

Equilibrium Thermodynamics I:

Introduction [tsc1]

Thermodynamic system and thermodynamic state:

All matter consists of particles. Particles are always in motion of one kind or another. Thermodynamic systems, which contain a macroscopic number of particles, are vibrant under all circumstances.

Thermodynamic systems at equilibrium are in thermodynamic states which are specified by a set of time-independent state variables. The time-dependence associated with particle motion is averaged out in this description.

Equilibrium thermodynamics identifies functional relations between state variables. Such relations are named equations of state. They must satisfy stability criteria associated with thermodynamic equilibrium.

A thermodynamic state is also called macrostate. It represents a macroscopic number of microstates, each of which describes the state of all particles in the thermodynamic system.

State variables:

In homogeneous systems, it is useful to distinguish between extensive and intensive state variables. Extensive variables are proportional to the size of the system, whereas intensive variables are independent of system size.

The first group of state variables are named thermodynamic functions. They come in (thermodynamically conjugate) pairs here listed side by side. The variables on the left (right) are extensive (intensive). The product of each pair has units of energy.

V : volume	p : pressure
S : entropy	T : temperature
M : magnetization	H : magnetic field
N : number of particles	μ : chemical potential
n : number of moles	$\bar{\mu}$: chemical potential
X : generic <i>extensive</i> variable	Y : generic <i>intensive</i> variable

Ratios of extensive variables, e.g. N/V (particle density), are intensive.

The second group of state variables are named thermodynamic potentials or free energies. They are all extensive, but can be rendered intensive by scaling, e.g. U/N (per particle) or U/V (per unit volume).

U : internal energy
 E : enthalpy
 A : Helmholtz free energy
 G : Gibbs free energy
 Ω : grand potential

The third group of state variables are named response functions. Some definitions make them extensive, other definitions make them intensive.

C_V : isochoric heat capacity	c_V : isochoric specific heat
C_p : isobaric heat capacity	c_p : isobaric specific heat
χ_T : isothermal susceptibility	
χ_S : adiabatic susceptibility	
	κ_T : isothermal compressibility
	κ_S : adiabatic compressibility
	α_p : thermal expansivity

Symbols vary between sources, especially for thermodynamic potentials.

In inhomogeneous systems, most intensive state variables become functions of position, whereas all extensive variables become integrals over position.

Equations of state:

The empirical specification of a thermodynamic system is traditionally expressed in the form of two kinds of equations of state.

- ▷ *Thermodynamic equation of state:*
Functional relation between thermodynamic variables.
For example: $pV = nRT$ (classical ideal gas).
- ▷ *Caloric equation of state:*
Temperature dependence of internal energy or heat capacity.
For example: $U = C_V T$ with $C_V = \text{const}$ (classical ideal gas).

The complete thermodynamic information about a system is encoded in this dual specification. In more complex systems, the thermodynamic equation of state consists of multiple relations.

Thermodynamic equation of state for a classical gas:

Classical ideal gas: $pV = nRT$,

$$n = N/N_A \quad (\text{number of moles}),$$

$$N_A = 6.022 \times 10^{23} \quad (\text{Avogadro's number}),$$

$$R = N_A k_B = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{gas constant}),$$

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad (\text{Boltzmann constant}).$$

$$\text{Van der Waals gas: } \left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT.$$

Ad-hoc generalization of ideal gas. Pressure reduction, $-an^2/V^2$, accounts for long-range attractive interaction. Exclusion volume, nb , accounts for short-range repulsive interaction.

$$\text{Virial expansion: } p = \frac{nRT}{V} \left[1 + \frac{n}{V} B_2(T) + \left(\frac{n}{V} \right)^2 B_3(T) + \dots \right].$$

Systematic generalization of ideal gas. The virial coefficients $B_n(T)$, accessible to specialized methods of analysis, represent particle interaction effects, which gain traction as the density n/V increases.

Encoding thermodynamic information:

The most concise way of encoding the complete specification of a thermodynamic system at equilibrium is in the form of a thermodynamic potential. All thermodynamic quantities of interest about a given system can directly be derived from a thermodynamic potential.

Strategies commonly pursued:

▷ *Equilibrium thermodynamics:*

Construct a thermodynamic potential from the empirical information contained in the thermodynamic and caloric equations of state. Then derive any thermodynamic quantity of interest from the thermodynamic potential.

▷ *Equilibrium statistical mechanics:*

Derive a thermodynamic potential (or partition function) from the microscopic specification of the system in the form of a many-body Hamiltonian. Then derive any thermodynamic quantity of interest from the thermodynamic potential.

Thermodynamic contacts:

The primary criterion in a classification of thermodynamic systems is the combination of thermodynamic contacts between system and environment.

- 1 *Mechanical interaction* (with work source).
Exchange of energy via work performance.
- 2 *Thermal interaction* (with heat reservoir).
Exchange of energy via heat transfer.
- 3 *Mass interaction* (with particle reservoir).
Exchange of energy via matter transfer.

Major types of thermodynamic systems:

- isolated system*: contact 1,
- closed system*: contacts 1, 2,
- open system*: contacts 1, 2, 3.

Additional combinations do exist. Superfluid helium confined by a porous material permits contacts 1 and 3 and prohibits contact 2.

Zeroth law of thermodynamics:

Mathematically speaking, thermodynamic equilibrium is an equivalence relation: it is postulated to be reflexive, symmetric, and transitive.

- Reflexivity: $A \equiv A$
A thermodynamic system A is in equilibrium with itself.
- Symmetry: $A \equiv B \Rightarrow B \equiv A$
If system A is in equilibrium with system B , then system B is in equilibrium with system A .
- Transitivity: $A \equiv B, B \equiv C \Rightarrow A \equiv C$
If system A is in equilibrium with system B and system B with system C , then system A is also in equilibrium with system C .

The zeroth law makes it possible to design a device (thermometer) that measures an attributes (empirical temperature) characteristic of systems in thermodynamic equilibrium with each other.

First law of thermodynamics:

Thermodynamic equilibrium states have a definite internal energy U with no memory about the source (work, heat, radiation, ...) of the energy content.

Internal energy is a state variable, but work and heat are not state variables.

Energy conservation in a thermodynamic process means that the internal energy may change if energy is imported or exported via work performance, heat transfer, radiation, or other means energy exchange.

Second law of thermodynamics:

Heat flows spontaneously from high to low temperatures.

This empirical fact limits the use of the energy contained in a thermodynamic system for work performance. It puts a limit to the efficiency of heat engines. It makes some thermodynamic processes irreversible.

The second law establishes the entropy S and the absolute temperature T as state variables.

Third law of thermodynamics:

The entropy difference between any two equilibrium states approaches zero as their absolute temperature approaches zero.

A consequence of this empirical fact (grounded in quantum mechanics) is that there exists no thermodynamic process by which $T = 0$ can be reached in a finite number of steps.

In a nutshell, the zeroth, first, second, and third laws are encapsulated in an equivalence, an equality, an inequality, and a limit, respectively.

Thermodynamic processes:

The study of equilibrium thermodynamics cannot do without processes that connect equilibrium states. Processes necessarily disturb the equilibrium.

Generic process:

- During a generic process between equilibrium states, some of the thermodynamic variables may not be defined.
- Information about changes in all thermodynamic variables during a generic process can be obtained if we connect the same initial and final equilibrium states by a quasi-static process.

Quasi-static process:

- A quasi-static process involves infinitesimal steps between equilibrium states along a definite path in the space of state variables.
- The equations of state remain satisfied as the thermodynamic variables change during a quasi-static process.

Adiabatic process:

- During an adiabatic process the system is thermally isolated. There is no heat transfer. Changes are caused by work performance.
- An adiabatic process must not be too fast in order not to produce entropy within the system.
- In some practical applications, an adiabatic process must not be too slow in order to prevent significant heat exchange between the system and the environment.

Reversible and irreversible processes:

- In an isolated system, the entropy (to be defined) stays constant during a reversible process and increases during an irreversible process.
- Quasi-static processes can be reversible or irreversible.

Differentials:

The differential,

$$dF = c_1(x_1, x_2)dx_1 + c_2(x_1, x_2)dx_2,$$

expresses the infinitesimal change of some quantity along an infinitesimal step of a path in the plane of the independent variables x_1, x_2 .

We assume that c_1 and c_2 are arbitrary differentiable functions.

In general, the integral of dF between any two points (a_1, a_2) and (b_1, b_2) depends on the path. For paths (i) and (ii) we can write,

$$\int_{(i)} dF = \int_{a_1}^{b_1} dx_1 c_1(x_1, a_2) + \int_{a_2}^{b_2} dx_2 c_2(b_1, x_2).$$

$$\int_{(ii)} dF = \int_{a_2}^{b_2} dx_2 c_2(a_1, x_2) + \int_{a_1}^{b_1} dx_1 c_2(x_1, b_2).$$

If the functions c_1 and c_2 satisfy the condition,

$$\frac{\partial c_1}{\partial x_2} = \frac{\partial c_2}{\partial x_1},$$

then dF is an exact differential,

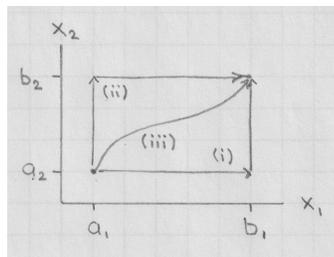
$$dF = \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2,$$

of a function $F(x_1, x_2)$, and its integration between two point is guaranteed to be path-independent:

$$\int_{(a_1, a_2)}^{(b_1, b_2)} dF = F(b_1, b_2) - F(a_1, a_2),$$

The distinction between exact and inexact differentials is important in thermodynamics.

- The differentials of state variables are exact. Integrating the differential of a state variable along a closed path is then zero as it must be.
- Thermodynamics also deals with differentials that are not state variable such as dQ (heat) and dW (work). In cyclic processes (along closed paths), the net heat transfer and work performance are nonzero, in general.



Exercises:

- ▷ Fast heat [tex143]
- ▷ Expansion and compression of nitrogen gas [tex144]
- ▷ Bathtub icebreaker [tex145]
- ▷ Exact and inexact differentials I [tex5]
- ▷ Exact and inexact differentials II [tex146]
- ▷ Exact and inexact differentials III [tex168]

Additional materials:

- ▷ Thermodynamics overview [tln2]
- ▷ Equations of state for ideal gas and real fluid [tsl12]
- ▷ Physical constants [tsl47]
- ▷ Relevant textbooks [tln90]