

Review of Thermodynamics. 1: The Basic Laws

What is Thermodynamics?

- *Idea:* The study of states of physical systems that can be characterized by macroscopic variables, usually equilibrium states (mechanical, thermal or chemical), and possible transformations between them. It started as a phenomenological subject motivated by practical applications, but it gradually developed into a coherent framework that we will view here as the macroscopic counterpart to the statistical mechanics of the microscopic constituents, and provides the observational context in which to verify many of its predictions.
- *Plan:* We will mostly be interested in internal states, so the allowed processes will include heat exchanges and the main variables will always include the internal energy and temperature. We will recall the main facts (definitions, laws and relationships) of thermodynamics and discuss physical properties that characterize different substances, rather than practical applications such as properties of specific engines. The connection with statistical mechanics, based on a microscopic model of each system, will be established later.

States and State Variables for a Thermodynamical System

- *Energy:* The internal energy E is the central quantity in the theory, and is seen as a function of some complete set of variables characterizing each state. Notice that often energy is the only relevant macroscopic conservation law, while momentum, angular momentum or other quantities may not need to be considered.
- *Extensive variables:* For each system one can choose a set of extensive variables (S, \vec{X}) whose values specify the equilibrium states of the system; S is the entropy and the \vec{X} are quantities that may include V , $\{N_i\}$, q , \vec{M} , \vec{p} , \vec{L} , ... (For a substance i , the variable N_i can be any measure of the amount of matter, such as number of particles or moles, or mass.) One equation of state expresses E as a function of (S, \vec{X}) .
- *Intensive variables:* A set of variables (T, \vec{f}) , each conjugate to one of the extensive variables. The temperature T is conjugate to S , and the other conjugate pairs (\vec{X}, \vec{f}) are defined by the fact that when no heat is exchanged, the energy change in an infinitesimal process can be written as $dE = \vec{f} \cdot d\vec{X}$; for example, $(V, -p)$, (N_i, μ_i) , (q, Φ) , (\vec{M}, \vec{B}) , etc. Intensive variables play an important role in equilibrium states.
- *Other equations of state:* Once values for a complete set of state variables (one variable for each pair (X, f)) are specified, values for all other variables can be obtained using equations of state. For a neutral, single-species, non-magnetic gas described by T , V and N , they are $p(T, V, N)$, $S(T, V, N)$ and $\mu(T, V, N)$.
- *Physical processes:* Reversible ones are represented by lines in this space. Questions of interest for us may include finding the value of any state variable after any given transformation, or calculating the response of state variables to any change in the external parameters. Later, using statistical mechanics, our goals will include deriving the equations of state and response functions from models of the microscopic interactions.

Zeroth Law: Systems in Thermal Equilibrium Have the Same Temperature

- *Statement:* If system A is in equilibrium (thermal, mechanical, chemical, ...) with systems B and C , then systems B and C are in equilibrium with each other. It amounts to the possibility of establishing universal scales for the corresponding intensive quantities. It has a statistical justification, as we will see soon.

First Law: Heat is a Form of Energy

- *Statement:* If Q is the heat transferred to a system in a physical process between thermodynamical states and W the work done on the system during that process, then the conservation of energy is expressed by

$$\Delta E = Q + W \quad \text{or, infinitesimally,} \quad dE = \delta Q + \delta W .$$

The process need not be reversible. If it is, it can be represented as a curve α in the thermodynamical state space, and the work $W = \int_{\alpha} \delta W = \int \vec{f} \cdot d\vec{X}$ can be expressed as a sum of contributions from variations of each of the extensive variables; the intensive coefficients \vec{f} can be seen as generalized forces. We will see how the heat Q transferred in a reversible transformation can be expressed after introducing the second law.

- *Remark:* If we can account for all forms of work W , the first law can be taken as a definition of the heat exchanged $Q = \Delta E - W$; this is often convenient calculationally. However, conceptually we can also call heat any spontaneous energy flow resulting purely from a difference in temperature; work is then the remaining part of ΔE . Notice that ΔE only depends on the initial and final states, while Q and W are path-dependent.

Second Law: Heat Flows From Hotter to Colder Systems

- *Statements:* (Kelvin) No thermodynamic transformation can have as sole effect that of extracting heat from a system and converting it entirely into work; (Clausius) No thermodynamic transformation can have as sole effect that of extracting heat from a colder system and delivering it to a hotter system. [But be careful when applying this to $T < 0$ systems!] For our purposes, a statement in terms of entropy will be more useful, since entropy is more directly related to a microscopic, statistical point of view.

- *Entropy statement:* There exists an extensive state variable $S(E, \vec{X})$, normally taken to be a monotonically increasing function of E (but there are exceptions!), such that, if $A \mapsto B$ is an adiabatic transformation (one with $Q = 0$) between *any* accessible states, $\Delta S \geq 0$; it follows that $\Delta S = 0$ in a reversible adiabatic process.

- *Remarks:* Notice that (i) although S is a function of state like E , because it is not a conserved quantity unlike E it is not “exchanged”, “absorbed” or “stored”, and (ii) in thermodynamics one can only calculate entropy *differences* ΔS ; Systems for which S decreases with E have $T < 0$; (iii) There exist non-extensive definitions of entropy (Tsallis entropy).

Fundamental Identity of Thermodynamics

- *Derivation:* Using the fact that $\Delta S = 0$ for a reversible adiabatic transformation we can derive a useful identity that expresses the first law for any reversible transformation. If the transformation is adiabatic,

$$dS \equiv \left. \frac{\partial S}{\partial E} \right|_{\vec{X}} dE + \left. \frac{\partial S}{\partial \vec{X}} \right|_E \cdot d\vec{X} = 0 .$$

This means that, if we define $T := (\partial S / \partial E|_{\vec{X}})^{-1}$, an intensive quantity (usually positive), and substitute

$$dE = \delta Q + \vec{f} \cdot d\vec{X} , \quad \text{with} \quad \delta Q = 0 ,$$

into the expression for dS we get the relationship $\partial S / \partial \vec{X}|_E = -T^{-1} \vec{f}$ between state functions, which does not refer to any specific type of transformation, so the differential dS can be identically written

$$dS = \frac{1}{T} dE - \frac{1}{T} \vec{f} \cdot d\vec{X} , \quad \text{or} \quad dE = T dS + \vec{f} \cdot d\vec{X} ,$$

where we consider E as a function of the extensive thermodynamical variables (S, \vec{X}) and the relevant $\vec{f} \cdot d\vec{X}$ terms that appear in the equation depend on the type of system considered. For example,

$$dE = T dS - p dV + \mu dN - \vec{B} \cdot d\vec{M} + \Phi dq + \dots$$

- *Relationship with the first law:* If we take the intensive variables $(T, \vec{f}) = (T, p, \mu, \dots)$ to be given by suitable derivatives of E , for example $T := \partial E / \partial S|_V$ and $p := -\partial E / \partial V|_S$, then the last equation is an identity. Applying the first law to a reversible, infinitesimal transformation tells us then that this p is in fact the thermodynamic pressure and that in this case $\delta Q = T dS$.

Third Law: It Is Impossible to Cool a System to Absolute Zero Temperature

- *Statements:* Some equivalent statements are (i) The entropy of a system approaches a minimum finite value (possibly zero) as $T \rightarrow 0$; (ii) No (finite) physical process can lead to a system reaching absolute zero; (iii) The heat capacity of the system goes to zero as $T \rightarrow 0$ —we will come back to this.

- *Comment:* As we’ll see, the third “law” is not satisfied by some important models of physical systems.

Reading

- *Kennett:* Appendix B is a primer/overview similar to this one in level and amount of detail. Many books on statistical mechanics have chapters on Thermodynamics. For books that discuss these topics, see below.
- *Books with summaries:* Chandler, Secs 1.1–1.4; Kardar, Secs 1.1–1.6 and 1.10; Mattis & Swendsen, Secs 3.1–3.4; Plischke & Bergersen, Secs 1.1–1.2; Reichl, Secs 3.1–3.4; Reif, Ch 3; Schwabl, Ch 5.
- *Undergraduate textbooks with good treatments:* Schroeder 2000; Gould & Tobochnik 2010; Huang 2010.