

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, then it coincides with the universe.*

Definition 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 1.8. 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 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.

Definition 1.10. We define the *infinitesimal work* as the non-exact differential one-form

$$\bar{d}W = X dY, \quad (1)$$

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, \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 1.2. *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 $pV - nRT = pV - Nk_B T = 0$.*

Definition 1.12. Let \mathcal{S} be a system. We define its *caloric equation of state* as an equation that relates its internal 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*

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

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

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

Definition 1.13. Thermodynamical coefficient.

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

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

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

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

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

$$\beta := \frac{1}{p} \frac{\partial p}{\partial T} \Big|_V. \quad (6)$$

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

$$\frac{\partial x}{\partial y} \Big|_z \frac{\partial y}{\partial z} \Big|_x \frac{\partial z}{\partial x} \Big|_y = -1. \quad (7)$$

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

$$\alpha = \beta p k_T, \quad \frac{\partial \alpha}{\partial p} \Big|_T = - \frac{\partial k_T}{\partial T} \Big|_p. \quad (8)$$

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 constant x* as

$$C_x := \frac{\bar{d}Q}{\bar{d}T} \Big|_x. \quad (9)$$

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 1.10. Being in equilibrium is an equivalence relation.

Axiom 3. First version from last year.

Axiom 4. Second statement from last year,

$$dU = \bar{d}Q + \bar{d}W. \quad (10)$$

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

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

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

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

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

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

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

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad (14)$$

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

$$\eta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{Q_1/Q_2 - 1} \quad (15)$$

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 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 1.22. 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 between two given thermal sources, the Carnot machine is the most efficient one.

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

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \quad (16)$$

Corollary 1.19. For the heat engine and refrigerator we have

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

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

$$T = T_R \frac{Q_1}{Q_2}. \quad (18)$$

Theorem 1.21. Let γ 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,

$$\oint_{\gamma} \frac{1}{T} \bar{d}Q \leq 0. \quad (19)$$

Corollary 1.22. Let γ be a cyclic reversible process. Then,

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

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

$$dS := \frac{1}{T} \bar{d}Q^{\text{rev}}, \quad \Delta S = \int_{\gamma} \frac{1}{T} \bar{d}Q^{\text{rev}}. \quad (21)$$

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

$$\int_A^B \frac{1}{T} \bar{d}Q \leq \Delta S = S(B) - S(A), \quad (22)$$

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

$$\Delta S \geq 0, \quad (23)$$

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

Corollary 1.25. For every process

$$\Delta S_{\text{universe}} \geq 0. \quad (24)$$

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

$$T dS = dU - \bar{d}W^{\text{rev}} = dU - X dY. \quad (25)$$

Proposition 1.27. Let $\mathcal{S}_1, \mathcal{S}_2$ be two thermodynamical 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 thermal equilibrium.

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

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

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

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

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

Corollary 1.30. 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

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

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

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

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

$$T dS = C_V dT + T \frac{\alpha}{k_T} dV. \quad (32)$$

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

$$T dS = C_p dT - TV \alpha dp = \quad (33)$$

$$\frac{C_v k_T}{\alpha} dp + \frac{C_p}{\alpha V} dV. \quad (34)$$

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

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

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

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V, \quad T \frac{\alpha}{k_T} = \left. \frac{\partial S}{\partial V} \right|_T, \quad C_p = T \left. \frac{\partial S}{\partial T} \right|_p, \quad (36)$$

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

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 fluid,

$$\lim_{T \rightarrow 0} S_V(T) = \lim_{T \rightarrow 0} S_p(T) = 0. \quad (38)$$

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,

$$\lim_{T \rightarrow 0} \Delta S = 0. \quad (39)$$

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

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

$$\lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_V = \lim_{T \rightarrow 0} \alpha = 0, \quad (40)$$

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 freedom. Then, its Gibbs equation has the form

$$dU = T dS + \sum_{i=1}^k X_i dY_i + \sum_{i=1}^r \mu_i dN_i, \quad (41)$$

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 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

$$U(S, Y_1, \dots, Y_k, N_1, \dots, N_r). \quad (42)$$

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

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

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

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

Corollary 2.4. Let \mathcal{S} be a thermodynamical system and T, C_i, μ_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 2.5. 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 $f : \mathbb{R}^r \times \mathbb{R}^{s-r} \rightarrow \mathbb{R}$ 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

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

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

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

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

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

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

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

$$S dT + \sum_{i=1}^k Y_i dX_i + \sum_{i=1}^r N_i d\mu_i = 0. \quad (48)$$

Definition 2.3. 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

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

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

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,

$$dU = T dS - p dV + \mu dN \quad (51)$$

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

and the Euler's form of U is

$$U = TS - pV + \mu N \quad (53)$$

Definition 2.5. Let \mathcal{S} be a thermodynamical system formed by a monocomponent fluid. We define the *enthalpy* of \mathcal{S} as the Legendre transformation in volume of the energy.

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

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

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

$$dH = T dS + V dp + \mu dN, \quad (56)$$

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

and the Euler's form of H is

$$H = TS + \mu N. \quad (58)$$

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 transformation in entropy of the energy.

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

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

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

$$dF = -p dV - S dT + \mu dN, \quad (61)$$

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

and the Euler's form of F is

$$F = -PV + \mu N. \quad (63)$$

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 transformation in entropy and volume of the energy.

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

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

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

$$dG = -S dT + V dp + \mu dN, \quad (66)$$

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

and the Euler's form of G is

$$G = \mu N. \quad (68)$$

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 transformation in entropy and number of particle of the energy.

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

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

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

$$d\Phi = -p dV - S dT - N d\mu, \quad (71)$$

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

and the Euler's form of Φ is

$$\Phi = -pV. \quad (73)$$