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## Chapter 1

# Fundamentals

## 1.1 Definitions and previous concepts

**Definition 1.1.1.** We define a *thermodynamical system*  $\mathcal{S}$  as a system of particles where  $n \gg 1$ .

**Axiom 1.** *Every system evolves to an equilibrium state.*

**Definition 1.1.2.** Let  $\mathcal{S}$  be a thermodynamical system and  $x$  a state variable of  $\mathcal{S}$ . We say

1.  $x$  is *extensive* if and only if it varies when dividing  $\mathcal{S}$  in partitions,
2.  $x$  is *intensive* if and only if it does not varies when dividing  $\mathcal{S}$  in partitions, and
3.  $x$  is *specific* if and only if it is the result from dividing an extensive variable by the number of particles of  $\mathcal{S}$ .

### 1.1.1 System, environment and universe

**Definition 1.1.3.** We define a *system*  $\mathcal{S}$  as the region we are studying.

**Definition 1.1.4.** We define the environment as the region different from  $\mathcal{S}$  that interacts with  $\mathcal{S}$ .

**Definition 1.1.5.** Let  $\mathcal{S}$  be a system. We define the universe as the system formed by the system and its environment.

**Definition 1.1.6.** Let  $\mathcal{S}$  be a system. We say

1.  $\mathcal{S}$  is *open* if and only if it can exchange matter and energy with the environment.
2.  $\mathcal{S}$  is *closed* if and only if it can exchange energy but not matter with the environment.
3.  $\mathcal{S}$  is *isolated* if and only if it can exchange neither energy nor matter with the environment.

**Proposition 1.1.1.** *Let  $\mathcal{S}$  be a system. If  $\mathcal{S}$  is isolated, then it coincides with the universe.*

### 1.1.2 Interactions

**Definition 1.1.7.** Let  $\mathcal{S}_1, \dots, \mathcal{S}_r$  be  $r$  thermodynamical systems that interact between them. Then, we call the union of  $\mathcal{S}_1, \dots, \mathcal{S}_r$  as a *system*  $\mathcal{S}$  and every  $\mathcal{S}_i$  a *subsystem* of  $\mathcal{S}$ .

**Definition 1.1.8.** Wall

**Definition 1.1.9.** Let  $\mathcal{S}_1, \mathcal{S}_2$  be two systems and  $w(\mathcal{S}_1, \mathcal{S}_2)$  be their wall. Then, we say

1.  $w$  is *thermal* if and only if  $\mathcal{S}_1, \mathcal{S}_2$  can exchange energy in form of heat and *adiabatic* if and only if they cannot.
2.  $w$  is *mechanical* if and only if  $\mathcal{S}_1, \mathcal{S}_2$  can exchange energy in form of work and *rigid* if and only if they cannot do it in form of compression-expansion work.
3.  $w$  is *material* if and only if  $\mathcal{S}_1, \mathcal{S}_2$  can exchange particles and *impermeable* if and only if they cannot.

### 1.1.3 Work

**Definition 1.1.10.** We define the *infinitesimal work* as the non-exact differential one-form

$$\bar{d}W = X dY, \quad (1.1)$$

where  $X$  is the *force* or *cause* and  $Y$  the *displacement* or *consequence*. We also say  $X$  and  $Y$  are *conjugate variables*.

### 1.1.4 Thermal equation of state

**Definition 1.1.11.** Let  $\mathcal{S}$  be a system and  $x_1, \dots, x_r$  its state variables. We define its *thermal equation of state* as an equation  $\phi(x_1, \dots, x_r) = 0$  that relates the state variables.

**Proposition 1.1.2.** Let  $\mathcal{S}$  be a system with conjugate variables  $X, Y$ . Then, its thermal equation of state is  $\phi(X, Y, T, N) = 0$ , and if the system is closed,  $\phi(X, Y, T) = 0$ .

**Corollary 1.1.3.** Let  $\mathcal{S}$  be a system formed by a monocomponent fluid. Then, its thermal equation of state is  $\phi(p, V, T, N) = 0$ .

**Corollary 1.1.4.** Let  $\mathcal{S}$  be a system formed by a monoatomic ideal gas. Then, its thermal equation of state is  $pV - nRT = pV - Nk_B T = 0$ .

### 1.1.5 Caloric equation of state

**Definition 1.1.12.** Let  $\mathcal{S}$  be a system. We define its *caloric equation of state* as an equation that relates its intern energy or entropy, its mass and two of its thermal variables.

**Corollary 1.1.5.** Let  $\mathcal{S}$  be a system with a caloric equation of state  $\psi(U, X, Y) = 0$ . Then, there exists a function  $f$  such that  $U = f(X, Y)$  and  $\psi(f(X, Y), X, Y) = 0$ . The same can be said substituting  $U$  by  $S$ .

**Proposition 1.1.6.** Let  $\mathcal{S}$  be a system formed by a monocomponent fluid. Then, its caloric equations of state are

$$\varphi_1(U, T, V, N) = 0, \quad \varphi_2(U, T, p, N) = 0, \quad \varphi_3(U, V, p, N) = 0, \quad (1.2)$$

$$\psi_1(S, T, V, N) = 0, \quad \psi_2(S, T, p, N) = 0, \quad \psi_3(S, V, p, N) = 0. \quad (1.3)$$

**Corollary 1.1.7.** Let  $\mathcal{S}$  be a system formed by a monoatomic ideal gas. Then, its caloric equation of state is  $U - \frac{3}{2}Nk_B T = 0$ .

## 1.2 Thermodynamical coefficients and heat capacities

**Definition 1.2.1.** Thermodynamical coefficient.

**Definition 1.2.2.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *coefficient of thermal expansion* as

$$\alpha := \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p. \quad (1.4)$$

**Definition 1.2.3.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *compressibility* as

$$k_T := -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_T. \quad (1.5)$$

**Definition 1.2.4.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *piezometric coefficient* as

$$\beta := \frac{1}{p} \left. \frac{\partial p}{\partial T} \right|_V. \quad (1.6)$$

**Theorem 1.2.1** (Reciprocity theorem). Let  $\Phi(x, y, z) = 0$  be an equation. Then,

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1. \quad (1.7)$$

**Corollary 1.2.2.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,

$$\alpha = \beta p k_T, \quad \left. \frac{\partial \alpha}{\partial p} \right|_T = - \left. \frac{\partial k_T}{\partial T} \right|_p. \quad (1.8)$$

**Definition 1.2.5.** Let  $\mathcal{S}$  be a thermodynamical system and  $x$  one of its state variables. We define the *heat capacity of  $\mathcal{S}$  at constant  $x$*  as

$$C_x := \left. \frac{\bar{d}Q}{dT} \right|_x. \quad (1.9)$$

### 1.3 Zeroth law of thermodynamics

**Axiom 2.** Let  $\mathcal{A}, \mathcal{B}, \mathcal{C}$  be three thermodynamical systems. If  $\mathcal{A}, \mathcal{B}$  are in equilibrium with  $\mathcal{C}$ , then each one is in equilibrium with the other.

**Corollary 1.3.1.** Being in equilibrium is an equivalence relation.

### 1.4 First law of thermodynamics

**Axiom 3.** First version from last year.

**Axiom 4.** Second statement from last year,

$$dU = \bar{d}Q + \bar{d}W. \quad (1.10)$$

#### 1.4.1 Relations between heat capacities

**Proposition 1.4.1** (Mayer's relation). Let  $\mathcal{S}$  be a thermodynamical system and  $X, Y$  its conjugate variables. Then,

$$C_x - C_y = \left( \left. \frac{\partial U}{\partial Y} \right|_T - X \right) \left. \frac{\partial Y}{\partial T} \right|_X. \quad (1.11)$$

**Proposition 1.4.2.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,

$$C_p - C_V = \left( \left. \frac{\partial U}{\partial V} \right|_T - p \right) V\alpha, \quad C_V = \left. \frac{\partial U}{\partial T} \right|_V, \quad C_p = \left. \frac{\partial U}{\partial T} \right|_p + pV\alpha. \quad (1.12)$$

#### 1.4.2 Ideal gas

**Proposition 1.4.3.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent ideal gas. Then,

$$\alpha = \frac{1}{T}, \quad k_t = \frac{1}{p}, \quad C_p - C_v = nR. \quad (1.13)$$

### 1.5 Second law of thermodynamics

#### 1.5.1 Thermal machines

**Definition 1.5.1.** Heat engine.

**Definition 1.5.2.** Refrigerator.

**Definition 1.5.3.** Converter.

**Definition 1.5.4.** Efficiency.

**Proposition 1.5.1.** Let  $\mathcal{M}$  be a heat engine. Then, its efficiency is given by

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (1.14)$$

**Proposition 1.5.2.** Let  $\mathcal{M}$  be a refrigerator. Then, its efficiency is given by

$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{Q_1/Q_2 - 1} \quad (1.15)$$

**Proposition 1.5.3.** *Let  $\mathcal{M}$  be a conversor. Then, its efficiency is 1.*

**Axiom 5** (Kelvin's statement). *There is not any cyclic process that transforms entirely heat into work.*

**Axiom 6** (Clausius' statement). *There is not any cyclic process capable of transferring heat from a cold body to a hot one without consuming energy.*

**Definition 1.5.5.** We define the *Carnot heat engine* as a reversible engine based on a reversible cycle called *Carnot cycle*, formed by two isothermal and two adiabatic processes.

### 1.5.2 Carnot's theorem

**Theorem 1.5.4** (Carnot's theorem). *Among all heat engines that work between two given thermal sources, the Carnot machine is the most efficient one.*

**Proposition 1.5.5.** *For any reversible engine operating between two thermal sources of temperatures  $T_1$  and  $T_2$ ,*

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \quad (1.16)$$

**Corollary 1.5.6.** *For the heat engine and refrigerator we have*

$$\eta_k = 1 - \frac{T_2}{T_1}, \quad \eta_r = \frac{1}{T_1/T_2 - 1}. \quad (1.17)$$

**Definition 1.5.6.** We define the *Carnot thermometer* as the thermometer that obtains the temperature of a system  $\mathcal{S}_1$  by using a Carnot engine that works between  $\mathcal{S}_1$  and another system  $\mathcal{S}_2$  at different temperature.

**Proposition 1.5.7.** *The Carnot thermometer gives a scale of temperatures with one fixed point, given by the expression*

$$T = T_R \frac{Q_1}{Q_2}. \quad (1.18)$$

### 1.5.3 Clausius theorem

**Theorem 1.5.8.** *Let  $\gamma$  be a cyclic process formed by infinitesimal processes such that each one realizes an exchange of heat  $\bar{d}Q$  at a temperature  $T$  that we consider constant in every subprocess. Then,*

$$\oint_{\gamma} \frac{1}{T} \bar{d}Q \leq 0. \quad (1.19)$$

**Corollary 1.5.9.** *Let  $\gamma$  be a cyclic reversible process. Then,*

$$\oint \frac{1}{T} \bar{d}Q^{\text{rev}} = 0. \quad (1.20)$$

**Definition 1.5.7.** Let  $\mathcal{S}$  be a thermodynamical system. We define the *entropy* as the state function determined by

$$dS := \frac{1}{T} \bar{d}Q^{\text{rev}}, \quad \Delta S = \int_{\gamma} \frac{1}{T} \bar{d}Q^{\text{rev}}. \quad (1.21)$$

**Proposition 1.5.10.** *Let  $\mathcal{S}$  be a thermodynamical system and  $\gamma$  a path that goes from the state  $A$  to  $B$ . Then, for every process*

$$\int_A^B \frac{1}{T} \bar{d}Q \leq \Delta S = S(B) - S(A), \quad (1.22)$$

*and the equality is reached if and only if the process is reversible.*

**Corollary 1.5.11.** *Let  $\mathcal{S}$  be an isolated thermodynamical system. Then, for every process*

$$\Delta S \geq 0, \quad (1.23)$$

*and the equality is reached if and only if the process is reversible.*

**Corollary 1.5.12.** *For every process*

$$\Delta S_{\text{universe}} \geq 0. \quad (1.24)$$

**Corollary 1.5.13** (Gibb's equation). *Let  $\mathcal{S}$  be a thermodynamical system and  $X, Y$  its conjugate variables. Then,*

$$T dS = dU - \bar{d}W^{\text{rev}} = dU - X dY. \quad (1.25)$$

**Proposition 1.5.14.** *Let  $\mathcal{S}_1, \mathcal{S}_2$  be two therodynamical system at temperature  $T_1, T_2$  with  $T_1 > T_2$ . If the system  $\mathcal{S} = \mathcal{S}_1 \cup \mathcal{S}_2$  is isolated, then there will be a heat flux going from  $\mathcal{S}_1$  to  $\mathcal{S}_2$  until reaching the theral equilibrium.*

**Proposition 1.5.15.** *Let  $\mathcal{M}_h$  be a heat engine and  $\mathcal{M}_r$  a refrigerator. Then,*

$$W_k^{\text{max}} = Q_1 - Q_2^{\text{min}} = Q_1 \left( 1 - \frac{T_f}{T_c} \right), \quad \eta_k^{\text{max}} = 1 - \frac{T_f}{T_c}, \quad (1.26)$$

$$W_r^{\text{min}} = Q_1^{\text{min}} - Q_2 = Q_2 \left( \frac{T_c}{T_f} - 1 \right), \quad \eta_r^{\text{max}} = \frac{1}{T_c/T_f - 1}. \quad (1.27)$$

#### 1.5.4 TdS equations for a fluid

**Proposition 1.5.16** (Compatibility conition). *Let  $\mathcal{S}$  be a closed thermodynamical system and  $X, Y$  its conjugate variables. Then,*

$$\left. \frac{\partial U}{\partial Y} \right|_T = -T \left. \frac{\partial X}{\partial T} \right|_Y + X. \quad (1.28)$$

**Corollary 1.5.17.** *Let  $\mathcal{S}_1$  be a thermodynamical system formed by a monocomponent fluid and  $\mathcal{S}_2$  a magnetic system. Then, for these system respectively*

$$\left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p, \quad \left. \frac{\partial U}{\partial M} \right|_T = -T \left. \frac{\partial H}{\partial T} \right|_M + H. \quad (1.29)$$

**Corollary 1.5.18.** *Let  $\mathcal{S}$  be a closed thermodynamical system formed by a monocomponent fluid. Then,*

$$\left. \frac{\partial S}{\partial V} \right|_T = \frac{\alpha}{k_T}, \quad T dS = C_V dT + T \frac{\alpha}{k_T} dV. \quad (1.30)$$

**Proposition 1.5.19.** *Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid, Then,*

$$T dS = C_p dT - TV\alpha dp = \frac{C_v k_T}{\alpha} dp + \frac{C_p}{\alpha V} dV. \quad (1.31)$$

**Proposition 1.5.20** (Mayer's relation). *Let  $\mathcal{S}$  be a closed thermodynamical system formed by a monocomponent fluid. Then,*

$$C_p - C_v = \frac{TV\alpha^2}{k_T}. \quad (1.32)$$

**Proposition 1.5.21.** *Let  $\mathcal{S}$  be a closed thermodynamical system fromed by a monocomponent fluid. Then,*

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V, \quad T \frac{\alpha}{k_t} = \left. \frac{\partial S}{\partial V} \right|_T, \quad C_p = T \left. \frac{\partial S}{\partial T} \right|_p, \quad (1.33)$$

$$\alpha V = - \left. \frac{\partial S}{\partial p} \right|_T, \quad \frac{C_V k_T}{\alpha T} = \left. \frac{\partial S}{\partial p} \right|_V, \quad \frac{V_p}{\alpha V T} = \left. \frac{\partial S}{\partial V} \right|_p. \quad (1.34)$$



## 1.6 Third law of Thermodynamics

**Axiom 7** (Planck's postulate). *For every system and every process such that  $T$  tends to the absolute zero, the entropy will also tend to zero. Then, for a fluid,*

$$\lim_{T \rightarrow 0} S_V(T) = \lim_{T \rightarrow 0} S_p(T) = 0. \quad (1.35)$$

**Axiom 8** (Nernst's postulate). *It is impossible for every process, independent of how ideal it is, to reduce the entropy of a system until the absolute zero in a finite number of steps. That is, it would be necessary an infinite number of steps to reduce the temperature of a system to zero, which means that the absolute zero is inaccessible in practice. Equivalently,*

$$\lim_{T \rightarrow 0} \Delta S = 0. \quad (1.36)$$

**Proposition 1.6.1.** *Planck's postulate implies Nernst's postulate.*

**Proposition 1.6.2.** *Let  $S$  be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_V = \lim_{T \rightarrow 0} \alpha = 0, \quad (1.37)$$

*whereas  $k_T$  does not necessarily tends to zero.*



## Chapter 2

# Formal structure of Thermodynamics

## 2.1 Fundamental equation in the representation of energy

**Proposition 2.1.1.** *Let  $\mathcal{S}$  be a thermodynamical system formed by  $r$  components and with  $k$  degrees of freedom. Then, its Gibbs equation has the form*

$$dU = T dS + \sum_{i=1}^k X_i dY_i + \sum_{i=1}^r \mu_i dN_i, \quad (2.1)$$

where  $X_i, Y_i$  are its conjugate variables.

**Definition 2.1.1.** Let  $\mathcal{S}$  be a thermodynamical system formed by  $r$  components and with  $k$  degrees of freedom. Let  $Y_1, \dots, Y_k$  be its extensive state variables and  $N_1, \dots, N_r$  the numbers of particles of each component. We define the *fundamental equation in representation of energy* of the system as

$$U(S, Y_1, \dots, Y_k, N_1, \dots, N_r). \quad (2.2)$$

**Proposition 2.1.2.** *Let  $\mathcal{S}$  be a thermodynamical system and  $U = U(S, Y_1, \dots, Y_k, N_1, \dots, N_r)$  its fundamental equation in representation of energy. If  $U$  is defined in an open set  $W \subseteq \mathbb{R}^{1+k+r}$  and is of class  $C^1(W)$ , then*

$$T = \left. \frac{\partial U}{\partial S} \right|_{\mathbf{Y}, \mathbf{N}}, \quad X_i = \left. \frac{\partial U}{\partial Y_i} \right|_{S, Y_{j \neq i}, \mathbf{N}}, \quad \mu_i = \left. \frac{\partial U}{\partial N_i} \right|_{S, \mathbf{Y}, N_{j \neq i}}. \quad (2.3)$$

**Proposition 2.1.3.** *Let  $\mathcal{S}$  be a thermodynamical system  $\Phi(U, S, \mathbf{Y}, \mathbf{N}) = 0$  its fundamental equation. If  $\phi$  is defined in an open set  $W \subseteq \mathbb{R}^{2+k+r}$ , is of class  $C^1(W)$  and all partial derivatives are not zero, then for all  $i = 1, \dots, k$  and  $j = 1, \dots, r$  we can obtain the following functions*

$$T = T(S, \mathbf{Y}, \mathbf{N}), \quad X_i = X_i(S, \mathbf{Y}, \mathbf{N}), \quad \mu_i = \mu_i(S, \mathbf{Y}, \mathbf{N}). \quad (2.4)$$

**Corollary 2.1.4.** *Let  $\mathcal{S}$  be a thermodynamical system and  $T, C_i, \mu_i$  variables with functions  $f_j$  of variables  $(S, \mathbf{Y}, \mathbf{N})$ . If the functions  $f_j$  are defined in open sets  $W_j$ , are of class  $C^1(W_i)$  and  $\partial f_j / \partial S, \partial f_j / \partial X_i \neq 0 \forall i$ , then we can obtain*

- The caloric equation of state for entropy  $S = S(T, \mathbf{Y}, \mathbf{N})$
- The thermal equations of state  $X_i = X_i(T, \mathbf{Y}, \mathbf{N})$ ,
- The caloric equation of state  $U = U(T, \mathbf{Y}, \mathbf{N})$ .

**Proposition 2.1.5.** *Let  $\mathcal{S}$  be a thermodynamical system and  $\Psi(U, S, Y_1, \dots, Y_k, N_1, \dots, N_r) = 0$  its fundamental equation. Then, there are  $k+1$  caloric equations of state for energy and  $k+1$  for entropy.*

## 2.2 Euler's form for energy

### 2.2.1 Homogeneous functions

**Definition 2.2.1.** Let  $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \rightarrow \mathbb{R}$  be a function where  $(x_1, \dots, x_r) \in \mathbb{R}^r$  are the extensive variables. We say  $f$  is *homogeneous* if and only if

$$f(\lambda x_1, \dots, \lambda x_r, x_{r+1}, \dots, x_s) = \lambda^n f(x) \quad (2.5)$$

for some  $n$ . In that case, we call  $n$  the *degree of homogeneity*.

### 2.2.2 Homogeneity criteria

**Proposition 2.2.1.** *Let  $\mathcal{S}$  be a thermodynamical system. Then,  $U$  is an homogeneous function of degree 1 and  $X_i$  homogeneous functions of degree 0.*

## 2.3 Euler's theorem for homogeneous functions

**Proposition 2.3.1.** *Let  $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \rightarrow \mathbb{R}$  be an homogeneous function of degree  $n$ . Then,*

$$nf(x_1, \dots, x_r, x_{r+1}, \dots, x_s) = \sum_{i=1}^r x_i \frac{\partial f}{\partial x_i} \Big|_{x_{j \neq i}}. \quad (2.6)$$

**Proposition 2.3.2.** *Let  $\mathcal{S}$  be a thermodynamical system. Then,*

$$U(S, Y_1, \dots, Y_k, N_1, \dots, N_r) = TS + \sum_{i=1}^k X_i Y_i + \sum_{i=1}^r \mu_i N_i. \quad (2.7)$$

We call this expression Euler's form of energy.

**Proposition 2.3.3** (Gibbs-Duhem equation). *Let  $\mathcal{S}$  be a thermodynamical system. Then,*

$$S dT + \sum_{i=1}^k Y_i dX_i + \sum_{i=1}^r N_i d\mu_i = 0. \quad (2.8)$$

## 2.4 Legendre transformation. Thermodynamical potential

**Definition 2.4.1.** Let  $f : \mathbb{R}^k \times \mathbb{R}^{n-k} \rightarrow \mathbb{R}$  be a function of class  $C^1$ . We define its *Legendre transformation* as

$$\mathcal{L}_{x_1, \dots, x_k}[y(x)] = y(p_1, \dots, p_k, x_{k+1}, \dots, x_n) - \sum_{i=1}^k x_i p_i, \text{ where } p_i = \frac{\partial f}{\partial x_i} \Big|_{x_{j \neq i}}. \quad (2.9)$$

**Definition 2.4.2.** Thermodynamical potential

**Proposition 2.4.1.** *Thermodynamical potentials contain the same information as the fundamental equation*

**Proposition 2.4.2.** *Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,*

$$dU = T dS - p dV + \mu dN \quad (2.10)$$

$$T = \frac{\partial U}{\partial S} \Big|_{V, N}, \quad p = -\frac{\partial U}{\partial V} \Big|_{S, N}, \quad \mu = \frac{\partial U}{\partial N} \Big|_{S, V}, \quad (2.11)$$

and the Euler's form of  $U$  is

$$U = TS - pV + \mu N \quad (2.12)$$

### 2.4.1 Entalpy

**Definition 2.4.3.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *entalpy* of  $\mathcal{S}$  as the Legendre trasnformation in volume of the energy.

$$H(S, p, N) := \mathcal{L}_v[U(S, V, N)] = U + pV, \text{ where } p = \frac{\partial U}{\partial V} \Big|_{S, N}. \quad (2.13)$$

**Proposition 2.4.3.** *Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,*

$$dH = T dS + V dp + \mu dN, \quad (2.14)$$

$$T = \frac{\partial H}{\partial S} \Big|_{p, N}, \quad V = \frac{\partial H}{\partial p} \Big|_{S, N}, \quad \mu = \frac{\partial H}{\partial N} \Big|_{S, p}, \quad (2.15)$$

and the Euler's form of  $H$  is

$$H = TS + \mu N. \quad (2.16)$$

### 2.4.2 Helmholtz free energy

**Definition 2.4.4.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *Helmholtz free energy* of  $\mathcal{S}$  as the Legendre transformation in entropy of the energy.

$$F(T, V, N) := \mathcal{L}_S[U(S, V, N)] = U - TS, \text{ where } T = \left. \frac{\partial U}{\partial S} \right|_{V, N}. \quad (2.17)$$

**Proposition 2.4.4.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,

$$dF = -p dV - S dT + \mu dN, \quad (2.18)$$

$$S = -\left. \frac{\partial F}{\partial T} \right|_{V, N}, \quad p = -\left. \frac{\partial F}{\partial V} \right|_{T, N}, \quad \mu = \left. \frac{\partial F}{\partial N} \right|_{T, N}, \quad (2.19)$$

and the Euler's form of  $F$  is

$$F = -PV + \mu N. \quad (2.20)$$

### 2.4.3 Gibbs free energy

**Definition 2.4.5.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *Gibbs free energy* of  $\mathcal{S}$  as the Legendre transformation in entropy and volume of the energy.

$$G(T, p, N) := \mathcal{L}_{S, V}[U(S, V, N)] = U - TS + pV, \text{ where } T = \left. \frac{\partial U}{\partial S} \right|_{V, N}, \quad p = \left. \frac{\partial U}{\partial V} \right|_{T, N}. \quad (2.21)$$

**Proposition 2.4.5.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,

$$dG = -S dT + V dp + \mu dN, \quad (2.22)$$

$$S = -\left. \frac{\partial G}{\partial T} \right|_{p, N}, \quad V = \left. \frac{\partial G}{\partial p} \right|_{T, N}, \quad \mu = \left. \frac{\partial G}{\partial N} \right|_{T, p}, \quad (2.23)$$

and the Euler's form of  $G$  is

$$G = \mu N. \quad (2.24)$$

### 2.4.4 Grand potential

**Definition 2.4.6.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. We define the *grand potential* of  $\mathcal{S}$  as the Legendre transformation in entropy and number of particle of the energy.

$$\Phi(T, V, \mu) := \mathcal{L}_{S, N}[U(S, V, N)] = U - TS - \mu N, \text{ where } T = \left. \frac{\partial U}{\partial S} \right|_{V, N}, \quad \mu = \left. \frac{\partial U}{\partial N} \right|_{S, V}. \quad (2.25)$$

**Proposition 2.4.6.** Let  $\mathcal{S}$  be a thermodynamical system formed by a monocomponent fluid. Then,

$$d\Phi = -p dV - S dT - N d\mu, \quad (2.26)$$

$$p = -\left. \frac{\partial \Phi}{\partial V} \right|_{\mu, T}, \quad S = -\left. \frac{\partial \Phi}{\partial T} \right|_{V, \mu}, \quad N = -\left. \frac{\partial \Phi}{\partial \mu} \right|_{V, T}. \quad (2.27)$$

and the Euler's form of  $\Phi$  is

$$\Phi = -pV. \quad (2.28)$$

## 2.5 Maxwell relations