# 1 Fundamentals of equilibrium thermodynamics

**Definition 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 1.2.** 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 $\mathcal{S}$.

**Definition 1.3.** We define a *system* $\mathcal{S}$ as the region we are studying.

**Definition 1.4.** We define the environment as the region different from $\mathcal{S}$ that interacts with $\mathcal{S}$.

**Definition 1.5.** Let $\mathcal{S}$be a system. We define the universe as the system formed by the system and its environment.

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

**Definition 1.7.** Let $\mathcal{S}_1, \ldots, \mathcal{S}_r$ be $r$ thermodynamical systems tha interact between them. Then, we call the union of $\mathcal{S}_1, \ldots, \mathcal{S}_r$ as a *system* $\mathcal{S}$ and every $\mathcal{S}_i$ a *subsystem of* $\mathcal{S}$.

**Definition 1.8.** Wall

**Definition 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 het and *adiabtic* 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 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.

**Definition 1.10.** We define the *infinitessimal work* as the non-exact differntial one-form

$$\bar{\mathrm{d}}W = X\,\mathrm{d}Y\,, \tag{1}$$

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

**Definition 1.11.** Let $\mathcal{S}$ be a system and $x_1, \ldots, x_r$ its state variables. We define its *thermal equation of state* as an equation $\phi(x_1, \ldots, x_r) = 0$ that relates the state variables.

**Proposition 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 1.3.** *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 1.4.** *Let $\mathcal{S}$ be a system formed by a monoatomic ideal gas. Then, its thermal equation of state is $pV - nRT = pV - Nk_BT = 0$.*

**Definition 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 1.5.** *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 1.6.** *Let $\mathcal{S}$ be a system formed by a monocomponent fluid. Then, its caloric equations of state are*

$$\varphi_1(U, T, V, N) = 0,\ \varphi_2(U, T, p, N) = 0,\ \varphi_3(U, V, p, N) = 0, \tag{2}$$

$$\psi_1(S, T, V, N) = 0,\ \psi_2(S, T, p, N) = 0,\ \psi_3(S, V, p, N) = 0. \tag{3}$$

**Corollary 1.7.** *Let $\mathcal{S}$ be a system formed by a monoatomic ideal gas. Then, its caloric equation of state is $U - \frac{3}{2}Nk_BT = 0$.*

**Definition 1.13.** Thermodynaical coefficient.

**Definition 1.14.** Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. We define the *coefficient of thermal expansion* as

$$\alpha := \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p. \tag{4}$$

**Definition 1.15.** Let $\mathcal{S}$ be a thermodynmaical system formed by a monocomponent fluid. We define the *compressibility* as

$$k_T := -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T. \tag{5}$$

**Definition 1.16.** Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. We define the *piezometric coefficient* as

$$\beta := \frac{1}{p}\left.\frac{\partial p}{\partial T}\right|_V. \tag{6}$$

**Theorem 1.8** (Reciprocity theorem)**.** *Let $\Phi(x, y, z) = 0$ be an equation. Then,*

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1. \tag{7}$$

**Corollary 1.9.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\alpha = \beta p k_T,\ \left.\frac{\partial \alpha}{\partial p}\right|_T = -\left.\frac{\partial k_T}{\partial T}\right|_p. \tag{8}$$

**Definition 1.17.** Let $\mathcal{S}$ be a thermodynamical system and $x$ one of its state variables. We define the *heat capacity of $\mathcal{S}$ at constatn $x$* as

$$C_x := \left.\frac{\bar{d}Q}{\mathrm{d}T}\right|_x. \tag{9}$$

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

**Corollary 1.10.** *Being in equilibrium is an equivalence relation.*

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

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

$$\mathrm{d}U = \bar{\mathrm{d}}Q + \bar{\mathrm{d}}W. \tag{10}$$

**Proposition 1.11** (Mayer's relation)**.** *Let $\mathcal{S}$ be a thermodynamical system and $X, Y$ its conjugate variables. Then,*

$$C_x - C_y = \left(\left.\frac{\partial U}{\partial Y}\right|_T - X\right)\left.\frac{\partial Y}{\partial T}\right|_X. \tag{11}$$

**Proposition 1.12.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$C_p - C_V = \left(\left.\frac{\partial U}{\partial V}\right|_T - p\right)V\alpha,\ C_V = \left.\frac{\partial U}{\partial T}\right|_V,\ C_p = \left.\frac{\partial U}{\partial T}\right|_p + pV\alpha. \tag{12}$$

**Proposition 1.13.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent ideal gas. Then,*

$$\alpha = \frac{1}{T},\ k_t = \frac{1}{p},\ C_p - C_v = nR. \tag{13}$$

**Definition 1.18.** Heat engine.

**Definition 1.19.** Refrigerator.

**Definition 1.20.** Conversor.

**Definition 1.21.** Efficiency.

**Proposition 1.14.** *Let $\mathcal{M}$ be a heat engine. Then, its efficiency is given by*

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{14}$$

**Proposition 1.15.** *Let $\mathcal{M}$ be a refrigerator. Then, its efficiency is given by*

$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{Q_1/Q_2 - 1} \tag{15}$$

**Proposition 1.16.** *Let $\mathcal{M}$ be a conversor. Then, its efficiency is 1.*

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

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

**Definition 1.22.** 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.

**Theorem 1.17** (Carnot's theorem)**.** *Among all heat engines that work bewteen two given thermal sources, the Carnot machine is the omst efficient one.*

**Proposition 1.18.** *For any reversible engine operating between two thermal sources of temperatures $T_1$ and $T_2$,*

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{16}$$

**Corollary 1.19.** *For the heat engine and refrigerator we have*

$$\eta_k = 1 - \frac{T_2}{T_1},\ \eta_r = \frac{1}{T_1/T_2 - 1}. \tag{17}$$

**Definition 1.23.** 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 1.20.** *The Carnot thermometer gives a scale of temperatures with one fixed point, given by the expression*

$$T = T_R\frac{Q_1}{Q_2}. \tag{18}$$

**Theorem 1.21.** *Let $\gamma$ be a cyclic process formed by infinitessimal 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,*

$$\oint_\gamma \frac{1}{T}\bar{d}Q \le 0. \tag{19}$$

**Corollary 1.22.** *Let $\gamma$ be a cyclic reversible process. Then,*

$$\oint \frac{1}{T}\bar{d}Q^{\text{rev}} = 0. \tag{20}$$

**Definition 1.24.** Let $\mathcal{S}$ be a thermodynamical system. We define the *entropy* as the state function determined by

$$\mathrm{d}S \coloneqq \frac{1}{T}\bar{\mathrm{d}}Q^{\mathrm{rev}},\ \Delta S = \int\limits_{\gamma} \frac{1}{T}\bar{\mathrm{d}}Q^{\mathrm{rev}}. \tag{21}$$

**Proposition 1.23.** *Let $\mathcal{S}$ be a thermodynamical system and $\gamma$ a path that goes from the state $A$ to $B$. Then, for every process*

$$\int\limits_{A}^{B} \frac{1}{T}\bar{\mathrm{d}}Q \leq \Delta S = S(B) - S(A), \tag{22}$$

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

**Corollary 1.24.** *Let $\mathcal{S}$ be an isolated thermodynamical system. Then, for every process*

$$\Delta S \geq 0, \tag{23}$$

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

**Corollary 1.25.** *For every process*

$$\Delta S_{\text{universe}} \geq 0. \tag{24}$$

**Corollary 1.26** (Gibb's equation)**.** *Let $\mathcal{S}$ be a thermodynamical system and $X, Y$ its conjugate variables. Then,*

$$T\,\mathrm{d}S = \mathrm{d}U - \bar{\mathrm{d}}W^{\mathrm{rev}} = \mathrm{d}U - X\,\mathrm{d}Y\,. \tag{25}$$

**Proposition 1.27.** *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 1.28.** *Let $\mathcal{M}_h$ be a heat engine and $\mathcal{M}_r$ a refrigerator. Then,*

$$W_k^{\max} = Q_1 - Q_2^{\min} = Q_1\left(1 - \frac{T_f}{T_c}\right),\ \eta_k^{\max} = 1 - \frac{T_f}{T_c}, \tag{26}$$

$$W_r^{\min} = Q_1^{\min} - Q_2 = Q_2\left(\frac{T_c}{T_f} - 1\right),\ \eta_r^{\max} = \frac{1}{T_c/T_f - 1}. \tag{27}$$

**Proposition 1.29** (Compatibility conition)**.** *Let $\mathcal{S}$ be a closed thermodynamical system and $X, Y$ its conjugate variables. Then,*

$$\left.\frac{\partial U}{\partial Y}\right|_T = -T\left.\frac{\partial X}{\partial T}\right|_Y + X. \tag{28}$$

**Corollary 1.30.** *Let $\mathcal{S}_1$ be a thermodynamical system formed by a monocomponent fliud and $\mathcal{S}_2$ a magnetic system. Then, for these system respectively*

$$\left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_V - p, \tag{29}$$

$$\left.\frac{\partial U}{\partial M}\right|_T = -T\left.\frac{\partial H}{\partial T}\right|_M + H. \tag{30}$$

**Corollary 1.31.** *Let $\mathcal{S}$ be a closed thermodynamical system formed by a monocomponent fluid. Then,*

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\alpha}{k_T}, \tag{31}$$

$$T\,\mathrm{d}S = C_V\,\mathrm{d}T + T\frac{\alpha}{k_T}\,\mathrm{d}V\,. \tag{32}$$

**Proposition 1.32.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid, Then,*

$$T\,\mathrm{d}S = C_p\,\mathrm{d}T - TV\alpha\,\mathrm{d}p = \tag{33}$$

$$\frac{C_v k_T}{\alpha}\,\mathrm{d}p + \frac{C_p}{\alpha V}\,\mathrm{d}V\,. \tag{34}$$

**Proposition 1.33** (Mayer's relation)**.** *Let $\mathcal{S}$ be a closed thermodynamical system formed by a monocomponent fluid. Then,*

$$C_p - C_v = \frac{TV\alpha^2}{k_T}. \tag{35}$$

**Proposition 1.34.** *Let $\mathcal{S}$ be a closed thermodynamical system fromed by a monocomponent fluid. Then,*

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V,\ T\frac{\alpha}{k_t} = \left.\frac{\partial S}{\partial V}\right|_T,\ C_p = T\left.\frac{\partial S}{\partial T}\right|_p, \tag{36}$$

$$\alpha V = -\left.\frac{\partial S}{\partial p}\right|_T,\ \frac{C_V k_T}{\alpha T} = \left.\frac{\partial S}{\partial p}\right|_V,\ \frac{V_p}{\alpha V T} = \left.\frac{\partial S}{\partial V}\right|_p. \tag{37}$$

**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 fluic,*

$$\lim_{T\to 0} S_V(T) = \lim_{T\to 0} S_p(T) = 0. \tag{38}$$

**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,*

$$\lim_{T\to 0} \Delta S = 0. \tag{39}$$

**Proposition 1.35.** *Planck's postulate implies Nernst's postulate.*

**Proposition 1.36.** *Let $\mathcal{S}$ be a thermodunamical system formed by a monocomponent fluid. Then,*

$$\lim_{T\to 0} C_p = \lim_{T\to 0} C_V = \lim_{T\to 0} \alpha = 0, \tag{40}$$

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

## 2 Formal structure of thermodynamics

**Proposition 2.1.** *Let $\mathcal{S}$ be a thermodynamical system formed by $r$ components and with $k$ degrees of reedom. Then, its Gibbs equation has the form*

$$\mathrm{d}U = T\,\mathrm{d}S + \sum_{i=1}^{k} X_i\,\mathrm{d}Y_i + \sum_{i=1}^{r} \mu_i\,\mathrm{d}N_i\,, \tag{41}$$

*where $X_i, Y_i$ are its conjugate variables.*

**Definition 2.1.** 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 exptensive 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

$$U(S, Y_i, \dots, Y_k, N_1, \dots, N_r). \tag{42}$$

**Proposition 2.2.** *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*

$$T = \left.\frac{\partial U}{\partial S}\right|_{\mathbf{Y},\mathbf{N}},\; X_i = \left.\frac{\partial U}{\partial Y_i}\right|_{S, Y_{j\neq i}, \mathbf{N}},\; \mu_i = \left.\frac{\partial U}{\partial N_i}\right|_{S, \mathbf{Y}, N_{j\neq i}}. \tag{43}$$

**Proposition 2.3.** *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 zer, then for all $i = 1, \dots, k$ and $j = 1, \dots r$ we can obtain the following functions*

$$T = T(S, \mathbf{Y}, \mathbf{N}),\; X_i = X_i(S, \mathbf{Y}, \mathbf{N}),\; \mu_i = \mu_i(S, \mathbf{Y}, \mathbf{N}). \tag{44}$$

**Corollary 2.4.** *Let $\mathcal{S}$ be a thermodynamical system and $T, C_i, \mu_i$ variables with functions $fj$ 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 2.5.** *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.*

**Definition 2.2.** Let $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \longrightarrow \mathbb{R}$ 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

$$f(\lambda x_1, \dots, \lambda x_r, x_{r+1}, \dots, x_s) = \lambda^n f(x) \tag{45}$$

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

**Proposition 2.6.** *Let $\mathcal{S}$ be a thermodynamical system. Then, $U$ is an homogeneous function of degree 1 and $X_i$ homogeneous functions of degree 0.*

**Proposition 2.7.** *Let $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \longrightarrow \mathbb{R}$ be an homogeneous function of degree $n$. Then,*

$$nf(x_1, \dots, x_r, x_{r+1}, \dots, x_s) = \sum_{i=1}^{r} x_i \left.\frac{\partial f}{\partial x_i}\right|_{x_{j\neq i}}. \tag{46}$$

**Proposition 2.8.** *Let $\mathcal{S}$ be a thermodynamical system. Then,*

$$U(S, Y_1, \dots, Y_k, N_1, \dots, N_r) = TS + \sum_{i=1}^{k} X_i Y_i + \sum_{i=1}^{r} \mu_i N_i. \tag{47}$$

*We call this expression Euler's form of energy.*

**Proposition 2.9** (Gibbs-Duhem equation)**.** *Let $\mathcal{S}$ be a thermodynamical system. Then,*

$$S\,\mathrm{d}T + \sum_{i=1}^{k} Y_i\,\mathrm{d}X_i + \sum_{i=1}^{r} N_i\,\mathrm{d}\mu_i = 0. \tag{48}$$

**Definition 2.3.** Let $f : \mathbb{R}^k \times \mathbb{R}^{n-k} \longrightarrow \mathbb{R}$ be a function of class $C^1$. We define its *Legendre transformation* as

$$\mathcal{L}_{x_1,\dots,x_k}[y(x)] = y(p_1, \dots, p_k, x_{k+1}, \dots, x_n) - \tag{49}$$

$$\sum_{i=1}^{k} x_i p_i, \text{ where } p_i = \left.\frac{\partial f}{\partial x_i}\right|_{x_{j\neq i}}. \tag{50}$$

**Definition 2.4.** Thermodynamical potential

**Proposition 2.10.** *Thermodynamical potentials contain the same information as the fundamental equation*

**Proposition 2.11.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \tag{51}$$

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N},\; p = -\left.\frac{\partial U}{\partial V}\right|_{S,N},\; \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}, \tag{52}$$

*and the Euler's form of $U$ is*

$$U = TS - pV + \mu N \tag{53}$$

**Definition 2.5.** 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.

$$H(S, p, N) := \mathcal{L}_v[U(S, V, N)] = U + pV, \tag{54}$$

$$\text{where } p = \left.\frac{\partial U}{\partial V}\right|_{S,N}. \tag{55}$$

**Proposition 2.12.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N\,, \tag{56}$$

$$T = \left.\frac{\partial H}{\partial S}\right|_{p,N},\; V = \left.\frac{\partial H}{\partial p}\right|_{S,N},\; \mu = \left.\frac{\partial H}{\partial N}\right|_{S,p}, \tag{57}$$

*and the Euler's form of $H$ is*

$$H = TS + \mu N. \tag{58}$$

**Definition 2.6.** Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. We define the *Helmholtz free energy* of $\mathcal{S}$ as the Legendre trasnformation in entropy of the energy.

$$F(T,V,N) \coloneqq \mathcal{L}_S[U(S,V,N)] = U - TS, \tag{59}$$

$$\text{where } T = \left.\frac{\partial U}{\partial S}\right|_{V,N}. \tag{60}$$

**Proposition 2.13.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T + \nu\,\mathrm{d}N\,, \tag{61}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N},\ p = -\left.\frac{\partial F}{\partial V}\right|_{T,N},\ \mu = \left.\frac{\partial F}{\partial N}\right|_{T,N}, \tag{62}$$

*and the Euler's form of $F$ is*

$$F = -PV + \mu N. \tag{63}$$

**Definition 2.7.** Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. We define the *Gibbs free energy* of $\mathcal{S}$ as the Legendre trasnformation in entropy and volume of the energy.

$$G(T,p,N) \coloneqq \mathcal{L}_{S,V}[U(S,V,N)] = U - TS + pV, \tag{64}$$

$$\text{where } T = \left.\frac{\partial U}{\partial S}\right|_{V,N},\ p = \left.\frac{\partial U}{\partial V}\right|_{T,N}. \tag{65}$$

**Proposition 2.14.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N\,, \tag{66}$$

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N},\ V = \left.\frac{\partial G}{\partial p}\right|_{T,N},\ \mu = \left.\frac{\partial G}{\partial N}\right|_{T,p}, \tag{67}$$

*and the Euler's form of $G$ is*

$$G = \mu N. \tag{68}$$

**Definition 2.8.** Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. We define the *grand potential* of $\mathcal{S}$ as the Legendre trasnformation in entropy and number of particle of the energy.

$$\Phi(T,V,\mu) \coloneqq \mathcal{L}_{S,N}[U(S,V,N)] = U - TS - \mu N, \tag{69}$$

$$\text{where } T = \left.\frac{\partial U}{\partial S}\right|_{V,N},\ \mu = \left.\frac{\partial U}{\partial N}\right|_{S,V}. \tag{70}$$

**Proposition 2.15.** *Let $\mathcal{S}$ be a thermodynamical system formed by a monocomponent fluid. Then,*

$$\mathrm{d}\Phi = -p\,\mathrm{d}V - S\,\mathrm{d}T - N\,\mathrm{d}\mu\,, \tag{71}$$

$$p = -\left.\frac{\partial \Phi}{\partial V}\right|_{\mu,T},\ S = -\left.\frac{\partial \Phi}{\partial T}\right|_{V,\mu},\ N = -\left.\frac{\partial \Phi}{\partial \mu}\right|_{V,T}. \tag{72}$$

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

$$\Phi = -pV. \tag{73}$$

# 3 Magnetic systems

**Definition 3.1.** Let $\mathcal{S}$ be a magnetic system. We say $\mathcal{S}$ is a *standard magnetic system* if and only if

1. $\mathcal{S}$ is homogeneous and isotropus.
2. $\mathbf{H}$ is uniform.
3. The volume of $\mathcal{S}$ is fixed.
4. $\mathcal{S}$ is a closed system.

**Proposition 3.1.** *Let $\mathcal{S}$ be a standard magnetic system. Then,*

1. *$\mathbf{M}, \mathbf{B}$ are uniform.*
2. *There is no compression-expansion work.*

**Proposition 3.2.** *Let $\mathcal{S}$ be a standard magnetic system. Then,*

$$\bar{\mathrm{d}}W_{\to\mathcal{S}} = \mu_0 H\,\mathrm{d}M\,, \qquad \mathrm{d}U_{\mathcal{S}} = T\,\mathrm{d}S + \mu_0 H\,\mathrm{d}M\,. \tag{74}$$

**Proposition 3.3.** *Let $\mathcal{S}$ be a standard magnetic system. Then, without $\mathbf{B}$ the system does not have energy and*

$$U = U_{\mathcal{S}} + E_p = U_{\mathcal{S}} - \mu_0 \left\langle \mathbf{H}, \sum_{i=1}^{N} \boldsymbol{\mu}_i \right\rangle_I, \tag{75}$$

*whwere $U$ is the energy of the uniiverse, $U_{\mathcal{S}}$ and $\mathbf{E}_p$ the energy interactions between dipoles and $\mathbf{B}_{ext}$.*

**Definition 3.2.** Let $\mathcal{S}$ be a standard magnetic system. We say $\mathcal{S}$ is uniform if $\boldsymbol{\mu}_i = \boldsymbol{\mu}$ for all $i$.

**Proposition 3.4.** *Let $\mathcal{S}$ be a uniform satandard magnetic system. Then,*

$$M = N\mu_z, \qquad U = U_{\mathcal{S}} - \mu_0 M\,\mathrm{d}H\,, \tag{76}$$

$$\mathrm{d}U = T\,\mathrm{d}S - \mu_0 M\,\mathrm{d}H \tag{77}$$

**Proposition 3.5.** *Let $\mathcal{S}$ be a uniform standard magnetic system. Then, the $T\,\mathrm{d}S$ equations and Maxwell's relations can be obtaines from the case of a monocomponent fluid by the mapping*

$$p \longmapsto \mu_0 M, \qquad V \longmapsto H. \tag{78}$$

**Proposition 3.6.** *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$T = \left.\frac{\partial U}{\partial S}\right|_{H}, \qquad M = -\frac{1}{\mu_0}\left.\frac{\partial U}{\partial H}\right|_{S}, \tag{79}$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{H}, \qquad \frac{\mu_0 M}{T} = \left.\frac{\partial S}{\partial H}\right|_{U}. \tag{80}$$

**Proposition 3.7.** *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$\mathrm{d}F = -\mu_0 M\,\mathrm{d}H - S\,\mathrm{d}T\,, \tag{81}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{H}, \qquad M = -\frac{1}{\mu_0}\left.\frac{\partial F}{\partial H}\right|_{T}. \tag{82}$$

**Proposition 3.8.** *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$U = -\left.\frac{\partial \ln Z}{\partial \beta}\right|_H, \qquad C_H = \left.\frac{\partial U}{\partial T}\right|_H = T\left.\frac{\partial S}{\partial T}\right|_H, \tag{83}$$

$$C_M = \left.\frac{\partial U}{\partial T}\right|_M + \mu_0 M \left.\frac{\partial H}{\partial T}\right|_M = T\left.\frac{\partial S}{\partial T}\right|_M. \tag{84}$$

**Definition 3.3.** Let $\mathcal{S}$ be a magnetic system. We define the *magnetic susceptibility* as

$$\xi = \left.\frac{\partial M}{\partial H}\right|_T. \tag{85}$$

**Definition 3.4.** Let $\mathcal{S}$ be a magnetic system. Then,

1. We say $\mathcal{S}$ is *paramagnetic* if and only if $\xi > 0$ and there is no interaction between dipoles from the system.
2. We say $\mathcal{S}$ is *ferromagnetic* if and only if $\xi > 0$ and maintains $\mathbf{M}$ after removing $\mathbf{H}_{\text{ext}}$.
3. We say $\mathcal{S}$ is diamagnetic if and only if $\xi < 0$.

**Proposition 3.9.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$H_1 = \alpha\cos\theta, \qquad Z = Z_1^N, \qquad Z_1 = \frac{4\pi}{\alpha}\sinh\alpha, \tag{86}$$

$$\rho(\theta,\varphi) = \frac{\alpha e^{\alpha\cos\theta}}{4\pi\sinh\alpha}, \qquad \alpha = \beta\mu_0\mu H. \tag{87}$$

**Definition 3.5** (Langevin function)**.** We define the *Langeving function* as

$$L(x) = \coth x - \frac{1}{x}. \tag{88}$$

**Proposition 3.10.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$U = -N\mu_0\mu H L(\alpha), \qquad M = N\mu L(\alpha), \tag{89}$$

$$S = k_B N\left[\ln\left(\frac{4\pi}{\alpha}\sinh\alpha\right) - \alpha\coth\alpha + 1\right] \tag{90}$$

**Proposition 3.11.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$C_H = k_B N\left(1 - \frac{\alpha^2}{\sinh^2\alpha}\right), \tag{91}$$

$$C_M = k_B N\left(\alpha^2 - \frac{\alpha^2}{\sinh^2\alpha}\right), \tag{92}$$

$$\chi = \frac{\mu N}{H}\left(\frac{1}{\alpha} - \frac{\alpha}{\sinh^2\alpha}\right). \tag{93}$$

**Proposition 3.12.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at high temperature limit we have $\alpha \ll 1$ and at low temperature limit $\alpha \gg 1$.*

**Proposition 3.13.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at high temperature limit*

$$U \approx -\frac{N\mu_0^2\mu^2}{3k_b}\frac{H^2}{T}, \qquad M \approx \frac{N\mu^2\mu_0}{3k_B}\frac{H}{T}, \tag{94}$$

$$S \approx k_B N\ln(4\pi). \tag{95}$$

**Proposition 3.14.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at low temperature limit*

$$U \approx -N\mu_0\mu H, \qquad M \approx N\mu, \tag{96}$$

$$S \approx k_B N\ln\alpha. \tag{97}$$

**Proposition 3.15.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at high temperature limit*

$$C_H \approx 0, \tag{98}$$

$$C_M \approx k_B N(\alpha - 1), \tag{99}$$

$$\chi \approx \frac{\mu N}{H}\frac{2}{3}\alpha^2. \tag{100}$$

**Proposition 3.16.** *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at low temperature limit*

$$C_H \approx k_B N(1 - 4\alpha^2 e^{-2\alpha}), \tag{101}$$

$$C_M \approx k_B N\alpha^2, \tag{102}$$

$$\chi \approx \frac{\mu N}{H}\frac{1}{\alpha}. \tag{103}$$

**Proposition 3.17.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$\epsilon_\uparrow = -\mu_0\mu H, \qquad \epsilon_\downarrow = \mu_0\mu H, \qquad \Omega = \frac{N!}{N_\downarrow! N_\uparrow!}. \tag{104}$$

**Proposition 3.18.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$U = -N\mu_0\mu H\tanh\alpha, \qquad M = N\mu\tanh\alpha, \tag{105}$$

$$S = -\alpha\tanh\alpha + \ln(2\cosh\alpha). \tag{106}$$

**Proposition 3.19.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, the dipoles are independent and*

$$H_1 = \pm\alpha, \qquad Z = Z_1^N, \qquad Z_1 = 2\cosh\alpha, \tag{107}$$

$$p(\sigma_i) = \frac{e^{\alpha\sigma_i}}{2\cosh\alpha}, \qquad \alpha = \beta\mu_0\mu H. \tag{108}$$

**Proposition 3.20.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$C_H = k_B N\frac{\alpha^2}{\cosh^2\alpha}, \tag{109}$$

$$C_M = k_B N\left[-\alpha\tanh\alpha + \alpha\coth\alpha - \alpha^2\operatorname{sech}^2\alpha\right], \tag{110}$$

$$\chi = \frac{\mu N}{H}\frac{\alpha}{\cosh^2\alpha}. \tag{111}$$

**Proposition 3.21.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at high temperature limit*

$$U \approx -\frac{N\mu_0^2\mu^2}{k_B}\frac{H^2}{T}, \tag{112}$$

$$M \approx \frac{N\mu^2\mu_0}{k_B}\frac{H}{T}, \tag{113}$$

$$S \approx k_B N\ln 2. \tag{114}$$

**Proposition 3.22.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at low temperature limit*

$$U \approx -N\mu_0\mu H, \tag{115}$$

$$M \approx N\mu, \tag{116}$$

$$S \approx 0. \tag{117}$$

**Proposition 3.23.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at high temperature limit*

$$C_H \approx k_B N\alpha^2, \tag{118}$$

$$C_M \approx k_B N(1-2\alpha^2), \tag{119}$$

$$\chi \approx \frac{\mu N}{H}\alpha^2. \tag{120}$$

**Proposition 3.24.** *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at low temperature limit*

$$C_H \approx k_B N 4\alpha^2 \mathrm{e}^{-2\alpha}, \tag{121}$$

$$C_M \approx k_B N 4\alpha^2 \mathrm{e}^{-2\alpha}, \tag{122}$$

$$\chi \approx k_B N 4\alpha \mathrm{e}^{-2\alpha}. \tag{123}$$