THERMODYNAMICS, STATISTICAL PHYSICS AND THEIR LAWS

Fernando del Río
Departamento de Física, Universidad Autónoma Metropolitana, México, DF, México

Víctor Romero-Rochín
Instituto de Física, Universidad Nacional Autónoma de México, México, DF, México

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Contents

Summary

Thermodynamics, one of the best established physical disciplines, is built on four general statements or Laws of wide applicability. These laws account for the internal properties and behavior of macroscopic systems; this chapter is devoted, in the first place, to give a concise but rigorous treatment of them. In second place, the most basic concepts of Statistical Mechanics are presented together with the central postulate of this discipline. The presentation is entirely self-contained and can be regarded as an

introduction to more ample or specialized treatments. Basic concepts of Thermodynamics such as heat, temperature, energy and entropy are defined and developed. Statistical Mechanics is introduced as the theoretical framework spanning the gap between the macroscopic and microscopic description of the state of macroscopic systems. The applicability of Thermodynamics to systems in steady or stationary states far from equilibrium, such as living organisms is briefly considered.

1. Introduction: On the Nature and Importance of Thermodynamic Laws

The laws of Thermodynamics constitute a set of very general statements about the behavior of macroscopic bodies that supersedes the details of their microscopic nature. They apply equally well to gases, solids, magnets, biological systems, etc. The laws tell us about properties such as temperature, pressure, volume, magnetization, polarization, specific heats and chemical reaction constants, among many others, but also about quantities a bit more elusive to grasp such as energy, entropy or enthalpy.

There is a wide consensus among physicists today that we know the dynamical laws explaining the behavior of systems at the microscopic level, namely, the laws of Quantum Mechanics with the laws of Classical Mechanics as a limiting case; the latter applicable also to the motion of macroscopic bodies. However, systems with a large number of atoms and molecules show subtle regularities in their internal behavior that are independent of microscopic details. These regularities are summarized strikingly in the Laws of Thermodynamics. The ultimate explanation for the validity of the laws rests, finally, on the fact that all matter is composed of atoms and molecules and that any macroscopic body has inordinate large numbers of them. For instance, one cubic centimeter of air at 25° C and atmospheric pressure, contains 10^{19} molecules!

The thermodynamic laws have a very wide range of validity. They were discovered during the Industrial Revolution in the XIX century, but it was not until the middle of the XX century when they were completely understood, at least for systems in equilibrium.

It is a general fact of nature that any macroscopic system that is kept isolated from its surroundings will eventually, after a time long enough, reaches a state in which two things happen: First, all its thermodynamic variables become appreciably constant with time and, second, all macroscopic fluxes of energy, momentum or substance within the system are very close to zero. Such a state is said to be one of *thermodynamic equilibrium* (This essential assumption, that all isolated systems eventually reach a state of thermodynamic equilibrium, is incorporated into the Second Law). Although most systems around us are not in equilibrium, states of thermodynamic equilibrium are particularly important for the logical coherence of Thermodynamics.

The fact that thermodynamic laws take their most rigorous expression for strict equilibrium states does not imply that they are not applicable, in some circumstances, to systems away from equilibrium. The laws do apply more generally in two important ways: First, certain processes connecting states of equilibrium—termed quasi-static—serve as limiting cases of processes out of equilibrium. Analysis of these limiting processes sets rigorous bounds to the attributes of the more general transformations. Second, many systems are out of equilibrium in a global sense whilst locally they may

be considered in equilibrium. For instance, the Earth's atmosphere is strictly not in equilibrium: It sustains noticeable currents and winds and its temperature is neither constant nor uniform all over the globe. However, at a smaller scale and for not-very-long periods of time, parts of it can be considered in equilibrium. That is why it makes sense to talk, for instance, about the temperature of a city at a definite time of a given day. Thermodynamic laws apply to each part of the system and, therefore, have consequences on the properties of the system as a whole.

Among the great variety of systems away from equilibrium, many show strong regularities in their thermodynamic properties. Due to the presence of gravitational forces on Earth and, especially, because of the continuous flux of energy coming from the Sun, many systems around us are away from equilibrium but still exhibit some kind of stability; the atmosphere is also an example of this. Living organisms, from bacteria to human beings, constitute the most notorious examples of systems out of equilibrium that remain in steady states for relatively long times. The steady condition of living systems is maintained essentially by the energy flux from the Sun, and that of the atmosphere necessitates both the Sun and gravity. We shall elaborate in the following further on the relevance of the laws for these systems.

The laws are four in number:

1. The Zeroth Law establishes the existence of temperature as a measurable quantity that, together with other thermodynamic properties, defines the state of equilibrium of a system.
2. The First Law states that energy is conserved and defines it as a thermodynamic state variable; it constitutes one of the most profound statements about how Nature behaves.
3. The Second Law sets very strict limits on the way processes –or transformations in a body– occur. Many important predictions of Thermodynamics involve this law and we shall dwell more deeply on it.
4. The Third Law establishes the existence of the absolute zero of temperature and the impossibility of reaching it in a finite time.

The importance of these laws rests on their very wide applicability. Nevertheless, the reader must become aware that they are not "in order" (namely, First goes first, Second goes second, and so on). They must be taken as a coherent set of laws, each at the same level of importance as the others. Some predictions may need the use of one or two laws, but most follow from the use of all of them in unison.

The main consequences of the laws are that they allow us to predict which things may happen in Nature and which do not. They also set constraints to the ways in which natural processes occur.

The laws refer sometimes to easily observable phenomena, enabling us to understand these as part of a consistent and ordered picture of the world. For instance, any person has surely noticed that when two bodies of different temperatures are put in contact, the hotter body cools down while the initially colder body heats up; things never happen in

the reverse way. Another fact of common experience is that the volume of a body always diminishes upon compression. These two seemingly disconnected facts become related by the rationale of the thermodynamic laws.

The purposes of this chapter are threefold: First, to express rigorously the laws of Thermodynamics and its main concepts, but without entering into proofs. These can be found in specialized texts. Second, to show how the validity of the laws rests on two grounds: On the laws that govern the microscopic behavior of physical systems and on the fact that macroscopic systems have a very large number of particles; the theory that bridges these two extremes is called Statistical Physics. The last purpose is to illustrate these ideas by several key examples.

2. Thermodynamic Systems and Their Description

2.1. Thermodynamic Systems

Thermodynamic systems consist of a large number of microscopic elements. All the systems on whose observation the thermodynamic laws have been built are confined within some finite and macroscopic volume V. Hence special care must be taken when discussing the thermodynamics of spatially unbound systems, with uncertain boundaries, such as the Universe. The microscopic constituents of thermodynamic systems may be particles such as molecules, atoms, photons, electrons, etc., or more abstract entities such as spins or oscillation modes. Any macroscopic body can be treated as a thermodynamic system. The Sun, the Earth, the water of a lake, a stone, an animal, a given part of the atmosphere, the leaf of a plant and a locomotive, are all examples of thermodynamic systems. A system is separated from the rest of the universe by its *boundary*, which may correspond to an actual wall −as for a gas in a vessel− or to a mathematical surface (infinitely thin surface) −as for that separating a liquid from its overlaying vapor; definition of a system requires sometimes to specify some condition other than the boundary, as when referring to the water vapor within a given volume of humid air. A given system may be influenced by other physical systems beyond its boundary, which are called the *surroundings* of the system. In this chapter, unless otherwise specified, the word *system* will mean a thermodynamic one.

A system may exchange energy with its surroundings. A broad and useful classification of systems follows the types of interaction allowed for by their boundaries: *Isolated* systems are those whose boundaries prevent any kind of energy exchange with their surroundings; impermeable boundaries −those inhibiting the transport of any kind of particle− surround *closed* systems, whereas an *open* system can exchange mass, i.e. particles, with its surroundings. The conditions needed for a certain type of interaction to hold are called *constraints*.

Thermodynamics focuses on the *internal state* of systems and studies those actions able to affect those states. It is not concerned at all with the motion of the center of mass of the macroscopic system under scrutiny –a subject of Classical Mechanics–, which is therefore assumed to be at rest and with vanishing total angular momentum.

Standard thermodynamic treatments apply to systems that are macroscopic in the three spatial dimensions. The laws are equally valid for systems that are not macroscopic in one or two of their dimensions, such as very thin films, powders, finely grained materials or fluids confined within very narrow and long pores; however, one should be very careful in applying the laws to these systems.

2.2. Thermodynamic Variables

The internal state of a thermodynamic system –and of any macroscopic subsystem of it– is described by means of thermodynamic variables such as temperature θ, pressure P, molar specific heats c_V and c_P, dielectric constant δ, etc. All these are physical quantities that apply either to the whole system or to any of its macroscopic parts. A thermodynamic state is defined by the values of the thermodynamic properties and these are thus called also *state variables*. If some macroscopic parts of a system are moving, description of these motions is part of the specification of the state.

A *global* thermodynamic variable refers to a property of the whole system, whereas a *local* variable $X(\mathbf{r})$ refers to a 'point' $\mathbf{r}$ in space. Actually, $X(\mathbf{r})$ means the value of X measured over a sub-volume $\Delta V(\mathbf{r})$ centered on the point $\mathbf{r}$. Here ΔV has to be small enough to be treated as a 'point' from the macroscopic point of view but at the same time big enough to contain a very large number of particles. Local variables are in general functions of position and time, $X(\mathbf{r},t)$, while global variables depend only on time, $X(t)$. Typical global variables are the volume V, the quantity of substance of component α, denoted by n_α and measured in moles, and the total number of moles $n = \Sigma\, n_\alpha$, with $\alpha = 1, 2, \ldots, c$ and c being the number of different components or species. The composition of a system is determined by the relative abundance of the different species, given usually by the set of molar fractions $\{x_\alpha\}$ with $x_\alpha = n_\alpha/n$. The shape of a system, however, does not usually affect the value of its thermodynamic properties and hence it is not a relevant quantity; thin films, porous media and finely grained materials, and systems in non-uniform external fields are among the exceptions.

The volume V and the total number of moles n define the size of a system S. Varying this size by a factor ξ means a new system S' with the same composition $\{x_\alpha\}$ as S but with $n' = \xi n$ moles in a volume $V' = \xi V$. In this respect, most relevant thermodynamic variables belong to either one of two distinct types: An *extensive* variable X is such that when the size of the system is modified by the factor ξ it acquires the new value $X' = \xi X$. In contrast, an *intensive* variable is left invariant when the system suffers a change in size and $X' = X$. Again, systems with a very large area-to-volume ratio, among others, may require the introduction of nonextensive variables. For example, the energy of a system constituted by two thin subsystems sharing a common interface will not be equal to the sum of the energies of the subsystems.

Many thermodynamic variables are measured directly in the laboratory or in the field by means of macroscopic instruments; any one of these variables X is the time average of a corresponding instantaneous dynamical quantity $X_{\mathrm{inst}}(t)$ that evolves with the dynamics of the microscopic elements of the system:

$$X(t) = \frac{1}{\Delta t} \int_t^{t+\Delta t} X_{\text{inst}}(t')\, dt'. \tag{1}$$

This average is taken over a time Δt satisfying two requirements in order to represent a true thermodynamic average: First, Δt has to be short enough for the measurement to be considered instantaneous from the macroscopic point of view and, second, Δt has to be long enough to 'average out' the instantaneous fluctuations due to motions of only a few molecules. These conditions on the definition of average gives due sense to assertions like 'the barometric pressure was 750 mmHg at 8 O'clock': It means that the pressure was measured as an average over a time Δt of, say, a millisecond and taken starting at 8 O'clock. However, some thermodynamic variables, such as the entropy S, cannot be measured directly in terms of 'macroscopically instantaneous' averages but are defined in terms of other directly measurable variables. This connection between thermodynamic and microscopic dynamical variables is provided for by Statistical Physics, a subject to be treated in Section 5.

2.3. Equilibrium and Interactions

The time needed by an isolated system to reach equilibrium is called the relaxation time. This time is roughly proportional to the spatial length of a system and inversely proportional to the speed with which matter or energy flow through the system: particle diffusion, heat conductivity or the speed of sound. Once in equilibrium, the thermodynamic variables do not change appreciably over the time during which the system is being observed and $X = $ constant. States in which thermodynamic variables are constant but with nonzero fluxes of energy, substance or momentum are called *stationary* or *steady*. Many systems out of equilibrium are in states such that every sub-volume $\Delta V(\mathbf{r})$ has had time enough to reach internal equilibrium. In that case, the system is said to be in *local equilibrium* and standard Thermodynamics may be applied locally.

Systems in thermodynamic equilibrium show one or more macroscopic and homogeneous regions, called *phases*, like the solid, liquid and gaseous phases exhibited by pure substances. When external fields are weak and constant, local properties are uniform over each phase, but when external fields are not negligible, properties $X(\mathbf{r})$ will vary from point to point and one speaks of non-uniform systems.

The study of systems in thermodynamic equilibrium, of their changes of state and of the effects produced by different kinds of process is the direct subject matter of Classical Thermodynamics and its laws.

Two thermodynamic systems brought into contact will interact with each other by interchanging energy. The type of energy interchanged depends on the nature of the boundary between the systems and of the constrictions being applied. Based on experience, all these interactions are conveniently classified in three broad types:

1. *Mechanical interactions*. In these, the forces exerted by systems on each other may perform mechanical work. A uniform and electrically-neutral pure fluid,

which we will take here as illustration due to its simplicity, exerts a pressure $P = F_\perp/a$, where $F_\perp$ is the normal component of the force F that the fluid exerts on an element of its boundary surface and a is the area of that element; $F_\perp$ is taken as positive when the force is directed outwards from the fluid. The force $F_\perp$ (or the pressure P) performs an amount of work $\delta W = PdV$ when the surface is displaced so that the volume of the fluid changes by an amount dV. More in general, Classical Mechanics and Electrodynamics prescribe the existence of generalized forces, F_j, their corresponding generalized displacements $d\ell_j$ and the work $\delta W_j = F_j d\ell_j$ that they may perform. The variables F_j and ℓ_j are considered conjugate of each other. Mechanical interactions may involve contact forces other than pressure –such as surface tension and (linear) tension– or force fields –gravitational, electric or magnetic. The specific form of $F_j d\ell_j$ for these and other cases are found in textbooks.

2. *Chemical, mass or particle interactions*. These occur when the boundary of a system is permeable to the transfer of one or more types of substance or particle. Transfer to S of an infinitesimal quantity dn_α of substance of species α implies a transfer of energy $dA_\alpha = \mu_\alpha dn_\alpha$ where μ_α is the chemical potential of species α in S.

3. *Thermal interaction*. This occurs when the boundary of S is *diathermic*, i.e., when it allows the transfer of a quantity of heat δQ between the systems. A boundary resistant to the transfer of heat is called an *insulating* or *adiabatic* wall.

When two systems interact mechanically, chemically, thermally or in any combination of the three, the corresponding type of equilibrium may be reached in each case. For a general type of interaction the systems are said to reach *thermodynamic* equilibrium. A non trivial consequence of the Thermodynamic laws is that if two systems, initially not in equilibrium, are allowed to equilibrate spontaneously by either mechanical or chemical interactions, they will always end up sharing the same temperature: They will equilibrate *thermally*, in addition to the mechanical or chemical equilibrium.

In equilibrium, all the interacting and macroscopic subsystems in which any system may be partitioned are in thermodynamic equilibrium with each other. The system is then said to be in a state of *internal equilibrium*.

3. The Thermodynamic Laws

3.1. Temperature and the Zeroth Law

The 'Zeroth' Law states that thermal equilibrium is *transitive*. This means that if system S_1 is in a state of equilibrium with S_2 and separately with S_3, then it follows that S_2 and S_3 are in mutual equilibrium. This simple statement implies the existence of the temperature as an intensive state thermodynamic property. The temperature θ is such that any two systems S_1 at θ_1 and S_2 at θ_2 will be in mutual equilibrium if and only if $\theta_2 = \theta_1$.

Mechanical and chemical equilibria are also transitive and have intensive variables associated to them. Two fluids exerting contact forces on each other will have, in equilibrium, equal pressures. Chemical equilibrium between systems S and S′ on interchange of species α, occurs if and only if the chemical potential μ_α is equal in both systems: $\mu_\alpha = \mu'_\alpha$.

The simplest thermodynamic system consists of n moles of a pure substance in a single phase and in absence of external fields. Among the many thermodynamic variables that may be defined –and measured– for this system, only two of them are independent, while the rest depend on these two. Possible pairs of independent variables are, for instance, (P,V), (θ,V) or (P,θ). Let the number of independent variables be denoted by λ_F. For a pure homogeneous substance $\lambda_F = 2$. Addition of new types of particle makes λ_F larger while the appearance of more phases –due to the conditions imposed by their mutual equilibrium– makes λ_F to decrease. This leads to Gibbs' phase rule, that for a non-reacting system of c components in ϕ phases reads: $\lambda_F = 2 + c - \phi$. However, not *any* set of λ_F variables is independent and hence sufficient to specify the state. Once a particular set of λ_F independent variables has been chosen, the state is determined by their values $(X_1, X_2, \ldots, X_\lambda)$ so that the remaining variables depend on them: $X_i = X_i(X_1, X_2, \ldots, X_\lambda)$. A relation expressing this dependency is called an *equation of state*. Any given system has specific equations of state, a simple example being the relation $P = P(\theta,V)$ for a pure fluid. It is important to note that Classical Thermodynamics sets general restrictions on the properties of systems and on their equations of state but does not provide us with information about the specific properties, or equation of state, of any particular system. These have to be measured in experiments or calculated by means of Statistical Mechanics.

A good definition of any physical variable should point the way to measure it. How is temperature measured? Choosing θ as independent variable and keeping constant the remaining independent variables one finds that $X_i = X_i(\theta)$ so that X_i can be calculated when θ is measured and vice-versa. A thermometer is then a system with a property X_T that is particularly sensitive to changes in θ when the rest of the variables are kept fixed. We obtain θ by allowing the thermometer to reach thermal equilibrium with the system of interest and then measuring X_T. The Zeroth Law then guaranties that all systems for which the thermometer gives the same reading of X_T will be at the same temperature. By convention, the international standard of temperature is defined with respect to the *triple point* of water, the state of pure water in which three phases –solid I, liquid and vapor– coexist. In this state, water has $\lambda_F = 0$ so that its temperature θ_{tp} is unique.

A thermometer of a particular type has a specific function $X_T(\theta)$ and hence there are as many different 'temperatures' as there are types of thermometer. Especially important is the constant-volume ideal-gas thermometer. In this device, a dilute gas is kept at constant volume, put into thermal contact with the system whose temperature is to be determined and its pressure P measured, then, the gas is put in contact with water at its triple point and the pressure P_{tp} recorded. The pair of measurements (P, P_{tp}) is repeated

with successively smaller quantities of gas, so that both $P \to 0$ and $P_{tp} \to 0$. The ideal-gas temperature θ_{id} is then defined as the limit

$$\theta_{id} = \theta_{tp} \lim_{P \to 0} \left(P/P_{tp} \right),$$

The value of θ_{id} in a given state is found to be independent of the chemical nature of the gas used. In the Kelvin temperature scale $\theta_{tp} = 273.16\,\text{K}$, where K is the symbol for *kelvin*, the unit of temperature in the International System of units. The temperature t in the common Celsius scale is obtained from $t/^{\circ}\text{C} = \theta/\text{K} - 273.15$. In this chapter, θ will denote the ideal-gas temperature.

By 'ideal gas' it is meant any gas in the limit of vanishing pressure. After arduous and careful experimentation, Boyle, Mariotte, Amontons, Charles, Gay Lussac and Avogadro obtained the ideal-gas equation. It reads,

$$PV = nR\theta, \tag{2}$$

where $R = 8.314510\ \text{J mol}^{-1}\ \text{K}^{-1}$ is the Universal Gas Constant. This simple equation has played a very important role in the history of Thermodynamics and in the early stages of Statistical Mechanics.

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Biographical Sketches

Fernando del Río, obtained the First Degree in Physics, National University of Mexico (UNAM, 1963) and Ph D in Physics, University of California, Berkeley (1969). Is *Distinguished Professor*, Physics Department, at the Universidad Autónoma Metropolitana (UAM) in Mexico City and member of the National System of Researchers (SNI); is a former president of the Mexican Academy of Sciences (AMC) in 1988-1989, was appointed *Honorary Associate Professor* by the University of Sheffield, UK (1996) and received the *Academic Award* of the Mexican Physical Society in 1984. Has received the following awards by UAM: *Research Award* (1985), *Best Book in Sciences and Engineering* (1995) and *Teaching Award* (1999). In 2001, the Mexican Petroleum Institute (IMP) named the Laboratory of Thermodynamics and Phase Behaviour of the IMP Center at Cactus, Chiapas, as "Laboratorio Dr Fernando del Río Haza". His main scientific field of interest is the thermodynamics and statistical mechanics of fluids. Has published four books and more than 80 articles in specialised journals plus more than a hundred for the general public. For many years FDR was assistant editor of *Naturaleza*, a leading journal of science for the general public, and chief editor of *Ciencia*, Journal of the Mexican Academy of Sciences. Has been Visiting Professor at the Universities of Cornell, (1980-1981) and Complutense de Madrid (1989-1990), and has lectured at many universities of Europe, North and South America. Was Coordinator of the Program for the Improvement of Higher Education Teaching Staff (PROMEP) of the Ministry of Education (SEP). He is presently a consultant to the Under Secretary for Higher Education at SEP.

Víctor Romero-Rochín, was born on February 19, 1960, in Mazatlán, México. He received his B.Sc. degree (Physics) from the Universidad Autónoma Metropolitana in 1982, and his Ph.D. degree in Physics from the Massachusetts Institute of Technology in 1988. After a postdoctoral stay in the University of Chicago, he joined the Instituto de Fisica at UNAM, Mexico, in 1990, where he has been since then. He is currently tenured Full Professor (Investigador Titular "C"). He is actively involved in research, in teaching and in supervising students both at the undergraduate and the graduate level. His research interests are in the areas of Thermodynamics and Statistical Physics, ranging from systems both in equilibrium and non-equilibrium, inhomogeneous fluids and, recently, in the thermodynamics of Bose-Einstein condensates; he has also contributed in topics of Molecular Physics, especially in problems related to ultrafast spectroscopy. His contributions have been widely recognized in the international scientific literature and he has been invited to visit, collaborate and lecture in universities in United States (Princeton, MIT, Oregon, New Mexico), in Spain (Universitat de Barcelona) and Brazil (Universidade de Sao Paulo). He has been distinguished by the "Award on Scientific Research 1998" (Premio a la Investigación) by the Mexican Academy of Sciences, the "Award for Young Scientific Researchers 1998" (Distinción para Jóvenes Académicos) by the National University in Mexico, and he has also been awarded the highest level (Nivel III) by the National Researchers System (Sistema Nacional de Investigadores, Mexico).