

## Alternative set of thermodynamic potentials [tln9]

Intensive variables:  $\alpha = -\frac{\mu}{T}$ ,  $\beta = \frac{1}{T}$ ,  $\gamma = \frac{p}{T}$

The following four thermodynamic potentials are related to each other via Legendre transform.

**Entropy** (microcanonical potential):

$$S(U, V, N) = \alpha N + \beta U + \gamma V, \quad dS = \alpha dN + \beta dU + \gamma dV$$

**Massieu function** (canonical potential):

$$\Phi(\beta, V, N) = S - \beta U = -A(T, V, N)/T, \quad d\Phi = \alpha dN - U d\beta + \gamma dV$$

**Kramers function** (grandcanonical potential):

$$\Psi(\beta, V, \alpha) = S - \beta U - \alpha N = -\Omega(T, V, \mu)/T, \quad d\Psi = -N d\alpha - U d\beta + \gamma dV$$

**Planck function**:

$$\Pi(\beta, \gamma, N) = S - \beta U - \gamma V = -G(T, p, N)/T, \quad d\Pi = \alpha dN - U d\beta - V d\gamma$$

Gibbs-Duhem relation:  $N d\alpha + U d\beta + V d\gamma = 0$

Distinct properties:

- Any spontaneous i.e. irreversible process at constant values of the natural independent variables is accompanied by an *increase* of the associated thermodynamic potential.
- The equilibrium state for fixed values of a set of natural independent variables is the state where the associated thermodynamic potential is a *maximum*.