beispielhafte Umformung

- $\left(\frac{\partial T}{\partial p}\right)_V \longleftrightarrow \frac{\partial^2 U}{\partial \ldots \partial \ldots}$?

- Vorgehen:

(i) $T = T(p,V) \longrightarrow dT = \boxed{\left(\frac{\partial T}{\partial p}\right)_V} dp + \left(\frac{\partial T}{\partial V}\right)_p dV$ (8.13)

(ii) Trafo: $p,V \longrightarrow S,V$ [kanon. Variable von U]

für $p = p(S,V) \longrightarrow dp = \left(\frac{\partial p}{\partial S}\right)_V dS + \left(\frac{\partial p}{\partial V}\right)_S dV$ (8.14)

in (8.13): $dT = \underbrace{\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial S}\right)_V}_{=\left(\frac{\partial T}{\partial S}\right)_V} dS + \underbrace{\ldots\ldots}_{\text{nicht wichtig}} dV$

$$\xrightarrow[p = -\frac{\partial U}{\partial V}]{T = \frac{\partial U}{\partial S}} \quad \left(\frac{\partial T}{\partial p}\right)_V = \frac{\left(\frac{\partial^2 U}{\partial S^2}\right)}{-\frac{\partial^2 U}{\partial V \partial S}} \qquad (8.15)$$

... siehe Beweis Teil 2 !!

d) direktes Vorgehen:

- $\left(\frac{\partial T}{\partial p}\right)_V \longleftrightarrow c_p,\ \alpha,\ \kappa_T$?
- Trafo: $p, V \longrightarrow T, p$ [kanon. Variable von g]

also: $V = V(T,p) \longrightarrow dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \quad (8.16)$

in (8.13): $0 = \underbrace{\left\{\left(\frac{\partial T}{\partial p}\right)_V + \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T\right\}}_{=0} dp + \underbrace{\left\{\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p - 1\right\}}_{=0} dT$

$$\left(\frac{\partial T}{\partial p}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \quad (8.17) \qquad \left(\frac{\partial T}{\partial V}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p^{-1} \quad (8.18)$$

$$\xrightarrow[(8.18)]{(8.17)} \quad \boxed{\left(\frac{\partial T}{\partial p}\right)_V = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p} = \frac{\kappa_T}{\alpha}} \quad (8.19)$$

e) allg. Rechenregeln:

(i) Geg: äquivalente Beziehungen

$$X = X(Y,Z) \longleftrightarrow Y = Y(X,Z) \longleftrightarrow Z = Z(X,Y) \quad (8.20)$$

Bsp: P, T, V (s.d))

Differential: $$dX = \left(\frac{\partial X}{\partial Y}\right)_Z dY + \left(\frac{\partial X}{\partial Z}\right)_Y dZ \quad (8.21)$$

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$$X = X(Y,Z) \longleftrightarrow Y = Y(X,Z) \longleftrightarrow Z = Z(X,Y) \quad (8.20)$$

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Differential: $$dX = \left(\frac{\partial X}{\partial Y}\right)_Z dY + \left(\frac{\partial X}{\partial Z}\right)_Y dZ \quad (8.21)$$

nun Trafo: $Y, Z \longrightarrow X, Z$

mit $$dY = \left(\frac{\partial Y}{\partial X}\right)_Z dX + \left(\frac{\partial Y}{\partial Z}\right)_X dZ \quad (8.22)$$

in (8.21):

$$0 = \underbrace{\left\{-1 + \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial X}\right)_Z\right\}}_{=0} dX + \underbrace{\left\{\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X + \left(\frac{\partial X}{\partial Z}\right)_Y\right\}}_{=0} dZ \quad (8.23)$$

$\longrightarrow$

$$\boxed{\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial Y}{\partial X}\right)_Z^{-1}} \quad (8.24) \quad \text{[Ableitungen umkehren!]}$$

$$\boxed{\left(\frac{\partial X}{\partial Y}\right)_Z = -\frac{\left(\frac{\partial X}{\partial Z}\right)_Y}{\left(\frac{\partial Y}{\partial Z}\right)_X}} \quad (8.25) \quad \text{[Art Kettenregel]}$$

NB: 2dim-Fläche lokal durch 2 Steigungen festgelegt

$\rightarrow$ 2 Ableitungen reichen!

(ii) Ersetze $Y \longrightarrow$ neue Variable $W(Y,Z)$: $X = X(Y,Z) = X(W(Y,Z),Z)$

Ableitungen? = Kettenregeln

Bsp: $W = \mu$

(1)
$$\boxed{\left(\frac{\partial X}{\partial Y}\right)_Z = \left(\frac{\partial X}{\partial W}\right)_Z \left(\frac{\partial W}{\partial Y}\right)_Z = \frac{\left(\frac{\partial X}{\partial W}\right)_Z}{\left(\frac{\partial Y}{\partial W}\right)_Z}} \quad (8.26)$$

(2) $\left(\frac{\partial X}{\partial Z}\right)_Y$?

$$dX \overset{(8.26)}{=} \underbrace{\left\{\left(\frac{\partial X}{\partial Z}\right)_W + \left(\frac{\partial X}{\partial W}\right)_Z \left(\frac{\partial W}{\partial Z}\right)_Y\right\}} dZ + \ldots \; dY$$

$$\boxed{\left(\frac{\partial X}{\partial Z}\right)_Y = \left(\frac{\partial X}{\partial Z}\right)_W + \left(\frac{\partial X}{\partial W}\right)_Z \left(\frac{\partial W}{\partial Z}\right)_Y} \quad (8.27)$$

- Verwende Regeln oder leite sie her!

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- Verwende Regeln oder leite sie her!

- <u>wichtiges Bsp:</u>

$$\boxed{c_p = c_V + \frac{TV\alpha^2}{N\kappa}} \quad (8.28)$$

Beweis: Starte von c_V und verwende Trafo: $T, V \longrightarrow T, P$

s. Übungen