

# Chapter 5

## Thermodynamic potentials

Thermodynamic potentials are *state functions* that, together with the corresponding equations of state, describe the equilibrium behavior of a system as a function of so-called "natural variables". The natural variables are a set of appropriate variables that allow to compute other state functions by partial differentiation of the thermodynamic potentials.

### 5.1 Internal energy $U$

The basic relation of thermodynamics is given by the equation

$$dU = TdS + \sum_{i=1}^m F_i dq_i + \sum_{j=1}^{\alpha} \mu_j dN_j , \quad (5.1)$$

where  $\{F, q\}$  denote the set of conjugate intensive and extensive variables that characterize a system. For instance, for a gas

$$\{F, q\} \rightarrow \{-P, V\},$$

and for a magnetic system

$$\{F, q\} \rightarrow \{\mathcal{B}, \mathcal{M}\} .$$

**Chemical potential.** The number of particles in the system is a natural extensive variable for the free energy, we did keep it hitherto constant. The number of particle of a distinct types  $j$  is denoted by  $N_j$  in (5.1), where  $j = 1, \dots, \alpha$ . The respective intensive variable,  $\mu$  (and respectively the  $\mu_j$ ), is denoted the *chemical potential*.

The chemical potential become identical to the *Fermi energy* for a gas of Fermions (at low temperatures, as we will discuss in Sect. 13.3). Note that diffusion processes (e.g. across a membrane) may change individual  $N_j$ . The number of particles needs therefore not to be constant.

**Internal energy of a gas.** Eq. (5.1) is equivalent to

$$dU = TdS - PdV + \mu dN , \quad \boxed{U = U(S, V, N)} \quad (5.2)$$

for a gas with one species of particle, which implies that

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N}, \quad -P = \left( \frac{\partial U}{\partial V} \right)_{S,N}, \quad \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}. \quad (5.3)$$

**Response functions.** The experimentally important *response* functions are obtained by second-order differentiation of the internal energy,

$$\left( \frac{\partial^2 U}{\partial S^2} \right)_{V,N} = \left( \frac{\partial T}{\partial S} \right)_{V,N} = \frac{T}{C_V}, \quad C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = T \left[ \left( \frac{\partial^2 U}{\partial S^2} \right)_{V,N} \right]^{-1}$$

$$\left( \frac{\partial^2 U}{\partial V^2} \right)_{S,N} = - \left( \frac{\partial P}{\partial V} \right)_{S,N} = \frac{1}{V \kappa_S}, \quad \kappa_S = \frac{1}{V} \left[ \left( \frac{\partial^2 U}{\partial V^2} \right)_{S,N} \right]^{-1}$$

**Maxwell relations.** A *Maxwell relation* follows, as discussed already in Sect. 4.4.2, from the differentiability of thermodynamic potentials. An example of a Maxwell relation derived from the differential of the internal energy  $U = U(S, V, N)$  is

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial N} \right) = \frac{\partial}{\partial N} \left( \frac{\partial U}{\partial V} \right), \quad \left( \frac{\partial \mu}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial N} \right)_V, \quad (5.4)$$

which relates the change of the chemical potential  $\mu$  with the volume  $V$  to the (negative of the) change of the pressure  $P$  with the number of particles  $N$ .

### 5.1.1 Monoatomic ideal gas

For the monoatomic ideal we did find hitherto

$$PV = nRT, \quad U = \frac{3}{2}nRT, \quad C_V = \frac{3}{2}nR.$$

We now use these relations to derive an expression for  $U$  in terms of its natural variables.

**Entropy.** We start with the entropy

$$\begin{aligned} S(T, V) - S(T_0, V_0) &= \frac{3nR}{2} \log \left( \frac{T}{T_0} \right) + nR \log \left( \frac{V}{V_0} \right) \\ &= \frac{3nR}{2} \log \left( \frac{U}{U_0} \right) + nR \log \left( \frac{V}{V_0} \right) \end{aligned}$$

of the ideal gas, as derived in Sect. 4.4.1, where we have used the ideal gas relation  $U = 3nRT/2$  to substitute  $T$  and  $T_0$  with  $U$  and  $U_0$  in the second step.

With  $C_V = 3nR/2$  we may write equivalently

$$\frac{S - S_0}{C_V} = \ln\left(\frac{U}{U_0}\right) + \frac{2}{3} \ln\left(\frac{V}{V_0}\right) = \ln\left[\frac{U}{U_0} \left(\frac{V}{V_0}\right)^{2/3}\right], \quad (5.5)$$

which can be solved for the internal energy as

$$\boxed{U(S, V) = U_0 \left(\frac{V_0}{V}\right)^{\gamma-1} e^{(S-S_0)/C_V}}, \quad \gamma = 5/3. \quad (5.6)$$

Eq. (5.6) is the fundamental equation for the ideal gas, with  $U(S, V)$  as the thermodynamic potential.  $S, V$  are the independent natural variables.

### 5.1.2 Thermodynamic potential vs. equation of state

The natural variables for  $U$  are  $S$  and  $V$ , which means that if the function  $U(S, V)$  is known for a given system we can obtain –all– thermodynamic properties of the system through the differentiation of  $U(S, V)$ . The *equation of state*

$$U = U(T, V, N) \quad (5.7)$$

for the internal energy  $U$  is on the contrary –not– a *thermodynamic potential*. This is because the first derivatives of (5.7) yield the specific heat  $C_V$  and the energy equation (4.12),

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V, \quad \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P,$$

but not the dependent variables  $S$  and  $P$ . Note the marked difference to (5.3).

### 5.1.3 Classical mechanics vs. thermodynamics

There is a certain analogy between the potential  $V$  and internal energy  $U$  of classical mechanics and thermodynamics respectively:

	Classical mechanics	Thermodynamics
Potential	$V(x, y, z)$	$U(S, V, N)$
Independent variables	$x, y, z$	$S, V, N$
Dependent variables	$F_x = -\frac{\partial V}{\partial x}$	$P = -\left(\frac{\partial U}{\partial V}\right)_S$

## 5.2 Legendre transformation

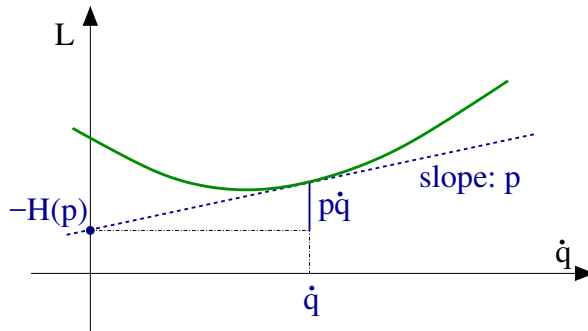
A disadvantage of using  $U(S, V, N)$  as a thermodynamic potential is that the natural variable  $S$  is difficult to control in the lab. For practical purposes, it is more convenient to deal with other thermodynamic potentials that can be defined by making use of the *Legendre transformation*.

**Legendre transformations in classical mechanics.** We recall the Legendre transformation connecting the Legendre function  $L(q, \dot{q})$  with the Hamilton function  $H(q, p)$ , where  $q$  is the generalized coordinate and,  $\dot{q}$  and  $p$  respectively the velocity and the momentum, with

$$p = \left( \frac{\partial L}{\partial \dot{q}} \right)_q,$$

at constant coordinate  $q$ , and

$$H(q, p) = p\dot{q} - L(q, \dot{q}). \quad (5.8)$$



A Legendre transformation is hence a variable transformation,  $\dot{q} \rightarrow p$ , where one of the variables, here the momentum  $p$ , is defined by the slope of original function, viz by the slope of the Lagrange function  $L(p, \dot{q})$ .

### 5.2.1 Legendre transformations in thermodynamics

As an example we consider the transformation

$$U(S, V, N) \rightarrow H(S, P, N),$$

from the internal energy  $U(S, V, N)$  to the enthalpy  $H(S, P, V)$ . The form is, as discussed shortly in Sect. 3.6,

$$H(S, P, N) = U(S, V, N) + PV, \quad P = - \left( \frac{\partial U}{\partial V} \right)_S. \quad (5.9)$$

Note that the pressure is defined as the (negative) slope of the internal energy  $U$  with respect to the volume  $V$ , in analogy to the transformation from the velocity  $\dot{q}$  to the momentum  $p = \partial L / \partial \dot{q}$  in classical mechanics. Note however the different sign conventions between (5.9) and (5.8).

**Differential.** The Legendre transformation (5.9) allows to evaluate with

$$dH = d(U + PV) = (TdS - PdV + \mu dN) + (PdV + VdP),$$

the differential  $dH$  of the enthalpy in terms of its natural variables  $S$ ,  $P$  and  $N$ . The result is

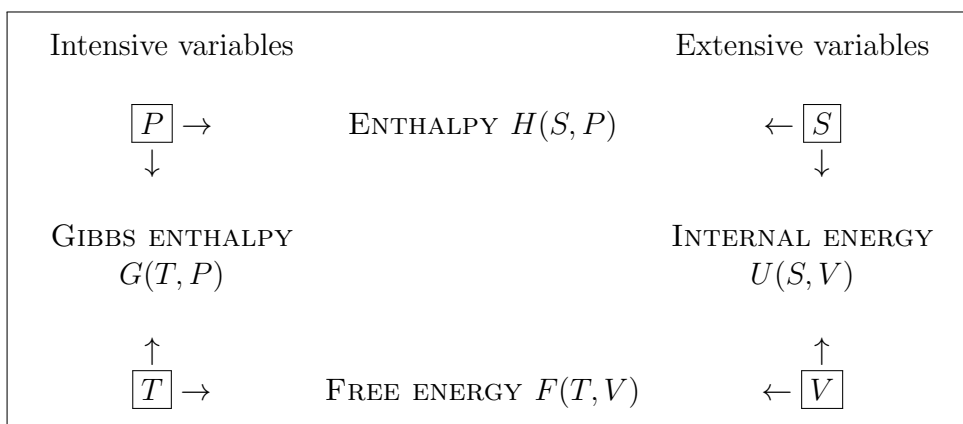
$$dH = TdS + VdP + \mu dN. \quad (5.10)$$

### 5.2.2 The four basic thermodynamic potentials

A thermodynamic potential for a system with variable number of particles should depend on  $\{\mu, N\}$  as well as a thermal variable and a mechanical variable, which can be (for a gas):

thermal:	$S$ (extensive)	$T$ (intensive)
mechanical:	$V$ (extensive)	$P$ (intensive)

The four possible combinations of these variables,



define four basic thermodynamic potentials:

- $U(S, V, N)$  – internal energy
- $H(S, P, N)$  – enthalpy
- $G(T, P, N)$  – Gibbs enthalpy
- $F(T, V, N)$  – free energy

**Gibbs enthalpy.** We did already discuss the differentials (5.2),  $dU = TdS - PdV + \mu dN$ , and (5.10) of respectively the free energy  $U(S, V, N)$  and of the enthalpy  $H(S, P, N)$ . For the Gibbs enthalpy one has in analogy

$$\boxed{G = U(S, V, N) - TS + PV}, \quad dG = -SdT + VdP + \mu dN. \quad (5.11)$$

**Free energy.** The natural variables  $T$ ,  $V$  and  $N$  of the free energy  $F = F(T, V, N)$  are straightforward to access experimentally. The free energy is hence an often considered thermodynamic potential. It obeys

$$\boxed{F = U(S, V, N) - TS}, \quad dF = -SdT - PdV + \mu dN. \quad (5.12)$$

**Differential relation between free and internal energy.** The Legendre transformation (5.12) between  $U$  and  $F$  allow to derive a differential relation between the free and

internal energy,

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

which can be written in terms of the inverse temperature  $\beta = 1/(k_B T)$  as

$$\boxed{U = \frac{\partial}{\partial \beta}(\beta F)}, \quad \frac{\partial}{\partial T} = \frac{\partial}{\partial(1/T)} \frac{\partial(1/T)}{\partial T} = \frac{-1}{T^2} \frac{\partial}{\partial(1/T)}. \quad (5.13)$$

It is generally easier to obtain explicit expressions for the internal energy  $U$  than for the free energy  $F$ . Above relation will be for this reason fundamental to the formulation of statistical mechanics, as discussed later on in Sect. 9.2, as it allows to identify  $F$ .

### 5.2.3 Maxwell relations

The differentiability of the thermodynamic potentials leads to various Maxwell relations, such as the one given by Eq. (5.4). There are furthermore four Maxwell relations relating  $T$ , respectively  $S$  to  $P$  respectively  $V$ . We drop in the following the dependence on the number of particles  $N$ .

$U(S, V)$	$dU = TdS - PdV$	$\boxed{\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V}$
$H(S, P)$	$dH = TdS + VdP$	$\boxed{\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P}$
$G(T, P)$	$dG = -SdT + VdP$	$\boxed{\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P}$
$F(T, V)$	$dF = -SdT - PdV$	$\boxed{\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V}$

### 5.2.4 Entropy

The differential of the entropy  $S = S(U, V, N)$  is obtained rewriting (5.2) as

$$\boxed{dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN}. \quad (5.14)$$

The conjugate (natural) intensive variables are here  $1/T$  and  $P/T$  with respect to  $dU$  and  $dV$  respectively. It is hence not customary to perform Legendre transformations with respect to these variables.

### 5.3 Homogeneity relations

The thermodynamic potentials vary as *extensive* state properties if the volume and number of particles vary by a factor  $\lambda$ , i.e.,

$$\left. \begin{array}{l} V \rightarrow \lambda V \\ N_j \rightarrow \lambda N_j \end{array} \right\} \Rightarrow U \rightarrow \lambda U. \quad (5.15)$$

Note that long-range interactions between particles, such as the unscreened Coulomb interaction, may invalidate (5.15). Surface effects will contribute in addition for the case of a mesoscopic system.

**Extensive and intensive variables.** Temperature is intensive, but

$$dU = TdS - PdV + \sum_{j=1}^{\alpha} \mu_j dN_j$$

extensive. It follows likewise that

$$\begin{array}{ll} \text{extensive} & : U(S, V, N), H(S, P, N), G(T, P, N), F(T, V, N) \\ & : S(U, V, N), V, N \\ \text{intensive} & : T, P, \mu \end{array}$$

**Scaling.** Doubling the volume  $V$  will also double the free energy  $F(T, V, N)$ . All extensive functions, viz all thermodynamic potentials obey hence the scaling relations of the sort of

$$\begin{aligned} F(T, \lambda V, \lambda N) &= \lambda F(T, V, N) \\ G(T, P, \lambda N) &= \lambda G(T, P, N) \end{aligned} \quad (5.16)$$

These functional dependencies express the *homogeneity* of the equilibrium thermodynamic state.

**Gibbs-Duhem relation.** Scaling relations are generically of fundamental importance in physics. Here we use the *extensivity* of  $G$  and differentiate (5.16) with respect to  $\lambda$  (at  $\lambda = 1$ ),

$$\lambda G(T, P, N) = \frac{d}{d\lambda} G(T, P, \lambda N_1, \lambda N_2, \dots) \Big|_{\lambda=1} = \sum_{j=1}^{\alpha} \underbrace{\left( \frac{\partial G}{\partial (\lambda N_j)} \right)_{T, P, N_{i \neq j}} \Big|_{\lambda=1}}_{= \mu_j} N_j$$

We obtain then with

$$\boxed{G(T, P, N) = \sum_{j=1}^{\alpha} \mu_j N_j} \Rightarrow \text{Gibbs-Duhem relation.} \quad (5.17)$$

the *Gibbs-Duhem relation*.

**Chemical potential.** When there is only one class of particles ( $\alpha = 1$ ),

$$\boxed{G(T, P, N) = \mu N} . \quad (5.18)$$

The chemical potential may hence be interpreted as Gibbs enthalpy per particle.

**Representation of the internal energy.** The Gibbs-Duhem relation (5.18) allows to rewrite the other thermodynamic potential. We recall, e.g. the Legendre transform (5.11),

$$G = U - TS + PV, \quad \boxed{U = TS - PV + \mu N} .$$

Note, however, that this representation is only seemingly simple.

## 5.4 Grand canonical potential

In a system that interchanges particles with a reservoir, the chemical potential is constant and the number of particles changes accordingly. In order to describe such a system, we introduce the *grand canonical potential*  $\Omega(T, V, \mu)$  as the Legendre transform of  $F(T, V, N)$ , where the natural variable  $N$  is replaced by  $\mu$ ,

$$\boxed{\Omega(T, V, \mu) = F(T, V, N) - \mu N} , \quad \mu(T, V, N) = \left( \frac{\partial F}{\partial N} \right)_{T, V} . \quad (5.19)$$

The total differential of  $\Omega$  is

$$d\Omega = dF - \mu dN - Nd\mu, \quad \boxed{d\Omega = -SdT - PdV - Nd\mu} . \quad (5.20)$$

Through differentiation of  $\Omega$  we can calculate  $S$ ,  $P$  and  $N$  as

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} , \quad P = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu} , \quad N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V} .$$

**Thermal equation of state.** From the Gibbs Duhem relation (5.18),  $G = \mu N$ , it follows that

$$\Omega = F - \mu N = G - PV - \mu N = -PV, \quad F = G - PV$$

and hence that the *thermal equation of state*  $P = P(T, V)$ , see Eq. (4.11), takes the form

$$\boxed{P = - \frac{\Omega(T, V, \mu)}{V}} \Rightarrow \text{thermal equation of state} .$$

**Differential relation between  $\Omega$  and  $U$ .** With, (5.12),  $F = U - TS$ , we may write (5.19) as

$$\Omega = F - \mu N = U - TS - \mu N, \quad S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} .$$



Rearranging the terms then leads to

$$U - \mu N = \Omega + TS = \Omega - T \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu}, \quad \boxed{U - \mu N = \frac{\partial}{\partial \beta} (\beta \Omega)}, \quad (5.21)$$

where we have used in analogy to (5.13) that

$$1 - T \frac{\partial}{\partial T} = -T^2 \frac{\partial}{\partial T} \frac{1}{T} = \beta \frac{\partial}{\partial T} \beta, \quad \frac{\partial}{\partial T} = \frac{\partial}{\partial(1/T)} \frac{\partial(1/T)}{\partial T} = \frac{-1}{T^2} \frac{\partial}{\partial \beta}.$$

## 5.5 Equilibrium conditions

Our discussion of thermodynamic potentials dealt hitherto mostly with the *equilibrium state*. The second law of thermodynamics,

$$TdS \geq \delta Q = dU + PdV - \mu dN, \quad (5.22)$$

allows however also to study the impact of *irreversible processes*, that is the evolution of the system toward the equilibrium. We have used for (5.22) the differential form of (4.6) together with the generalized first law

$$dU = \delta Q + \delta W + \mu dN, \quad \delta W = -PdV,$$

where we have taken the  $\delta W$  appropriate for a gas.

**Equilibrium internal energy.** The entropy is an exact differential  $dS = \delta Q/T$  at equilibrium. One can then consider situations like

$$dU = TdS - PdV \quad \Rightarrow \quad \begin{cases} dU = -PdV & S = \text{const.} \quad (\text{work}) \\ dU = TdS & V = \text{const.} \quad (\text{heat}) \end{cases}$$

where selected state variables are constant. We will now generalize this discussion.

### 5.5.1 Principle of maximal entropy

Isolated systems are defined by

$$\left. \begin{array}{l} \delta Q = 0 \\ dV = 0 \\ dN = 0 \end{array} \right\} \Rightarrow dU = 0.$$

The second law (5.22) tells us then that

$$\begin{aligned} \Delta S &\geq 0 \\ dS &= 0 \quad \text{in equilibrium.} \end{aligned}$$

**Principle of maximal entropy.**

In all irreversible processes, under the conditions

$$U = \text{const.}, \quad V = \text{const.}, \quad N = \text{const.}$$

the entropy increases and is maximal in the stationary equilibrium.  
 $S$  evolves to a maximum under conditions of fixed  $U$ ,  $V$ ,  $N$ .

**Two isolated system.** Consider two isolated systems **1** and **2** separated by a wall, which is however movable and which allows for the exchange of energy and particles.

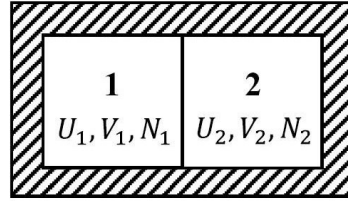
The variables  $V_1$ ,  $V_2$ ,  $U_1$ , and  $U_2$ ,  $N_1$ ,  $N_2$

must obey the following constraints:

$$U = U_1 + U_2 = \text{const.} \quad \Rightarrow \quad dU_1 = -dU_2$$

$$V = V_1 + V_2 = \text{const.} \quad \Rightarrow \quad dV_1 = -dV_2$$

$$N = N_1 + N_2 = \text{const.} \quad \Rightarrow \quad dN_1 = -dN_2$$



The total entropy of **1** and **2** is likewise a sum of the individual entropies:

$$S = S(U_1, V_1, N_1) + S(U_2, V_2, N_2) = S_1 + S_2 .$$

**Equilibrium conditions.** Both systems will interchange particles and energy until equilibrium is attained. In the equilibrium state

$$\begin{aligned} 0 &= dS = dS_1 + dS_2 \\ &= \left\{ \left( \frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} - \left( \frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \right\} dU_1 \\ &+ \left\{ \left( \frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \right\} dV_1 \\ &+ \left\{ \left( \frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} - \left( \frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} \right\} dN_1 \\ &= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 + \left( -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} \right) dN_1 . \end{aligned}$$

where we have used the steady-state version of the second law (5.22),  $dS = dU + PdV - \mu dN$ .

**Homogeneity condition.**  $U_1$ ,  $V_1$ , and  $N_1$  are independent variables. The prefactors of  $dU_1$ ,  $dV_1$ , and  $dN_1$  need hence to vanish individually:

$$T_1 = T_2 = T; \quad P_1 = P_2 = P; \quad \mu_1 = \mu_2 = \mu .$$

Instead of two systems we can subdivide a given system in an arbitrary number of ways. The system needs consequently to be homogeneous:

An isolated system in equilibrium has everywhere the same temperature, pressure and chemical potential.

### 5.5.2 Principle of minimal free energy

Closed systems in a reservoir with heat, but without work interchange, are defined by

$$\begin{aligned} \text{closed} &\Rightarrow N_j = \text{const} \Rightarrow dN_j = 0, \\ \text{in a reservoir} &\Rightarrow T = \text{const} \Rightarrow dT = 0, \\ \text{without work interchange} &\Rightarrow V = \text{const} \Rightarrow dV = 0. \end{aligned}$$

The second law of thermodynamics (5.22) reduces then to

$$TdS \geq dU + PdV - \mu dN = dU, \quad dV = 0 = dN .$$

**Principle of minimal free energy.** For constant temperature one has  $TdS = d(TS)$  and consequently that

$$0 \leq TdS - dU = d(TS - U), \quad \boxed{dF = d(U - TS) \leq 0} ,$$

where we have used (5.12), namely that  $F = U - TS$ .

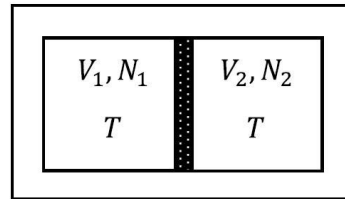
The free energy decreases and reaches a *minimum* at equilibrium,

$$\boxed{\begin{aligned} dF &\leq 0 \\ dF &= 0 \quad \text{in equilibrium} \end{aligned}}$$

for all irreversible processes characterized by a constant temperature  $T$ , volume  $V$  and particle number  $N$ .

**Composite system.** Consider a composite system in a heat reservoir at temperature  $T$ , whose particles can pass through the wall. It obeys the conditions

$$\begin{aligned} V &= V_1 + V_2 = \text{const.} \Rightarrow dV_1 = -dV_2 \\ N &= N_1 + N_2 = \text{const.} \Rightarrow dN_1 = -dN_2 \\ F &= F(T, V_1, N_1) + F(T, V_2, N_2) = F_1 + F_2 \end{aligned}$$



In equilibrium,

$$\begin{aligned} 0 &= dF = dF_1 + dF_2 \\ &= \left\{ \left( \frac{\partial F_1}{\partial V_1} \right)_{N_1, T} - \left( \frac{\partial F_2}{\partial V_2} \right)_{N_2, T} \right\} dV_1 \\ &+ \left\{ \left( \frac{\partial F_1}{\partial N_1} \right)_{V_1, T} - \left( \frac{\partial F_2}{\partial N_2} \right)_{V_2, T} \right\} dN_1 \\ &= \{-P_1 + P_2\} dV_1 + \{\mu_1 - \mu_2\} dN_1 . \end{aligned}$$

With  $V_1$  and  $N_1$  being independent variables it follows that

$$P_1 = P_2 = P, \quad \mu_1 = \mu_2 = \mu .$$

A closed system with constant volume  $V$  which is in contact with a heat bath at constant temperature  $T$  reaches an equilibrium state characterized by a uniform pressure  $P$  and chemical potential  $\mu$ .

**Principle of minimal Gibbs energy.** Generalizing above considerations we consider closed system in a heat reservoir, but at constant pressure  $P$  (previously  $V$  was constant). One can easily show that

$$dT = 0, \quad dN_j = 0, \quad dP = 0$$

implies that

$$\begin{aligned} dG &\leq 0 \\ dG &= 0 \quad \text{in equilibrium .} \end{aligned}$$

The Gibbs energy decreases in an irreversible process for a system with constant pressure  $P$  in contact with a heat bath at constant temperature  $T$ .  $G(T, P, N)$  reaches its minimum at equilibrium, which is characterized by a uniform chemical potential  $\mu$ .

### 5.5.3 Stationarity principles in information theory

From the microscopic point of view the equilibrium thermodynamic state is *stationary* in the sense that the positions and the velocities of the constituent particle change continuously. The ongoing reconfiguration of the microscopic state leaves however the macroscopic properties of the state intact.

**Stationary probability distribution functions.** A probability distribution functions  $p(y)$  quantifies the probability that the state  $y$  (an event) occurs, with

$$\int p(y)dy = 1, \quad p(y) \geq 0 .$$

It is the task of statistical mechanics to find the expression for  $p(y)$  (see Chap. 9) Statistical mechanics dealing hence with probability distribution functions which are stationary with respect to the reconfiguration of microscopic states.

**Entropy and disorder.** In statistical mechanics the entropy has, as we will discuss in Chap. 12, the form

$$S[p] = -k_B \langle \ln(p) \rangle = -k_B \int p(y) \ln(p(y)) dy .$$

It measures the amount of disorder in the sense that a flat (maximally disordered) distribution function  $p(y)$  has the largest entropy  $S[p]$ . Here we have written  $S = S[p]$  as a

functional of  $p = p(y)$ . This connection allows us to reinterpret the principle of maximal entropy derived in Sect. 5.5.1.

Irreversible processes increase the amount of disorder in isolated systems. The entropy of the universe can only increase.

**Entropy and information.** Information theory deals with information processing as described by probability distribution functions. The central quantity of information theory is the Shannon entropy

$$I[p] = - \int p(y) \log(p(y)) dy , \quad (5.23)$$

which is identical, apart from an overall factor,  $k_B$ , to the thermodynamic entropy. The Shannon entropy is however used as a measure of the *information content*. The context is here information transmitted via communication channels.

bit sequence	type	randomness	information content
..01010101..	ordered	zero	zero (predictable)
..00110101..	disordered	high	high

You do not learn anything new if you can predict what another person says.

**Shannon's source coding theorem.** A precise connections between the information-theoretical entropy  $I[p]$  and the information content of a communication channel is provided by the Shannon coding theorem, which states the  $I[p]$  provides a lower bound for lossless compression. Information is inevitably lost when compressing more.

**Life as a stationary state.** Life is by definition a stationary state of matter which retains its functionality despite the continuously ongoing turnover of its constituent elements. The proteins, enzymes and cells of our body have lifetimes ranging typically from hours to months.

**Equilibrium principles in the neurosciences.** The stationary equilibrium of the brain with both the environment and the body is dependent on a continuous flux of information. Information theoretical principles are consequently of widespread use in the neurosciences. An example is the free energy principle, as proposed by Carl Friston. It suggests that the brain may be minimizing the information-theoretical analog of the thermodynamic free energy (compare Sect. 5.5.2).

## 5.6 Summary of thermodynamic potentials

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
INTERNAL ENERGY $U$	$S, V, N$	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$ $P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$ $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
ENTROPY $S$	$U, V, N$	$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$ $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$ $-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,N}$	
FREE ENERGY $F = U - TS$	$T, V, N$	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$ $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $U = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T}\right)$
ENTHALPY $H = U + PV$	$S, P, N$	$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$ $V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$ $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
GIBBS ENTHALPY $G = H - TS = N\mu$	$T, P, N$	$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ $H = -T^2 \frac{\partial}{\partial T} \left(\frac{G}{T}\right)$

Potential	Natural independent variables	Conjugated dependent variables	Maxwell relations and others
GRAND CANONICAL POTENTIAL $\Omega = F - \mu N = -PV$	$T, V, \mu$	$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu}$ $P = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu}$ $N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V}$	
CHEMICAL POTENTIAL $\mu = \frac{G}{N}$	$T$ $P$	$s = \frac{S}{N} = - \left( \frac{\partial \mu}{\partial T} \right)_P$ $v = \frac{V}{N} = \left( \frac{\partial \mu}{\partial P} \right)_T$	

