
Y PHYSICAL SUPPLEMENT

Y.1 *Gibbs-Duhem relation and intensive state variables*

When constructing the various ensembles, we started at the fully extensive $E(S, V, N)$ for the microcanonical ensemble and ended up at $J(T, V, \mu)$ for the macrocanonical ensemble: Would there be a hypothetical ensemble with fully intensive state variables T, p and μ ? The answer is no, as one would lose all information about the actual size of the system and the amount of matter involved, and the mathematically accurate formulation is the \blacktriangleleft Gibbs-Duhem relation.

With the Euler-relation $U = TS - pV + \mu N$ as a starting point with the corresponding differential $dU = TdS - pdV + \mu dN$ for the case of three pairs of state variables we see that in every term there is always an intensive state variable associated with an extensive one. That means, that in principle one could define $8 = 2^3$ potentials, where 5 of those potentials have names

$U(S, V, N)$	energy	$dU = TdS - pdV + \mu dN$
$F(T, V, N)$	Helmholtz free energy	$dF = -SdT - pdV + \mu dN$
$G(T, p, N)$	free enthalpy (Gibbs)	$dG = -SdT + Vdp + \mu dN$
$H(S, p, N)$	enthalpy	$dH = TdS + Vdp + \mu dN$
$J(T, V, \mu)$	grand canonical potential	$dJ = -SdT - pdV - Nd\mu$

Computing the full differential of the Euler-relation $U = TS - pV + \mu N$ then suggests:

$$dU = TdS + SdT - pdV + Vdp + \mu dN + Nd\mu = TdS - pdV + \mu dN + SdT - Vdp + Nd\mu \quad (\text{Y.589})$$

When substituting the differential $dU = TdS - pdV + \mu dN$ one arrives at a relation between the intensive state variables:

$$SdT - Vdp + Nd\mu = 0 \quad (\text{Y.590})$$

implying that only 2 of the intensive state variables are actually independent, reducing the number of possible thermodynamic potentials for 3 pairs of state variables from 8 to 7.

Y.2 *Euler-relation*

The state variables S, V and N reflect the size of the thermodynamic system or the amount of matter present in the system, and for that purpose the energy U is necessarily a homogeneous function of order $\lambda = 1$ in these variables: Naturally one would think that the total internal energy of the system has this property,

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \quad (\text{Y.591})$$

and it is easy to imagine just λ copies of the system and to add up all extensive variables, such that the internal energy of the combined system is λ times larger, too. Differentiating this relation with respect to λ yields

$$U(S, V, N) = \underbrace{\frac{\partial U}{\partial(\lambda S)} \cdot \frac{\partial(\lambda S)}{\partial \lambda}}_{=S} + \underbrace{\frac{\partial U}{\partial(\lambda V)} \cdot \frac{\partial(\lambda V)}{\partial \lambda}}_{=V} + \underbrace{\frac{\partial U}{\partial(\lambda N)} \cdot \frac{\partial(\lambda N)}{\partial \lambda}}_{=N} \quad (\text{Y.592})$$

Setting λ , which was arbitrary, to $\lambda = 1$ then gives the Euler-relation

$$U(S, V, N) = \underbrace{\frac{\partial U}{\partial S}}_{=T} \cdot S + \underbrace{\frac{\partial U}{\partial V}}_{=-p} \cdot V + \underbrace{\frac{\partial U}{\partial N}}_{=\mu} \cdot N = TS - pV + \mu N \quad (\text{Y.593})$$

There is a differential version to the Euler-equation,

$$dU = TdS - pdV + \mu dN \quad (\text{Y.594})$$

as a differential of $U(S, V, N)$, which is suggested from the first and second law of thermodynamics:

$$dU = \delta Q + \delta W = TdS - pdV + \mu dN \quad (\text{Y.595})$$

which associate the change in thermal energy δQ with TdS and the change in mechanical energy δW with $-pdV + \mu dN$.