Contents

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, the it coincides with the universe.*

1.1.2   Interactions

Definition 1.1.7. 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 1.1.8. 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 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.

1.1.3   Work

Definition 1.1.10. We define the *infinitessimal work* as the non-exact differntial one-form

$$\bar{\mathrm{d}}W = X \, \mathrm{d}Y \,, \tag{1.1}$$

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 $x_1, \ldots, x_r$ 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 1.1.2. *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 $pV - nRT = pV - Nk_BT = 0$.*

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*

$$\varphi_1(U, T, V, N) = 0, \ \varphi_2(U, T, p, N) = 0, \ \varphi_3(U, V, p, N) = 0, \tag{1.2}$$
$$\psi_1(S, T, V, N) = 0, \ \psi_2(S, T, p, N) = 0, \ \psi_3(S, V, p, N) = 0. \tag{1.3}$$

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

1.2 Thermodynamical coefficients and heat capacities

Definition 1.2.1. Thermodynaical 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

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

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

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

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

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

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

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

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

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

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 constatn x* as

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

1.3   Zeroth law of thermodynamics

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 1.3.1. *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,*

$$\mathrm{d}U = \bar{\mathrm{d}}Q + \bar{\mathrm{d}}W.$$ (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,*

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

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

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

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

1.5   Second law of thermodynamics

1.5.1   Theral machines

Definition 1.5.1. Heat engine.

Definition 1.5.2. Refrigerator.

Definition 1.5.3. Conversor.

Definition 1.5.4. Efficiency.

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

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

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

$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{Q_1/Q_2 - 1}$$ (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 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 1.5.5. 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 bewteen two given thermal sources, the Carnot machine is the omst efficient one.*

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

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{1.16}$$

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

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

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*

$$T = T_R \frac{Q_1}{Q_2}. \tag{1.18}$$

1.5.3 Clausius theorem

Theorem 1.5.8. *Let γ 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,*

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

Corollary 1.5.9. *Let γ be a cyclic reversible process. Then,*

$$\oint \frac{1}{T} \bar{d}Q^{\mathrm{rev}} = 0. \tag{1.20}$$

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

$$\mathrm{d}S := \frac{1}{T} \bar{d}Q^{\mathrm{rev}}, \ \ \Delta S = \int_\gamma \frac{1}{T} \bar{d}Q^{\mathrm{rev}}. \tag{1.21}$$

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

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

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*

$$\Delta S \geq 0, \tag{1.23}$$

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

Corollary 1.5.12. *For every process*

$$\Delta S_{\text{universe}} \geq 0. \tag{1.24}$$

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

$$T \, dS = dU - \bar{d}W^{\text{rev}} = dU - X \, dY. \tag{1.25}$$

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,*

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

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

1.5.4 TdS equatios for a fluid

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

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

Corollary 1.5.17. *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*

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

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

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

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

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

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

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

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

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

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

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 fluic,*

$$\lim_{T \to 0} S_V(T) = \lim_{T \to 0} S_p(T) = 0. \tag{1.35}$$

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,*

$$\lim_{T \to 0} \Delta S = 0. \tag{1.36}$$

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

Proposition 1.6.2. *Let $\mathcal{S}$ be a thermodunamical system formed by a monocomponent fluid. Then,*

$$\lim_{T \to 0} C_p = \lim_{T \to 0} C_V = \lim_{T \to 0} \alpha = 0, \tag{1.37}$$

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 reedom. Then, its Gibbs equation has the form*

$$\mathrm{d}U = T\,\mathrm{d}S + \sum_{i=1}^{k} X_i\,\mathrm{d}Y_i + \sum_{i=1}^{r} \mu_i\,\mathrm{d}N_i\,, \tag{2.1}$$

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 $Y_1, \ldots, Y_k$ be its exptensive state variables and $N_1, \ldots, N_r$ the numbers of particles of each component. We define the *fundamental equation in representation of energy* of the system as

$$U(S, Y_i, \ldots, Y_k, N_1, \ldots, N_r). \tag{2.2}$$

Proposition 2.1.2. *Let $\mathcal{S}$ be a thermodynamical system and $U = U(S, Y_1, \ldots, Y_k, N_1, \ldots, N_r)$ 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*

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

Proposition 2.1.3. *Let $\mathcal{S}$ be a thermodynamical system $\Phi(U, S, \mathbf{Y}, \mathbf{N}) = 0$ its fundamental equation. If ϕ 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 $i = 1, \ldots, k$ and $j = 1, \ldots r$ we can obtain the following functions*

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

Corollary 2.1.4. *Let $\mathcal{S}$ be a thermodynamical system and T, C_i, μ_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 2.1.5. *Let $\mathcal{S}$ be a thermodynamical system and $\Psi(U, S, Y_1, \ldots, Y_k, N_1, \ldots, N_r) = 0$ 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 $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \longrightarrow \mathbb{R}$ be a function where $(x_1, \ldots, x_r) \in \mathbb{R}^r$ are the extensive variables. We say f is *homogeneous* if and only if

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

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

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

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

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

We call this expression Euler's form of energy.

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

$$S \, \mathrm{d}T + \sum_{i=1}^{k} Y_i \, \mathrm{d}X_i + \sum_{i=1}^{r} N_i \, \mathrm{d}\mu_i = 0. \tag{2.8}$$

2.4 Legendre transformation. Thermodynamical potential

Definition 2.4.1. *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*

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

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,*

$$\mathrm{d}U = T \, \mathrm{d}S - p \, \mathrm{d}V + \mu \, \mathrm{d}N \tag{2.10}$$

$$T = \left. \frac{\partial U}{\partial S} \right|_{V,N}, \ p = -\left. \frac{\partial U}{\partial V} \right|_{S,N}, \ \mu = \left. \frac{\partial U}{\partial N} \right|_{S,V}, \tag{2.11}$$

and the Euler's form of U is

$$U = TS - pV + \mu N \tag{2.12}$$

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.

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

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

$$\mathrm{d}H = T \, \mathrm{d}S + V \, \mathrm{d}p + \mu \, \mathrm{d}N, \tag{2.14}$$

$$T = \left. \frac{\partial H}{\partial S} \right|_{p,N}, \ V = \left. \frac{\partial H}{\partial p} \right|_{S,N}, \ \mu = \left. \frac{\partial H}{\partial N} \right|_{S,p}, \tag{2.15}$$

and the Euler's form of H is

$$H = TS + \mu N. \tag{2.16}$$

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 trasnformation in entropy of the energy.

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

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

$$\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T + \nu\,\mathrm{d}N\,, \tag{2.18}$$

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

and the Euler's form of F is

$$F = -PV + \mu N. \tag{2.20}$$

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 trasnformation in entropy and volume of the energy.

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

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

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N\,, \tag{2.22}$$

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

and the Euler's form of G is

$$G = \mu N. \tag{2.24}$$

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 trasnformation in entropy and number of particle of the energy.

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

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

$$\mathrm{d}\Phi = -p\,\mathrm{d}V - S\,\mathrm{d}T - N\,\mathrm{d}\mu\,, \tag{2.26}$$

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

and the Euler's form of Φ is

$$\Phi = -pV. \tag{2.28}$$

2.5   Maxwell relations

Chapter 3

Magnetic systems

3.1 Thermodynamics in magnetic systems

3.1.1 Introduction

Definition 3.1.1. 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 3.1.1. *Let $\mathcal{S}$ be a standard magnetic system. Then,*

 1. $\mathbf{M}, \mathbf{B}$ are uniform.

 2. There is no compression-expansion work.

Proposition 3.1.2. *Let $\mathcal{S}$ be a standard magnetic system. Then,*

$$\bar{\mathrm{d}}W_{\to \mathcal{S}} = \mu_0 H \, \mathrm{d}M\,, \qquad \mathrm{d}U_{\mathcal{S}} = T \, \mathrm{d}S + \mu_0 H \, \mathrm{d}M\,. \tag{3.1}$$

Proposition 3.1.3. *Let $\mathcal{S}$ be a standard magnetic system. Then, without $\mathbf{B}$ the system does not have energy and*

$$U = U_{\mathcal{S}} + E_p = U_{\mathcal{S}} - \mu_0 \left\langle \mathbf{H}, \sum_{i=1}^{N} \boldsymbol{\mu}_i \right\rangle_I, \tag{3.2}$$

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

3.1.2 Main properties

Proposition 3.1.4. *Let $\mathcal{S}$ be a uniform satandard magnetic system. Then,*

$$M = N\mu_z, \qquad U = U_{\mathcal{S}} - \mu_0 M \, \mathrm{d}H\,, \qquad \mathrm{d}U = T \, \mathrm{d}S - \mu_0 M \, \mathrm{d}H \tag{3.3}$$

Proposition 3.1.5. *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*

$$p \longmapsto \mu_0 M, \qquad V \longmapsto H. \tag{3.4}$$

Proposition 3.1.6. *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$T = \frac{\partial U}{\partial S}\bigg|_H, \qquad M = -\frac{1}{\mu_0} \frac{\partial U}{\partial H}\bigg|_S, \qquad \frac{1}{T} = \frac{\partial S}{\partial U}\bigg|_H, \qquad \frac{\mu_0 M}{T} = \frac{\partial S}{\partial H}\bigg|_U. \tag{3.5}$$

Proposition 3.1.7. *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$\mathrm{d}F = -\mu_0 M \, \mathrm{d}H - S \, \mathrm{d}T\,, \tag{3.6}$$

$$S = -\frac{\partial F}{\partial T}\bigg|_H, \qquad M = -\frac{1}{\mu_0} \frac{\partial F}{\partial H}\bigg|_T. \tag{3.7}$$

Proposition 3.1.8. *Let $\mathcal{S}$ be a uniform standard magnetic system. Then,*

$$U = -\frac{\partial \ln Z}{\partial \beta}\bigg|_H, \qquad C_H = \frac{\partial U}{\partial T}\bigg|_H = T\frac{\partial S}{\partial T}\bigg|_H, \qquad C_M = \frac{\partial U}{\partial T}\bigg|_M + \mu_0 M\frac{\partial H}{\partial T}\bigg|_M = T\frac{\partial S}{\partial T}\bigg|_M. \tag{3.8}$$

Definition 3.1.3. Let $\mathcal{S}$ be a magnetic system. We define the *magnetic susceptibility* as

$$\xi = \frac{\partial M}{\partial H}\bigg|_T. \tag{3.9}$$

3.1.3 Media classification

Definition 3.1.4. 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 $\xi < 0$.

3.2 Classical paramagnetism

Proposition 3.2.1. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$H_1 = \alpha \cos \theta, \qquad Z = Z_1^N, \qquad Z_1 = \frac{4\pi}{\alpha} \sinh \alpha, \qquad \rho(\theta, \varphi) = \frac{\alpha e^{\alpha \cos \theta}}{4\pi \sinh \alpha}, \qquad \alpha = \beta \mu_0 \mu H. \tag{3.10}$$

Definition 3.2.1 (Langevin function)**.** We define the *Langeving function* as

$$L(x) = \coth x - \frac{1}{x}. \tag{3.11}$$

Proposition 3.2.2. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$U = -N\mu_0 \mu H L(\alpha), \qquad M = N\mu L(\alpha), \qquad S = k_B N \left[\ln\left(\frac{4\pi}{\alpha} \sinh \alpha \right) - \alpha \coth \alpha + 1 \right] \tag{3.12}$$

3.2.1 Susceptibility and heat capacities

Proposition 3.2.3. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then,*

$$C_H = k_B N \left(1 - \frac{\alpha^2}{\sinh^2 \alpha} \right), \qquad C_M = k_B N \left(\alpha^2 - \frac{\alpha^2}{\sinh^2 \alpha} \right), \tag{3.13}$$

$$\chi = \frac{\mu N}{H} \left(\frac{1}{\alpha} - \frac{\alpha}{\sinh^2 \alpha} \right). \tag{3.14}$$

3.2.2 High/low temperature limits

Proposition 3.2.4. *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 3.2.5. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at high temperature limit*

$$U \approx -\frac{N\mu_0^2 \mu^2}{3k_b} \frac{H^2}{T}, \qquad M \approx \frac{N\mu^2 \mu_0}{3k_B} \frac{H}{T}, \qquad S \approx k_B N \ln(4\pi). \tag{3.15}$$

Proposition 3.2.6. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at low temperature limit*

$$U \approx -N\mu_0 \mu H, \qquad M \approx N\mu, \qquad S \approx k_B N \ln \alpha. \tag{3.16}$$

Proposition 3.2.7. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at high temperature limit*

$$C_H \approx 0, \qquad C_M \approx k_B N(\alpha - 1), \qquad \chi \approx \frac{\mu N}{H} \frac{2}{3} \alpha^2. \tag{3.17}$$

Proposition 3.2.8. *Let $\mathcal{S}$ be a classical uniform standard magnetic system. Then, at low temperature limit*

$$C_H \approx k_B N(1 - 4\alpha^2 e^{-2\alpha}), \qquad C_M \approx k_B N\alpha^2, \qquad \chi \approx \frac{\mu N}{H} \frac{1}{\alpha}. \tag{3.18}$$

3.3   Half spin paramagnetism

3.3.1   Microcanonic collectivity approach

Proposition 3.3.1. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$\epsilon_\uparrow = -\mu_0\mu H, \qquad \epsilon_\downarrow = \mu_0\mu H, \qquad \Omega = \frac{N!}{N_\downarrow! N_\uparrow!}. \tag{3.19}$$

Proposition 3.3.2. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$U = -N\mu_0\mu H \tanh\alpha, \qquad M = N\mu \tanh\alpha, \qquad S = -\alpha\tanh\alpha + \ln(2\cosh\alpha). \tag{3.20}$$

3.3.2   Canonic collectivity approach

Proposition 3.3.3. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, the dipoles are independent and*

$$H_1 = \pm\alpha, \qquad Z = Z_1^N, \qquad Z_1 = 2\cosh\alpha, \tag{3.21}$$

$$p(\sigma_i) = \frac{\mathrm{e}^{\alpha\sigma_i}}{2\cosh\alpha}, \qquad \alpha = \beta\mu_0\mu H. \tag{3.22}$$

3.3.3   Susceptibility and heat capacities

Proposition 3.3.4. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then,*

$$C_H = k_B N \frac{\alpha^2}{\cosh^2\alpha}, \qquad C_M = k_B N \left[-\alpha\tanh\alpha + \alpha\coth\alpha - \alpha^2\operatorname{sech}^2\alpha \right], \qquad \chi = \frac{\mu N}{H}\frac{\alpha}{\cosh^2\alpha}. \tag{3.23}$$

3.3.4   High/low temperature limits

Proposition 3.3.5. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at high temperature limit*

$$U \approx -\frac{N\mu_0^2\mu^2}{k_B}\frac{H^2}{T}, \qquad M \approx \frac{N\mu^2\mu_0}{k_B}\frac{H}{T}, \qquad S \approx k_B N \ln 2. \tag{3.24}$$

Proposition 3.3.6. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at low temperature limit*

$$U \approx -N\mu_0\mu H, \qquad M \approx N\mu, \qquad S \approx 0. \tag{3.25}$$

Proposition 3.3.7. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at high temperature limit*

$$C_H \approx k_B N\alpha^2, \qquad C_M \approx k_B N(1 - 2\alpha^2), \qquad \chi \approx \frac{\mu N}{H}\alpha^2. \tag{3.26}$$

Proposition 3.3.8. *Let $\mathcal{S}$ be a quantum standard magnetic system. Then, at low temperature limit*

$$C_H \approx k_B N 4\alpha^2 \mathrm{e}^{-2\alpha}, \qquad C_M \approx k_B N 4\alpha^2 \mathrm{e}^{-2\alpha}, \qquad \chi \approx k_B N 4\alpha \mathrm{e}^{-2\alpha}. \tag{3.27}$$