

# Equilibrium Thermodynamics III:

## Free Energies [tsc3]

We continue the development of the formalism of equilibrium thermodynamics for a fluid system with a single mode of work performance: change of volume  $V$  against pressure  $p$ .

It is straightforward to replace the extensive variable,  $X = V$ , and intensive variable,  $Y = -p$ , by another conjugate pair (e.g.  $X = M$  and  $Y = H$ ) for a different mode of work performance.

### Fundamental equation of thermodynamics:

The first and second laws of thermodynamics imply that

$$dU = TdS - pdV + \mu dN \quad (1)$$

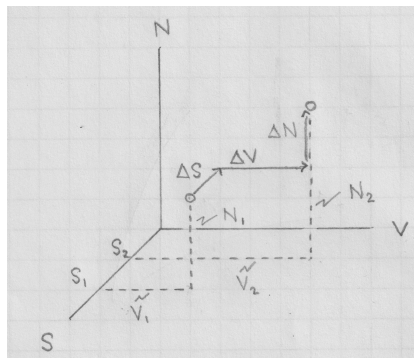
with

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

is the exact differential of a function  $U(S, V, N)$ .

Upon integration, the differential (1) connects two points in the 3-dimensional space spanned by  $S, V, N$  via a reversible process along a specific path.

The graph shows a specific path: first  $\Delta S$ , then  $\Delta V$ , and last  $\Delta N$ . However, the integral is path-independent.



Only quasi-static processes are represented by paths in  $(S, V, N)$ -space. This includes some, but not all irreversible processes.

For irreversible processes,  $dU < TdS - pdV + \mu dN$  holds.

$U, S, V, N$  are all extensive state variables.

Consequence:  $U(S, V, N)$  is a 1<sup>st</sup> order homogeneous function:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \quad \lambda > 0.$$

Set  $\lambda = 1 + \epsilon$  with  $\epsilon \ll 1$  and expand to first order:

$$U[(1 + \epsilon)S, (1 + \epsilon)V, (1 + \epsilon)N] = U + \underbrace{\frac{\partial U}{\partial S}}_T \epsilon S + \underbrace{\frac{\partial U}{\partial V}}_{-p} \epsilon V + \underbrace{\frac{\partial U}{\partial N}}_{\mu} \epsilon N = (1 + \epsilon)U.$$

The fundamental equation of thermodynamics (Euler's equation) follows:

$$U = TS - pV + \mu N. \quad (2)$$

The total differential of (2),

$$dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu, \quad (3)$$

disregards the functional relations contained in the differential (1) in the form of the partial derivatives that guarantee integrability.

We can extract these relations from the difference between (1) from (3), which is the Gibbs-Duhem equation,

$$SdT - Vdp + Nd\mu = 0,$$

a differential relationship between the intensive variables  $T, p, \mu$ . It can be integrated, for example, into a function  $\mu(T, p)$ .

In general, a system specified by  $m$  independent extensive variables possesses  $m - 1$  independent intensive variables.

Example for  $m = 3$ :  $S, V, N$  (extensive);  $S/N, V/N$  or  $p, T$  (intensive).

The complete specification of a thermodynamic system must involve at least one extensive variable, specifying the size of the system.

At fixed  $S, V, N$  any spontaneous process lowers the internal energy,  $dU < 0$ . This is implied by the inequality,  $dU < TdS - pdV + \mu dN$ , established earlier for irreversible processes.

The absence of spontaneous processes means that thermal equilibrium has been reached. Here the internal energy  $U$  assumes the lowest accessible value for fixed  $S, V, N$ .

### Analogy with mechanical equilibrium:

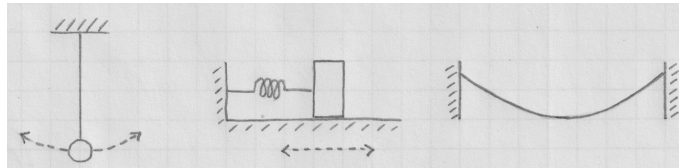
A physical pendulum in librational motion will reach mechanical equilibrium in state of minimum (gravitational) potential energy.

A harmonic oscillator in motion will reach mechanical equilibrium in a state of minimum (elastic) potential energy .

In both mechanical systems, dissipative forces (air resistance and friction) lead the way toward mechanical equilibrium.

Quite generally, mechanical equilibrium states can be identified as those that minimize the potential energy for given constraints.

For example, a rope with its ends fixed hangs (at mechanical equilibrium) in a shape that minimizes its gravitational potential energy.

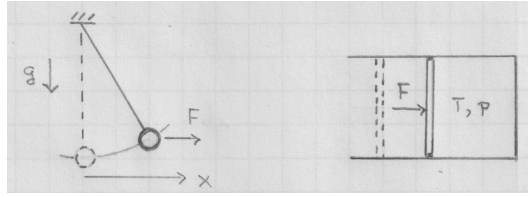


The internal energy  $U$  plays the role of a *thermodynamic potential*. For given constraints  $S, V, N$ , it assumes the lowest accessible value at thermal equilibrium.

### Free energy in a mechanical system:

Consider again a mechanical system such as the physical pendulum or, more generally, a massive object in some external potential.

- Energy can be stored in the mechanical system when some agent does work on it, e.g. by quasi-statically pulling the pendulum bob to a higher elevation.
- If the work involves only conservative forces, then all energy added can be retrieved as work performed by the system, e.g. by quasi-statically releasing the pendulum bob to the original lower elevation.
- If the work done also involves dissipative forces, e.g. air resistance or friction, then only part of the energy added is retrievable as work performed by the system.
- The retrievable part of the energy stored in the mechanical system is a potential energy. The fact that it can be extracted at no cost makes it a free energy.



### Free energy in a thermodynamic system:

Consider a thermodynamic system in contact with a work source and a heat reservoir. The example suggests a gas in a cylinder with a movable piston.

- Energy can be stored in the thermodynamic system when some agent does work on it, e.g. by pushing in the piston.
- If the work is done reversibly, then all the energy added can be retrieved as work performed by the system. If the piston is pushed in quasi-statically, the heat-flow from the gas to the reservoir is not wasteful and thus reversible.
- If the work is done irreversibly, e.g. by allowing a temperature difference between the gas and the heat bath, then only part of the energy added is retrievable as work performed by the system.
- The energy stored and retrievable as work is called *free energy*.
- The free energy stored in or retrieved from a thermodynamic system is expressed by a *thermodynamic potential*.
- The choice of thermodynamic potential depends on the constraints imposed on the system during storage and retrieval of free energy.

### Thermodynamic potentials for fluid system:

List of the five most common choices.

- *Internal energy*:  $U(S, V, N) = TS - pV + \mu N$ .
- *Enthalpy*:  $E(S, p, N) = U + pV = TS + \mu N$ .
- *Helmholtz free energy*:  $A(T, V, N) = U - TS = -pV + \mu N$ .
- *Gibbs free energy*:  $G(T, p, N) = U - TS + pV = \mu N$ .
- *Grand potential*:  $\Omega(T, V, \mu) = U - TS - \mu N = -pV$ .

There is no agreement on the use of symbols for thermodynamic potentials.

$E$  is often used for internal energy and  $H$  for enthalpy. The Helmholtz free energy is often denoted by  $F$ .

For other thermodynamic systems, the conjugate pair of variables  $p, V$  must be replaced appropriately, some times with a change in sign.

In magnetic systems, for example, we must interchange volume  $V$  by magnetization  $M$  and negative pressure  $-p$  by magnetic field  $H$ .

### Differentials of thermodynamic potentials:

$$\begin{aligned} dU &= TdS - pdV + \mu dN, & dE &= TdS + Vdp + \mu dN, \\ dA &= -SdT - pdV + \mu dN, & dG &= -SdT + Vdp + \mu dN, \\ d\Omega &= -SdT - pdV - Nd\mu, & \text{Magnet: } & -pdV \rightarrow HdM, Vdp \rightarrow -MdH. \end{aligned}$$

### Facts about thermodynamic potentials:

- All thermodynamic potentials of a system are related to each other via Legendre transform [tln77].
- Every thermodynamic potential has its distinct set of natural independent variables.
- Each thermodynamic potential encodes a complete macroscopic description of a thermodynamic system. All thermodynamic properties can be inferred from any thermodynamic potentials.
- Any quantity  $U, E, A, G, \Omega$  which is not expressed as a function of its natural independent variables is not a thermodynamic potential. Such quantities contain only partial thermodynamic information.
- In thermodynamics, thermodynamic potentials are inferred from empirical information (equations of state, response functions).
- In statistical mechanics, thermodynamic potentials are derived from microscopic information (interaction Hamiltonian).
- Any spontaneous i.e. irreversible process at constant values of the natural independent variables is accompanied by a decrease of the associated thermodynamic potential.
- The list of total differentials pertains to reversible processes. For irreversible processes, “=” must be replaced by “<”.
- The equilibrium state for fixed values of a set of natural independent variables is the state where the associated thermodynamic potential is a minimum.
- An alternative set of thermodynamic potentials with similar attributes and different combinations of variables is also in common use [tln9].

### Thermodynamic functions (for fluid system):

First partial derivatives of thermodynamic potentials with respect to natural independent variables are named *thermodynamic functions*.

$$\text{Entropy: } S = - \left( \frac{\partial A}{\partial T} \right)_{V,N} = - \left( \frac{\partial G}{\partial T} \right)_{p,N} = - \left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} .$$

$$\text{Temperature: } T = \left( \frac{\partial U}{\partial S} \right)_{V,N} = \left( \frac{\partial E}{\partial S} \right)_{p,N} .$$

$$\text{Volume: } V = \left( \frac{\partial E}{\partial p} \right)_{S,N} = \left( \frac{\partial G}{\partial p} \right)_{T,N} .$$

$$\text{Pressure: } p = - \left( \frac{\partial U}{\partial V} \right)_{S,N} = - \left( \frac{\partial A}{\partial V} \right)_{T,N} = - \left( \frac{\partial \Omega}{\partial V} \right)_{T,\mu} .$$

$$\text{Number of particles: } N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} .$$

$$\text{Chemical potential: } \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} = \left( \frac{\partial E}{\partial N} \right)_{S,p} = \left( \frac{\partial A}{\partial N} \right)_{T,V} = \left( \frac{\partial G}{\partial N} \right)_{T,p} .$$

### Substitutions for magnetic system:

The volume  $V$  is replaced by magnetization  $M$  and the negative pressure  $-p$  by the magnetic field  $H$ .

$$\text{Entropy: } S = - \left( \frac{\partial A}{\partial T} \right)_{M,N} = - \left( \frac{\partial G}{\partial T} \right)_{H,N} = - \left( \frac{\partial \Omega}{\partial T} \right)_{M,\mu} .$$

$$\text{Temperature: } T = \left( \frac{\partial U}{\partial S} \right)_{M,N} = \left( \frac{\partial E}{\partial S} \right)_{H,N} .$$

$$\text{Magnetization: } M = - \left( \frac{\partial E}{\partial H} \right)_{S,N} = - \left( \frac{\partial G}{\partial H} \right)_{T,N} .$$

$$\text{Magnetic field: } H = - \left( \frac{\partial U}{\partial M} \right)_{S,N} = - \left( \frac{\partial A}{\partial M} \right)_{T,N} = - \left( \frac{\partial \Omega}{\partial M} \right)_{T,\mu} .$$

$$\text{Number of particles: } N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,M} .$$

$$\text{Chemical potential: } \mu = \left( \frac{\partial U}{\partial N} \right)_{S,M} = \left( \frac{\partial E}{\partial N} \right)_{S,H} = \left( \frac{\partial A}{\partial N} \right)_{T,M} = \left( \frac{\partial G}{\partial N} \right)_{T,H} .$$

### Maxwell's relations:

Thermodynamic potentials are state variables. Their differentials are exact. Maxwell's relations are integrability conditions of exact differentials.

Lists of the most important Maxwell relations:

*Fluid system:*

$$\begin{aligned}dU = TdS - pdV &\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \\dE = TdS + Vdp &\Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \\dA = -SdT - pdV &\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \\dG = -SdT + Vdp &\Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

*Magnetic system:*

$$\begin{aligned}dU = TdS + HdM &\Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M \\dE = TdS - MdH &\Rightarrow \left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H \\dA = -SdT + HdM &\Rightarrow \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M \\dG = -SdT - MdH &\Rightarrow \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H\end{aligned}$$

### Additional relations involving thermodynamic potentials:

$$U = A + TS = A - T \left(\frac{\partial A}{\partial T}\right)_V = -T^2 \left(\frac{\partial(A/T)}{\partial T}\right)_V$$

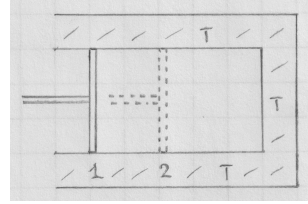
$$E = G + TS = G - T \left(\frac{\partial G}{\partial T}\right)_p = -T^2 \left(\frac{\partial(G/T)}{\partial T}\right)_p$$

$$G(T, p, N) = \mu(T, p)N$$

$$\Omega(T, V, \mu) = -p(T, \mu)V$$

## Free energy stored and retrieved:

Consider a classical ideal gas confined to a cylinder. The cylinder walls are in thermal contact with a heat reservoir at temperature  $T$ .



*Reversible cyclic process:* no wasteful heat flow

1. Push the piston in from position 1 to position 2 quasi-statically.  
The work on the system is done reversibly.

$$\Delta W_{12} = \int_1^2 F dx = \int_1^2 dA = \int_1^2 (-SdT - pdV) \text{ with } dT = 0, dV < 0.$$

$$\Rightarrow \Delta W_{12} = A_2 - A_1 > 0.$$

The work done is equal to the excess Helmholtz potential (free energy).

2. Move the piston out from position 2 to position 1 quasi-statically.

$$\Delta W_{21} = \int_2^1 dA = \int_2^1 (-SdT - pdV) \text{ with } dT = 0, dV > 0.$$

$$\Rightarrow \Delta W_{21} = A_1 - A_2 = -\Delta W_{12} < 0.$$

All the energy stored (in the form free energy) is converted back into work done by the system.

*Irreversible cyclic process:* some wasteful heat flow

1. Push the piston in from position 1 to position 2 rapidly.  
The initial and final equilibrium states are the same as previously, but the process requires more work. The gas heats up, which produces a larger pressure than in the quasi-static process.

$$\Rightarrow \Delta W_{12} > A_2 - A_1 > 0.$$

Only part of the work done on the system is stored as free energy.

2. (a) Move the piston out from position 2 to position 1 quasi-statically.

$$\Rightarrow |\Delta W_{21}| = |A_1 - A_2| < |\Delta W_{12}|.$$

All the free energy is converted back into work but that amount is smaller than the work previously done on the system.

- (b) Move the piston out from position 2 to position 1 rapidly.

$$\Rightarrow |\Delta W_{21}| < |A_1 - A_2| < |\Delta W_{12}|.$$

Only part of the available free energy is converted back into work, where the full amount of free energy is only part of the work previously done on the system.



### Response functions:

Second partial derivatives of thermodynamic potentials with respect to natural independent variables are named *response functions*.

Response functions describe how one thermodynamic function responds to a change in another thermodynamic function under controlled conditions, i.e. by keeping yet different thermodynamic functions constant.

Response functions are important because of their experimental accessibility. They are instrumental for the construction of (caloric and thermodynamic) equations of state from empirical information.

It is common practice to distinguish between *thermal* response functions (heat capacities) and *mechanical* response functions. The latter cover the response involving any kind of work.

### Thermal response functions:

Consider a fluid system with  $N = \text{const.}$

The generic definition of heat capacity is  $C \doteq dQ/dT$ , the rate at which heat must be added to a system to elicit a certain rate of temperature change.

Express the inexact differential  $dQ$  in two different ways using state functions:

$$dQ = TdS = \begin{cases} T \left( \frac{\partial S}{\partial T} \right)_V dT + T \left( \frac{\partial S}{\partial V} \right)_T dV & \text{for } S(T, V) \\ T \left( \frac{\partial S}{\partial T} \right)_p dT + T \left( \frac{\partial S}{\partial p} \right)_T dp & \text{for } S(T, p) \end{cases}$$
$$\Rightarrow C_V \doteq T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_V, \quad C_p = T \left( \frac{\partial S}{\partial T} \right)_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p$$

Equivalent expressions of  $C_V$  and  $C_p$  are inferred as first derivatives from the internal energy  $U(T, V)$  and enthalpy  $E(T, p)$ , respectively:

$$dU = TdS - pdV \quad \Rightarrow \quad C_V = \left( \frac{\partial U}{\partial T} \right)_V,$$

$$dE = TdS + Vdp \quad \Rightarrow \quad C_p = \left( \frac{\partial E}{\partial T} \right)_p.$$

Note that neither function  $U(T, V)$  or  $E(T, p)$  is a thermodynamic potential.

### Mechanical response functions:

- Isothermal compressibility:  $\kappa_T \doteq -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial p^2} \right)_T$
- Adiabatic compressibility:  $\kappa_S \doteq -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S = -\frac{1}{V} \left( \frac{\partial^2 E}{\partial p^2} \right)_S$
- Thermal expansivity:  $\alpha_p \doteq \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$

Relations with thermal response functions  $C_p, C_V$ :

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}, \quad C_p = \frac{TV\alpha_p^2}{\kappa_T - \kappa_S}, \quad C_V = \frac{TV\alpha_p^2\kappa_S}{\kappa_T(\kappa_T - \kappa_S)}$$
$$\Rightarrow C_p - C_V = \frac{TV\alpha_p^2}{\kappa_T} > 0$$

These are mechanical response functions in a strict sense for a fluid system.

Mechanical response functions in a broader sense include the magnetic response functions listed below.

### Magnetic response functions:

- Isothermal susceptibility:  $\chi_T \doteq \left( \frac{\partial M}{\partial H} \right)_T = - \left( \frac{\partial^2 G}{\partial H^2} \right)_T = \left( \frac{\partial^2 A}{\partial M^2} \right)_T^{-1}$
- Adiabatic susceptibility:  $\chi_S \doteq \left( \frac{\partial M}{\partial H} \right)_S = - \left( \frac{\partial^2 E}{\partial H^2} \right)_S$
- “You name it”:  $\alpha_H \doteq - \left( \frac{\partial M}{\partial T} \right)_H$

Relations with thermal response functions  $C_H, C_M$ :

$$\frac{C_H}{C_M} = \frac{\chi_T}{\chi_S}, \quad C_H = \frac{T\alpha_H^2}{\chi_T - \chi_S}, \quad C_M = \frac{T\alpha_H^2\chi_S}{\chi_T(\chi_T - \chi_S)}$$
$$\Rightarrow C_H - C_M = \frac{T\alpha_H^2}{\chi_T}$$

### Isothermal and adiabatic processes:

Here we establish useful relations between state variables pertaining to isothermal and adiabatic processes.

The relations are formulated separately for a fluid system and for a magnetic system. Intermediate steps are sketched for the fluid system.

*Fluid system:*

Start from  $TdS = dU + pdV$  with  $U = U(T, V)$

$$TdS = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV \stackrel{(a)}{=} C_V dT + \frac{1}{\alpha_p V} (C_p - C_V) dV$$

$$\text{Isotherm: } dT = 0 \Rightarrow TdS = \frac{1}{\alpha_p V} (C_p - C_V) dV \stackrel{(b)}{=} -\frac{\kappa_T}{\alpha_p} (C_p - C_V) dp$$

$$\text{Adiabate: } dS = 0 \Rightarrow dT = -\frac{1}{\alpha_p V} \frac{C_p - C_V}{C_V} dV \stackrel{(c)}{=} \frac{\kappa_S}{\alpha_p} \frac{C_p - C_V}{C_V} dp$$

(a) Use  $dE = dU + pdV - Vdp$ .

$$\Rightarrow C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial V}{\partial T}\right)_p = V\alpha_p.$$

(b) Use  $dV = \left(\frac{\partial V}{\partial p}\right)_T dp = -V\kappa_T dp$

(c) Use  $dV = -V\kappa_S dp$

*Magnetic system:*

Start from  $TdS = dU - HdM$  with  $U = U(T, M)$ .

$$TdS = \left(\frac{\partial U}{\partial T}\right)_M dT + \left[\left(\frac{\partial U}{\partial M}\right)_T - H\right] dM = C_M dT - \frac{1}{\alpha_H} (C_H - C_M) dM$$

$$\text{Isotherm: } dT = 0 \Rightarrow TdS = -\frac{1}{\alpha_H} (C_H - C_M) dM = -\frac{\chi_T}{\alpha_H} (C_H - C_M) dH$$

$$\text{Adiabate: } dS = 0 \Rightarrow dT = \frac{1}{\alpha_H} \frac{C_H - C_M}{C_M} dM = \frac{\chi_S}{\alpha_H} \frac{C_H - C_M}{C_M} dH$$

### Conditions for thermal equilibrium:

Consider a homogeneous fluid system in a rigid and insulated container which is divided into two compartments,  $A$  and  $B$ , by a fictitious partition.

Internal energy, volume, and number of particles are conserved:

$$U = U_A + U_B = \text{const}, \quad V = V_A + V_B = \text{const}, \quad N = N_A + N_B = \text{const}.$$

The fictitious partitioning permits fluctuations of these extensive quantities between compartments constrained by the conservation laws:

$$dU_A = -dU_B, \quad dV_A = -dV_B, \quad dN_A = -dN_B.$$

At thermal equilibrium, the entropy  $S(U, V, N)$  is a maximum [tln9]. Hence its differential to first order must vanish:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN = 0.$$

This condition applied to the container with a fictitious partition reads,

$$\begin{aligned} dS &= \sum_{\alpha=A,B} \left[ \left( \frac{\partial S_\alpha}{\partial U_\alpha} \right)_{V_\alpha N_\alpha} dU_\alpha + \left( \frac{\partial S_\alpha}{\partial V_\alpha} \right)_{U_\alpha N_\alpha} dV_\alpha + \left( \frac{\partial S_\alpha}{\partial N_\alpha} \right)_{U_\alpha V_\alpha} dN_\alpha \right] \\ &= \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left( \frac{p_A}{T_A} - \frac{p_B}{T_B} \right) dV_A - \left( \frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dN_A = 0. \end{aligned}$$

In each of the three terms, at least one of the factors must vanish at equilibrium.

(i) In the case of a fictitious wall, we permit  $dU_A \neq 0$  (energy fluctuations),  $dV_A \neq 0$  (volume fluctuations), and  $dN_A \neq 0$  (fluctuations in particle number). In consequence, we must have,

$$T_A = T_B, \quad p_A = p_B, \quad \mu_A = \mu_B.$$

(ii) If the fictitious wall is replaced by a real, mobile, conducting wall, then particle fluctuations in the two compartments are suppressed,  $dN_A = 0$ . In this case,  $\mu_A \neq \mu_B$  is possible, but  $T_A = T_B$  and  $p_A = p_B$  must still hold.

(iii) If the mobile, conducting wall is replaced by a rigid, conducting wall, then volume fluctuations in the two compartments are also suppressed,  $dV_A = 0$ . In this case,  $p_A \neq p_B$  is possible in addition to  $\mu_A \neq \mu_B$ , but the condition  $T_A = T_B$  remains in place.

(iv) If the rigid conducting wall is replaced by a rigid insulating wall, then energy fluctuations in the two compartments are also suppressed:  $dU_A = 0$ . In this case,  $T_A \neq T_B$  is possible in addition to  $\mu_A \neq \mu_B$  and  $p_A \neq p_B$ .

How about the case (v) of a mobile insulating wall? Here we must reason differently. This is a situation where entropy fluctuations are prohibited, while energy fluctuations are permitted.

We cope with this situation by switching from the thermodynamic potential  $S(U, V, N)$  to the thermodynamic potential  $U(S, V, N)$ , which assumes a minimum at thermodynamic equilibrium.

The extremum condition is again a differential that vanishes to first order:

$$dU = TdS - pdV + \mu dN.$$

Applied to the container with compartments  $A$  and  $B$ , it becomes,

$$\begin{aligned} dU &= \sum_{\alpha=A,B} \left[ \left( \frac{\partial S_\alpha}{\partial S_\alpha} \right)_{V_\alpha N_\alpha} dU_\alpha + \left( \frac{\partial U_\alpha}{\partial V_\alpha} \right)_{S_\alpha N_\alpha} dV_\alpha + \left( \frac{\partial U_\alpha}{\partial N_\alpha} \right)_{A_\alpha V_\alpha} dN_\alpha \right] \\ &= (T_A - T_B) dS_A - (p_A - p_B) dV_A + (\mu_A - \mu_B) dN_A = 0. \end{aligned}$$

In each of the three terms, again at least one of the factors must vanish at equilibrium.

(v) A mobile insulating wall permits volume fluctuations,  $dV_A \neq 0$ , thus requires,  $p_A = p_B$ . It prohibits fluctuations in the number of particles,  $dN_A = 0$ , which allows  $\mu_A \neq \mu_B$ . Entropy fluctuations are also prohibited (no heat flow between compartments),  $dS_A = 0$ , which allows  $T_A \neq T_B$  at equilibrium.

Further combinations of equilibrium constraints will be discussed in the context of application.

Equilibrium conditions become more complex for inhomogeneous systems. In the presence of external fields, pressure and chemical potential may become non-uniform, while temperature remains uniform if heat flow is unconstrained.

### Stability of thermal equilibrium:

Consider a fluid system with  $N = \text{const}$  in thermal equilibrium at temperature  $T_0$  and pressure  $p_0$ . Any spontaneous deviation from that state must cause an increase in Gibbs free energy,

$$G(T_0, p_0) = U(S, V) - T_0 S + p_0 V.$$

Effects entropy fluctuations  $\delta S$  and volume fluctuations  $\delta V$ :

$$\begin{aligned} \delta G &= \left[ \left( \frac{\partial U}{\partial S} \right)_V - T_0 \right] \delta S + \left[ \left( \frac{\partial U}{\partial V} \right)_S + p_0 \right] \delta V \\ &+ \frac{1}{2} \left[ \left( \frac{\partial^2 U}{\partial S^2} \right) (\delta S)^2 + 2 \left( \frac{\partial^2 U}{\partial S \partial V} \right) \delta S \delta V + \left( \frac{\partial^2 U}{\partial V^2} \right) (\delta V)^2 \right] \end{aligned}$$

$$\text{Equilibrium condition: } \left( \frac{\partial U}{\partial S} \right)_V - T_0 = 0, \quad \left( \frac{\partial U}{\partial V} \right)_S + p_0 = 0$$

$$\text{Stability condition: } \left( \frac{\partial^2 U}{\partial S^2} \right) (\delta S)^2 + 2 \left( \frac{\partial^2 U}{\partial S \partial V} \right) \delta S \delta V + \left( \frac{\partial^2 U}{\partial V^2} \right) (\delta V)^2 > 0.$$

Condition for quadratic form to be positive definite:

$$\frac{\partial^2 U}{\partial S^2} > 0, \quad \frac{\partial^2 U}{\partial V^2} > 0, \quad \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left( \frac{\partial^2 U}{\partial S \partial V} \right)^2 > 0.$$

Implications:

$$\begin{aligned} \left( \frac{\partial^2 U}{\partial S^2} \right)_V &= \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0 \Rightarrow C_V > 0. \\ \left( \frac{\partial^2 U}{\partial V^2} \right)_S &= - \left( \frac{\partial p}{\partial V} \right)_S = \frac{1}{V \kappa_S} > 0 \Rightarrow \kappa_S > 0. \\ \left( \frac{\partial^2 U}{\partial S^2} \right)_V \left( \frac{\partial^2 U}{\partial V^2} \right)_S &> \left( \frac{\partial^2 U}{\partial S \partial V} \right)^2 \Rightarrow \left( \frac{\partial T}{\partial S} \right)_V \left[ - \left( \frac{\partial p}{\partial V} \right)_S \right] > \left( \frac{\partial T}{\partial V} \right)_S^2 \\ &\Rightarrow \left[ \frac{T}{C_V} \right] \left[ \frac{1}{V \kappa_S} \right] > \left( \frac{\partial T}{\partial V} \right)_S^2 > 0. \end{aligned}$$

Let us keep in mind that the thermal stability conditions for inhomogeneous systems are more complex.