

Alternative set of thermodynamic potentials [tln9]

The following four thermodynamic potentials are again related to each other via Legendre transform [tln77].

The naturally independent variables comprise different sets:

$$U, V, N. \quad (\text{extensive})$$
$$\alpha \doteq -\frac{\mu}{T}, \quad \beta \doteq \frac{1}{T}, \quad \gamma \doteq \frac{p}{T}. \quad (\text{intensive})$$

We list definitions, alternative names, relations to free energies introduced in [tsc3], and differentials.

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.