Chapter 1. Review of Thermodynamics

This chapter starts from a brief discussion of the subject of statistical physics and thermodynamics, and the relation between these two disciplines. Then I proceed to a review of the basic notions and relations of thermodynamics. Most of this material is supposed to be known to the reader from his or her undergraduate studies, so the discussion is rather brief.

1.1. Introduction: Statistical physics and thermodynamics

Statistical physics (alternatively called “statistical mechanics”) and thermodynamics are two different approaches to the same goal: a description of internal dynamics of large physical systems, notably those consisting of many, \( N \gg 1 \), identical particles – or other components. The traditional example of such a system is a human-scale portion of a gas, with the number \( N \) of molecules of the order of the Avogadro number \( N_A \sim 10^{23} \). The “internal dynamics” is an (admittedly loose) term meaning all the physics unrelated to the motion of the system as a whole. The most important example of the internal dynamics is the thermal motion of atoms and molecules.

The motivation for the statistical approach to such systems is straightforward: even if the laws governing the dynamics of each particle and their interactions were exactly known, and we had infinite computing resources at our disposal, calculating the exact evolution of the system in time would be impossible, at least because it is completely impracticable to measure the exact initial state each component, e.g., the initial position and velocity of each particle. The situation is further exacerbated by the phenomena of chaos and turbulence, and the quantum-mechanical uncertainty, which do not allow the exact calculation of final positions and velocities of the component particles even if their initial state is known with the best possible precision. As a result, in most situations only statistical predictions about behavior of such systems may be made, with the probability theory becoming a major part of the mathematical tool arsenal.

However, the statistical approach is not as bad as it may look. Indeed, it is almost self-evident that any measurable macroscopic variable characterizing a stationary system of \( N \gg 1 \) particles as a whole (think, e.g., about pressure \( P \) of a gas contained in a fixed volume \( V \)) is almost constant in time. Indeed, we will see below that, besides certain exotic exceptions, the relative fluctuations – either in time, or among macroscopically similar systems - of such a variable are of the order of \( 1/\sqrt{N} \), i.e. for \( N \sim N_A \) are extremely small. As a result, the average values of macroscopic variables may characterize the state of the system rather well. Their calculation is the main task of statistical physics. (Though the analysis of fluctuations is also an important task, but due to the fluctuation smallness, the analysis in most cases may be based on perturbative approaches – see Chapter 5.)

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2 See, e.g., Sec. 4 below. (Note that in these notes, the chapter number is dropped in references to figures, formulas, and sections within the same chapter.)
3 See, e.g., CM Chapters 8 and 9. (Acronyms CM, EM, and QM refer to other of my lecture note series.)
4 See, e.g., QM Chapter 1.
Let us have a look at typical macroscopic variables the statistical physics and thermodynamics should operate with. Since I have already mentioned pressure $P$ and volume $V$, let me start with this famous pair. First of all, note that volume is an extensive variable, i.e. a variable whose value for a system consisting of several noninteracting (or weakly interacting) parts is the sum of those of its parts. On the other hand, pressure is an example of intensive variables whose value is the same for different parts of a system - if they are in equilibrium. In order to understand why $P$ and $V$ form a natural pair of variables, let us consider the classical playground of thermodynamics, a portion of a gas contained in a cylinder, closed with a movable piston of area $A$ (Fig. 1). Neglecting friction between the walls and the piston, and assuming that it is being moved slowly enough (so that the pressure $P$, at any instant, is virtually the same for all parts of the volume), the elementary work of the external force $\mathcal{F} = -PA$, compressing the gas, at a small piston displacement $dx$, is

$$dW = \mathcal{F}dx = \left(\frac{\mathcal{F}}{A}\right)(Adx) = -PdV.$$  \hspace{1cm} (1.1)

It is clear that the last expression is more general than the model shown in Fig. 1, and does not depend on the particular shape of the system surface.$^5$

![Fig. 1.1. Compressing a gas.](image)

From the point of analytical mechanics,$^6$ $V$ and $(-P)$ is just one of many possible canonical pairs of generalized coordinates $q_j$ and generalized forces $\mathcal{F}_j$, whose products $dW_j = -\mathcal{F}_jdq_j$ give contribution to the total work of the environment on the system under analysis. For example, the reader familiar with the basics of electromagnetism knows that the elementary work of an electric field on a unit volume of a media is

$$dW = \mathbf{E} \cdot d\mathbf{D} = \sum_{j=1}^{3} E_j dD_j,$$  \hspace{1cm} (1.2)

so that the role of generalized coordinates is played by Cartesian components of the electric displacement $\mathbf{D}$, while the components of the electric field $\mathbf{E}$ serve as the corresponding generalized forces. Similarly, the elementary work of the magnetic field $\mathbf{H}$ is

$^5$ In order to prove that, it is sufficient to integrate the scalar product $dW = d\mathcal{F} \cdot d\mathbf{r}$, with $d\mathcal{F} = -Pn d^2r$, where $d\mathbf{r}$ is the surface displacement vector (see, e.g., CM Sec. 7.1), and $n$ is the outer normal, over the surface.

$^6$ See, e.g., CM Chapters 2 and 10.

$^7$ See, e.g., EM Eq. (3.82).

$^8$ See, e.g., EM Eq. (5.128). Note that Eqs. (2)-(3) are in SI units (used throughout this lecture series). In the Gaussian units, the right-hand parts of these relations have additional coefficients $1/4\pi$. 

\[ d\mathcal{W} = \mathbf{H} \cdot d\mathbf{B} = \sum_{j=1}^{3} \mathcal{H}_j d\mathbf{B}_j, \quad (1.3) \]

where \( \mathbf{B} \) is the magnetic induction. This list may be extended to other interactions (such as gravitation, surface tension in fluids, etc.). Following tradition, I will use the \( \{P, V\} \) pair in almost all the formulas below, as well in most instances but the reader should remember that they all are valid for any other pair \( \{\phi_j, q_j\} \).

Again, the specific relations between the variables of each pair listed above are typically affected by the statistics of the components (particles) of a body, but their definition is not based on statistics. The situation is very different for a very specific pair of variables, temperature \( T \) and entropy \( S \), although these “sister variables” participate in many formulas of thermodynamics exactly like one more canonical pair \( \{\phi_j, q_j\} \). However, the very existence of these two variables is due to statistics. Temperature \( T \) is an intensive variable that characterizes the degree of thermal “agitation” of system components. On the contrary, entropy \( S \) is an extensive variable that in most cases evades immediate perception by human senses; it is a qualitative measure of disorder of the system, i.e. the degree of our ignorance about its exact microscopic state.\(^9\)

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The reason for the appearance of the \( \{T, S\} \) pair of variables in formulas is that the statistical approach to large systems of particles brings some qualitatively new results, most notably the notion of irreversible time evolution of collective (macroscopic) variables describing the system. On one hand, such irreversibility looks absolutely natural in such phenomena as the diffusion of an ink drop in a glass of water. In the beginning, the ink molecules are located in a certain small part of system’s volume, i.e. to some extent ordered, while at the late stages of diffusion, the position of each molecule is essentially random. However, as a second thought, the irreversibility is rather surprising,\(^10\) taking into account that it takes place even if the laws governing the motion of system’s components are time-reversible – such as the Newton laws or the basic laws of quantum mechanics. Indeed, if, at a late stage of the diffusion process, we exactly reversed the velocities of all molecules simultaneously, the ink molecules would again gather (for a moment) into the original spot.\(^11\) The problem is that getting the information necessary for the exact velocity reversal is not practicable. This example shows a deep connection between the statistical mechanics and the information theory.

A qualitative discussion of the reversibility-irreversibility dilemma requires a strict definition of the basic notion of statistical mechanics (and indeed the probability theory), the statistical ensemble, and I would like to postpone it until the beginning of Chapter 2. In particular, in that chapter we will see that the basic law of irreversible behavior is the increase of entropy \( S \) in any closed system. Thus, statistical mechanics, without defying the “microscopic” laws governing evolution of system’s components,

\[ \text{\footnotesize 9 The notion of entropy was introduced into thermodynamics in the 1850s by R. Clausius, on the background of an earlier pioneering work by S. Carnot (see Sec. 7 below), as a variable related to “useful thermal energy” rather than a measure of disorder. In the absence of any clue of entropy’s microscopic origins (which had to wait for decades until the works by L. Boltzmann and J. Maxwell), this was an amazing intellectual achievement.} \]
\[ \text{\footnotesize 10 Indeed, as recently as in the late XIX century, the very possibility of irreversible macroscopic behavior of microscopically reversible systems was questioned by some serious scientists, notably by J. Loschmidt in 1876.} \]
\[ \text{\footnotesize 11 While quantum-mechanical effects, with their intrinsic uncertainty, are quantitatively important in this example, our qualitative discussion does not depend on them. A good example is the chaotic, but classical motion of a billiard ball on a 2D Sinai table – see CM Fig. 9.8.} \]
introduces on top of them some new “macroscopic” laws, intrinsically related to the evolution of information, i.e. the degree of our knowledge of the microscopic state of the system.

To conclude this brief discussion of variables, let me mention that as in all fields of physics, a very special role in statistical mechanics is played by energy $E$. In order to emphasize the commitment to disregard the motion of the system as a whole, in thermodynamics it is frequently called the internal energy, though for brevity, I will mostly skip the adjective. Its simplest example is the kinetic energy of the thermal motion of molecules in a dilute gas, but in general $E$ also includes not only the individual energies of all system’s components, but also their interactions with each other. Besides a few pathological cases of very-long-range interactions (such as the Coulomb interactions in plasma with uncompensated charge density), the interactions may be treated as local; in this case the internal energy is proportional to $N$, i.e. is an extensive variable. As will be shown below, other extensive variables with the dimension of energy are often very useful, including the (Helmholtz) free energy $F$, the Gibbs energy $G$, enthalpy $H$, and grand potential $\Omega$. (The collective name for such variables is thermodynamic potentials.)

Now, we are ready for a brief discussion of the relation between statistical physics and thermodynamics. While the task of statistical physics is to calculate the macroscopic variables discussed above, using this or that particular microscopic model of the system, the main role of thermodynamics is to derive some general relations between the average values of the macroscopic variables (called thermodynamic variables) that do not depend on specific models. Surprisingly, it is possible to accomplish such a feat using a few either evident or very plausible general assumptions (sometimes called the laws of thermodynamics), which find their proof in statistical physics. Such general relations allow us to reduce rather substantially the amount of calculations we have to do in statistical physics; in many cases it is sufficient to calculate from statistics just one or two variables, and then use thermodynamic relations to calculate all other properties of interest. Thus the thermodynamics, sometimes snubbed at as a phenomenology, deserves every respect not only as a discipline which is, in a certain sense, more general than statistical physics as such, but also as a very useful science. This is why the balance of this chapter is devoted to a brief review of thermodynamics.

1.2. The 2nd law of thermodynamics, entropy, and temperature

Thermodynamics accepts a phenomenological approach to entropy $S$, postulating that there is such a unique extensive measure of disorder, and that in a closed system, it may only grow in time, reaching its constant (maximum) value at equilibrium: \[ dS \geq 0. \] (1.4)

This postulate is called the 2nd law of thermodynamics – arguably its only substantial new law.

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12 Several other quantities, for example the heat capacity $C$, may be obtained as partial derivatives of the basic variables discussed above. Also, at certain conditions, the number of particles $N$ in the system is not fixed and may be also considered as an (extensive) variable.

13 Admittedly, some of these proofs are based on other (but deeper) postulates, for example the central statistical hypothesis – see Sec. 2.2.

14 Defined as a system completely isolated from the environment, i.e. the system with its internal energy fixed.

15 Implicitly, this statement also postulates the existence, in a closed system, of thermodynamic equilibrium, an asymptotically reached state in which all thermodynamic variables, including entropy, remain constant.
Surprisingly, this law, together with the additivity of $S$ in composite systems of non-interacting parts (as an extensive variable), is sufficient for a formal definition of temperature, and a derivation of its basic properties that comply with our everyday notion of this variable. Indeed, let us consider a particular case: a closed system consisting of two fixed-volume subsystems (Fig. 2) whose internal relaxation is very fast in comparison with the rate of the thermal flow (i.e. the energy and entropy exchange) between the parts. In this case, on the latter time scale, each part is always in some quasi-equilibrium state, which may be described by a unique relation $E(S)$ between its energy and entropy.\(^{16}\)

![Fig. 1.2. Composite thermodynamic system.](image)

Neglecting the interaction energy between the parts (which is always possible at $N \gg 1$, in the absence of long-range interactions), we may use the extensive character of variables $E$ and $S$ to write

\[ E = E_1(S_1) + E_2(S_2), \quad S = S_1 + S_2, \quad (1.5) \]

for the full energy and entropy of the system. Now let us calculate the following derivative:

\[ \frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} = \frac{dS_1}{dE_2} \frac{dE_2}{dE_1} + \frac{dS_2}{dE_2} \frac{d(E - E_1)}{dE_1}. \quad (1.6) \]

Since the total energy $E$ of the system is fixed and hence independent of its re-distribution between the sub-systems, $dE/dE_1 = 0$, and we get

\[ \frac{dS}{dE_1} = \frac{dS_1}{dE_2} - \frac{dS_2}{dE_2}. \quad (1.7) \]

According to the 2\(^{\text{nd}}\) law of thermodynamics, when the two parts reach the thermodynamic equilibrium, the total entropy $S$ reaches its maximum, so that $dS/dE_1 = 0$, and Eq. (7) yields

\[ \frac{dS_1}{dE_1} = \frac{dS_2}{dE_2}. \quad (1.8) \]

Thus we see that if a thermodynamic system may be partitioned into weakly interacting macroscopic parts, their derivatives $dS/dE$ should be equal in the equilibrium. The reciprocal of such derivative is called \textit{temperature}. Taking into account that our analysis pertains to the situation (Fig. 2) when both volumes $V_{1,2}$ are fixed, we may write this definition as

\[ \left( \frac{\partial E}{\partial S} \right)_T \equiv T, \quad (1.9) \]

\(^{16}\) Here we strongly depend on a very important (and possibly the least intuitive) aspect of the 2\(^{\text{nd}}\) law, namely that the entropy is the \textit{unique} measure of disorder, i.e. its only measure which may affect the system’s energy, or any other thermodynamic variable.
subscript $V$ meaning that volume is kept constant at differentiation. (Such notation is common and very useful in thermodynamics, with its broad range of variables.)

Note that according to Eq. (9), if temperature is measured in energy units (as I will do in this course for the brevity of notation), $S$ is dimensionless. The transfer to the SI or Gaussian units, i.e. to temperature $T_K$ measured in kelvins (not “degrees Kelvin”, please!), is given by relation $T = k_B T_K$, where the Boltzmann constant $k_B \approx 1.38 \times 10^{-23} \text{ J/K} = 1.38 \times 10^{-16} \text{ erg/K}.^{17}$ In these units, the entropy becomes dimensional: $S_K = k_B S$.

The definition of temperature, given by Eq. (9), is of course in a sharp contrast with the popular notion of $T$ as a measure of the average energy per particle. However, as we will repeatedly see below, it is most cases these two notions may be reconciled. In particular, let us list some properties of $T$, which are in accordance with our everyday notion of temperature:

(i) according to Eq. (9), temperature is an intensive variable (since both $E$ and $S$ are extensive), i.e., in a system of similar particles, independent of the particle number $N$;
(ii) temperatures of all parts of a system are equal at equilibrium – see Eq. (8);
(iii) in a closed system whose parts are not in equilibrium, thermal energy (heat) always flows from a warmer part (with higher $T$) to the colder part.

In order to prove the last property, let us come back to the closed, composite system shown in Fig. 2, and consider another derivative:

$$
\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{dS_1}{dt} \frac{dE_1}{dt} + \frac{dS_2}{dt} \frac{dE_2}{dt}.
$$

(1.10)

If the internal state of each part is very close to equilibrium (as was assumed from the very beginning) at each moment of time, we can use Eq. (9) to replace derivatives $dS_{1,2}/dE_{1,2}$ for $1/T_{1,2}$ and get

$$
\frac{dS}{dt} = \frac{1}{T_1} \frac{dE_1}{dt} + \frac{1}{T_2} \frac{dE_2}{dt}.
$$

(1.11)

Since in a closed system $E = E_1 + E_2 = \text{const}$, these time derivatives are related as $dE_2/dt = -dE_1/dt$, and Eq. (11) yields

$$
\frac{dS}{dt} = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt}.
$$

(1.12)

But in accordance with the 2nd law of thermodynamics, the derivative cannot be negative: $dS/dt \geq 0$. Hence,

$$
\left( \frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \geq 0.
$$

(1.13)

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17 For more exact value of this and other constants, see appendix CA: Selected Physical Constants. Note that both $T$ and $T_K$ define the absolute (also called “thermodynamic”) scale of temperature, in contrast to such artificial temperature scales as degrees Celsius (“centigrades”), defined as $T_C = T_K + 273.15$, or degrees Fahrenheit: $T_F = (9/5) T_C + 32$. 

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For example, if $T_1 > T_2$ (i.e. $1/T_1 < 1/T_2$), then $dE/dt \leq 0$, i.e. the warmer part gives energy to its colder counterpart.

Note also that at such a heat exchange, at fixed volumes $V_{1,2}$, and $T_1 \neq T_2$, increases the total system entropy, without performing any “useful” mechanical work.

1.3. The 1st and 3rd laws of thermodynamics, and heat capacity

Now let us consider a thermally insulated system whose volume $V$ may be changed by a deterministic force – see, for example, Fig. 1. Such system is different from the fully closed one, because its energy $E$ may be changed by the external force’s work – see Eq. (1):

$$dE = dW = -PdV.$$  \hspace{1cm} (1.14)

Let the volume change be so slow ($dV/dt \to 0$) that the system is virtually at equilibrium at any instant without much error. Such a slow process is called reversible, and in this particular case of a thermally insulated system, it is also called adiabatic. If pressure $P$ (or any a generalized external force $f_j$) is deterministic, i.e. is a predetermined function of time independent on the state of the system under analysis, it may be considered as coming from a fully ordered system, i.e. the one having zero entropy, with the total system completely closed. Since according to the second of Eqs. (5), the entropy of the total closed system should stay constant, $S$ of the system under analysis should stay constant on its own. Thus we arrive at a very important conclusion: an adiabatic process, the entropy of a system cannot change.\(^\text{18}\) This means that we can use Eq. (14) to write

$$P = -\left(\frac{\partial E}{\partial V}\right)_S.$$  \hspace{1cm} (1.15)

Let us now consider an even more general thermodynamic system that may also exchange thermal energy (“heat”) with the environment (Fig. 3).

For such a system, our previous conclusion about the entropy constancy is not valid, so that $S$, in equilibrium, may be a function of not only energy $E$, but also of volume $V$. Let us resolve this relation for energy: $E = E(S, V)$, and write the general mathematical expression for the full differential of $E$ as a function of these two independent arguments:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV.$$  \hspace{1cm} (1.16)

\(^{18}\) A general (not necessarily adiabatic) process conserving entropy is sometimes called isentropic.
This formula, based on the stationary relation $E = E(S, V)$, is evidently valid not only in equilibrium, but also for very slow, reversible\(^{19}\) processes. Now, using Eqs. (9) and (15), we may rewrite Eq. (16) as

$$dE = TdS - PdV.$$  \hfill (1.17)

The second term in the right-hand part of this equation is just the work of the external force, so that due to the conservation of energy,\(^{20}\) the first term has to be equal to the heat $dQ$ transferred from the environment to the system (see Fig. 3):

$$dE = dQ + d\mathcal{W},$$  \hfill (1.18)

$$dQ = TdS.$$  \hfill (1.19)

The last relation, divided by $T$ and then integrated along an arbitrary (but reversible!) process,

$$S = \int \frac{dQ}{T} + \text{const},$$  \hfill (1.20)

is sometimes used as an alternative definition of entropy $S$ - provided that temperature is defined not by Eq. (9), but in some independent way. It is useful to recognize that entropy (like energy) may be defined to an arbitrary constant, which does not affect any other thermodynamic observables. The common convention is to take

$$S \to 0 \text{ at } T \to 0.$$  \hfill (1.21)

This condition is sometimes called the \textit{3rd law of thermodynamics}, but it is important to realize that this is just a convention rather than a real law.\(^{21}\) Indeed, the convention corresponds well to the notion of the full order at $T = 0$ in some systems (e.g., perfect crystals), but creates ambiguity for other systems, e.g., amorphous solids (like the usual glasses) that may remain, for “astronomic” times, highly disordered even at $T \to 0$.

Now let us discuss the notion of \textit{heat capacity} that, by definition, is the ratio $dQ/dT$, where $dQ$ is the amount of heat that should be given to a system to raise its temperature by a small amount $dT$.\(^{22}\) (This notion is very important, because it may be most readily measured experimentally.) The heat capacity depends, naturally, on whether the heat $dQ$ goes only into an increase of the internal energy $dE$.

\(^{19}\) Let me emphasize that an adiabatic process is reversible, but not vice versa.

\(^{20}\) Such conservation, expressed by Eqs. (18)-(19), is sometimes called the \textit{1st law of thermodynamics}. While it (in contrast with the \textit{2nd law}) does not present any new law of nature on the top of mechanics, and in particular was already used de-facto to write the first of Eqs. (5) and Eq. (14), such grand name was quite justified in the mid-19\textsuperscript{th} century when the mechanical nature of the internal energy (thermal motion) was not at all clear. In this context, the names of two great scientists, J. von Mayer (who was first to conjecture the conservation of the sum of the thermal and macroscopic mechanical energies in 1841), and J. Joule (who proved the conservation experimentally two years later), have to be reverently mentioned.

\(^{21}\) Actually, the \textit{3rd law} (also called the \textit{Nernst theorem}) as postulated by W. Nernst in 1912 was different - and really meaningful: “It is impossible for any procedure to lead to the isotherm $T = 0$ in a finite number of steps.” I will discuss this postulate in the end of Sec. 6.

\(^{22}\) By this definition, the full heat capacity of a system is an \textit{extensive} variable. The capacity per either unit mass or per particle (i.e., an \textit{intensive} variable), is called the \textit{specific heat capacity} or just the \textit{specific heat}. Note, however, that in some texts, the last term is used for the heat capacity of the system as the whole as well, so that some caution is in order.
of the system (as it does if volume $V$ is constant), or also into the mechanical work $(-d \mathcal{W})$ that may be performed at expansion - as it happens, for example, if pressure $P$, rather than volume $V$, is fixed (the so-called *isobaric* process – see Fig. 4).\(^{23}\)

![Fig. 1.4. The simplest implementation of an isobaric process.](image)

Hence we should discuss two different quantities, the *heat capacity at fixed volume*,

$$C_V = \left( \frac{\partial Q}{\partial T} \right)_V \quad (1.22)$$

and *heat capacity at fixed pressure*

$$C_P = \left( \frac{\partial Q}{\partial T} \right)_P \quad (1.23)$$

and expect that for all “normal” (mechanically stable) systems, $C_P \geq C_V$. The difference between $C_P$ and $C_V$ is rather minor for most liquids and solids, but may be very substantial for gases – see Sec. 4.

### 1.4. Thermodynamic potentials

A technical disadvantage of Eqs. (22) and (23) is that $\partial Q$ is not a differential of a function of state of the system,\(^{24}\) and hence (in contrast with temperature and pressure) does not allow an immediate calculation of heat capacity, even if the relation between $E$, $S$, and $V$ is known. For $C_V$ the situation is immediately correctable, because at fixed volume, $d \mathcal{W} = -PdV = 0$ and hence, according to Eq. (18), $dQ = dE$. Hence we may write

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V \quad (1.24)$$

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\(^{23}\) A similar duality is possible for other pairs $\{q_j, F_j\}$ of generalized coordinates and forces as well. For example, if a long sample of a dielectric placed is into a parallel, uniform external electric field, value of field $\mathcal{E}$ is fixed, i.e. does not depend on sample’s polarization. However, if a thin sheet of such material is perpendicular to the field, then value of field $D$ is fixed – see, e.g., EM Sec. 3.4.

\(^{24}\) The same is true for work $\mathcal{W}$, and in some textbooks this fact is emphasized by using a special sign for differentials of these variables. I do not do this in my notes, because both $d\mathcal{W}$ and $dQ$ are still very much usual differentials: for example, $d\mathcal{W}$ is the difference between the mechanical work which has been done over our system by the end of the infinitesimal interval we are considering, and that done by the beginning of that interval.
so that in order to calculate \( C_V \) from a certain statistical-physics model, we only need to calculate \( E \) as a function of temperature and volume.

If we want to write similarly a convenient expression for \( C_P \), the best way is to introduce a new notion of so-called *thermodynamic potentials* - whose introduction and effective use is perhaps one of the most impressive formalisms of thermodynamics. For that, let us combine Eqs. (1) and (18) to write the “1st law of thermodynamics” in its most common form

\[
dQ = dE + PdV. \tag{1.25}
\]

At an isobaric process (Fig. 5), i.e. at \( P = \text{const} \), this expression is equivalent to

\[
(dQ)_P = dE + d(PV) = d(E + PV)_P. \tag{1.26}
\]

Thus, if we introduce a new function with the dimensionality of energy:

\[
H \equiv E + PV, \tag{1.27}
\]

called *enthalpy* (or, more rarely, the “heat function” or “heat contents”),\(^{25}\) we may rewrite Eq. (23) as

\[
C_P = \left( \frac{\partial H}{\partial T} \right)_P. \tag{1.28}
\]

Comparing Eq. (28) with (24) we see that for the heat capacity, enthalpy \( H \) plays the same role at fixed pressure as the internal energy \( E \) plays at fixed volume.

Now let us explore properties of the enthalpy for an arbitrary reversible process, i.e. lifting the restriction \( P = \text{const} \), but still keeping definition (27). Differentiating it, we get

\[
dH = dE + PdV + VdP, \tag{1.29}
\]

so that plugging in Eq. (17) for \( dE \), we see that two terms \( PdV \) cancel, yielding a very simple expression

\[
dH = TdS + VdP. \tag{1.30}
\]

This equation shows that if \( H \) has been found (say, experimentally measured or calculated for a certain microscopic model) as a function of entropy \( S \) and pressure \( P \), we can find temperature \( T \) and volume \( V \) by simple partial differentiation:

\[
T = \left( \frac{\partial H}{\partial S} \right)_P, \quad V = \left( \frac{\partial H}{\partial P} \right)_S. \tag{1.31}
\]

The comparison of the first of these relations with Eq. (9) shows that not only for the heat capacity, but for temperature as well, enthalpy plays the same role at fixed pressure as played by the intrinsic energy at fixed volume. Moreover, the comparison of the second of Eqs. (31) with Eq. (15) shows that the transfer between \( E \) to \( H \) corresponds to a simple swap of \((-P)\) and \( V \) in the expressions for the differentials of these variables.

This success immediately raises the question whether we could develop it further on, by defining other useful *thermodynamic potentials* – variables with the dimensionality of energy that would have

\[\text{Enthalpy: definition} \]

\[\text{Enthalpy: differential} \]

\[25\] This function (as well as the Gibbs free energy \( G \), see below), had been introduced in 1875 by J. Gibbs, though the term “enthalpy” was coined much later by H. Onnes.
similar properties, first of all a potential which would enable a similar swap of $T$ and $S$ in its full differential. We already know that the adiabatic processes is the reversible process with fixed entropy, so that now we should analyze a reversible process with fixed temperature. Such isothermal process may be implemented, for example, by placing the system under consideration into a thermal contact with a much larger system (called either the heat bath, or “heat reservoir”, or “thermostat”) that remains in thermodynamic equilibrium at all times – see Fig. 5.

Due to its large size, the heat bath temperature $T$ does not depend on what is being done with our system, and if the change is being done slowly enough (i.e. reversibly), that temperature is also the temperature of our system – see Eq. (8) and its discussion. Let us calculate the elementary work $d\mathcal{W}$ for such a reversible isothermal process. According to the general Eq. (18), $d\mathcal{W} = dE - dQ$. Plugging in $dQ$ from Eq. (19), for $T = \text{const}$ we get

$$ (d\mathcal{W})_T = dE - TdS = d(E - TS) = dF, \quad (1.32) $$

where the following combination,

$$ F \equiv E - TS, \quad (1.33) $$

is called the free energy (or the “Helmholtz free energy”, or just the “Helmholtz energy”\textsuperscript{26}). Just as we have done for the enthalpy, let us establish properties of this new thermodynamic potential for an arbitrary (not necessarily isothermal) small reversible variation of variables, while keeping definition (33). Differentiating this relation and using Eq. (17), we get

$$ dF = -SdT - PdV. \quad (1.34) $$

Thus, if we know function $F(T, V)$, we can calculate $S$ and $P$ by simple differentiation:

$$ S = -\left( \frac{\partial F}{\partial T} \right)_V, \quad P = -\left( \frac{\partial F}{\partial V} \right)_T. \quad (1.35) $$

It is easy to see that we can make the derivative system full and symmetric if we introduce one more thermodynamic potential. Indeed, we have shown that each of three already introduced thermodynamic potentials ($E$, $H$, and $F$) has especially simple full differential if it is considered a

\textsuperscript{26} After H. von Helmholtz (1821-1894). The last term was recommended by the most recent (1988) IUPAC’s decision, but I will use the first term, which prevails is physics literature. Its origin may stems from Eq. (32): $F$ is may be interpreted as the internal energy part which is “free” to be transferred to mechanical work - at a reversible, isothermal process only!
function of two canonical arguments: one of “thermal variables” (either \(S\) or \(T\)) and one of “mechanical variables” (either \(P\) or \(V\)):\(^{27}\)

\[ E = E(S, V), \quad H = H(S, P), \quad \text{and} \quad F = F(T, V). \] (1.36)

In this list of pair of 4 arguments, only one pair is missing: \((T, P)\). The thermodynamic function of this pair, which gives two other variables \((S\) and \(V)\) by simple differentiation, is called the Gibbs energy (or sometimes the “Gibbs free energy”): \(G = G(T, P)\). The way to define it in a symmetric way is evident from the so-called circular diagram shown in Fig. 6.

\[
\begin{array}{c|c|c}
S & H & P \\
\hline
E & +PV & -TS \\
\hline
V & F & T \\
\end{array}
\]

In this diagram, each thermodynamic potential is placed between its two canonical arguments – see Eq. (36). The left two arrows in Fig. 6a show the way the potentials \(H\) and \(F\) have been obtained from energy \(E\) – see Eqs. (27) and (33). This diagram hints that \(G\) has to be defined as shown by the right two arrows on that panel, i.e. as

\[
G \equiv E - TS + PV = H - TS = F + PV. \quad \text{(1.37)}
\]

In order to verify this idea, let us calculate the full differential of this new potential, using, e.g., the last form of Eq. (37) together with Eq. (32):

\[
dG = dF + d(PV) = (-SDT - PdV) + (PdV + VdP) = -SDT + VdP,
\]

so that if we know the function \(G(T, P)\), we can indeed readily calculate entropy and volume:

\[
S = -\left(\frac{\partial G}{\partial T}\right)_P, \quad V = \left(\frac{\partial G}{\partial P}\right)_T. \quad \text{(1.39)}
\]

The circular diagram completed in this way is a good mnemonic tool for describing Eqs. (9), (15), (31), (35), and (39), which express thermodynamic variables as partial derivatives of the thermodynamic potentials. Indeed, the variable in any corner of the diagram may be found as a derivative of any of two potentials that are not its immediate neighbors, over the variable in the opposite corner. For example, the red line in Fig. 6b corresponds to the second of Eqs. (39), while the blue line, to the second of Eqs. (31). At this, the derivatives giving variables of the upper row \((S\) and \(P)\) have to be

\(^{27}\) Note the similarity of this situation with that is analytical (classical) mechanics (see, e.g., CM Chapters 2 and 10): the Lagrangian function may be used to get simple equations of motion if it is expressed as a function of generalized coordinates and velocities, while is order to use the Hamiltonian function in a similar way, it has to be expressed as a function of the generalized coordinates and momenta.
taken with negative signs, while those giving the variables of the bottom row ($V$ and $T$), with positive signs.\footnote{There is also a wealth of other relations between thermodynamic variables that may be presented as second derivatives of the thermodynamic potentials, including four Maxwell relations such as $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, etc. (They may be readily recovered from the well-known property of a function of two independent arguments, say, $f(x, y)$: $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right)$. In this chapter, I will list only the thermodynamic relations that will be used later in the course; a more complete list may found, e.g., in Sec. 16 of the textbook by L. Landau and E. Lifshitz, \textit{Statistical Physics, Part 1}, 3\textsuperscript{rd} ed., Pergamon, 1980 (and later its re-printings).}

Now I have to justify the collective name “thermodynamic potentials” used for $E$, $H$, $F$, and $G$. For that, let us consider an \textit{irreversible} process, for example, a direct thermal contact of two bodies with different initial temperatures. As we have seen in Sec. 2, at such a process, the entropy may grow even without the external heat flow: $dS \geq 0$ at $dQ = 0$ – see Eq. (12). For a more general process with $dQ \neq 0$, this means that entropy may grow faster than predicted by Eq. (19), which has been derived for a reversible process, so that

$$dS \geq \frac{dQ}{T},$$

with the equality approached in the reversible limit. Plugging Eq. (40) into Eq. (18) (which, being just the energy conservation law, remains valid for irreversible processes as well), we get

$$dE \leq TdS - PdV.$$  \hfill (1.41)

Now we can use this relation to have a look at the behavior of other thermodynamic potentials in irreversible situations, still keeping their definitions given by Eqs. (27), (33), and (37). Let us start from the (very common) case when both temperature $T$ and volume $V$ are kept constant. If the process was reversible, according to Eq. (34), the full time derivative of free energy $F$ would equal zero. Equation (41) says that at the irreversible process it is not necessarily so: if $dT = dV = 0$, then

$$\frac{dF}{dt} = \frac{d}{dt} (E - TS) = \frac{dE}{dt} - T \frac{dS}{dt} \leq T \frac{dS}{dt} - T \frac{dS}{dt} = 0.$$  \hfill (1.42)

Hence, in the general (irreversible) situation, function $F$ can only decrease, but not increase in time. This means that $F$ eventually approaches its minimum value $F(T, S)$, which is given by the equations of reversible thermodynamics.

Thus in the case $T = \text{const}$, $V = \text{const}$, the free energy $F$, i.e. the difference $E - TS$, plays the role of the potential energy in the classical mechanics of dissipative processes: its minimum corresponds to the (in the case of $F$, thermodynamic) equilibrium of the system. This is one of the key results of thermodynamics, and I invite the reader to give it some thought. One of its possible handwaving interpretations is that the heat bath with fixed $T > 0$, i.e. with a substantial thermal agitation of its components, “wants” to impose thermal disorder in the system immersed in it by “rewarding” it (by lowering its $F$) for any increase of disorder.

Repeating the calculation for the case $T = \text{const}$, $P = \text{const}$, it is easy to see that in this case the same role is played by the Gibbs energy:

$$\frac{dG}{dt} = \frac{d}{dt} (E - TS + PV) = \frac{dE}{dt} - T \frac{dS}{dt} + P \frac{dV}{dt} \leq (T \frac{dS}{dt} - P \frac{dV}{dt}) - T \frac{dS}{dt} + P \frac{dV}{dt} = 0,$$  \hfill (1.43)
so that the thermal equilibrium now corresponds to the minimum of $G$ rather than $F$. One can argue very convincingly that the difference, $G - F = PV$ between these two potentials (also equal to $H - E$) has very little to do with thermodynamics at all, because this difference exists (although not much advertised) in classical mechanics as well.\(^{29}\) Indeed, the difference may be generalized as $G - F = -\mathcal{A}q_j$, where $q_j$ is any generalized coordinate and $\mathcal{A}$ is the corresponding generalized force - see Eq. (1) and its discussion. In this case the minimum of $F$ corresponds to the equilibrium of an autonomous system (with $\mathcal{A} = 0$), while the equilibrium position of the same system under the action of external force $\mathcal{A}$ is given by the minimum of $G$. Thus the external force “wants” the system to subdue to its effect, “rewarding” it by lowering its $G$. (The analogy with the “disorder pressure” by a heat bath, discussed in the last paragraph, is evident.)

For two remaining thermodynamic potentials, $E$ and $H$, the calculations similar to Eqs. (42) and (43) make less sense, because that would require taking $S = \text{const}$ (with $V = \text{const}$ for $E$, and $P = \text{const}$ for $H$), but it is hard to prevent the entropy from growing if initially it had been lower than its equilibrium value, at least on the long-term basis.\(^{30}\) Thus the circular diagram is not so symmetric after all: $G$ and/or $F$ are somewhat more useful for most practical calculations than $E$ and $H$.

One more important conceptual question is why the main task of statistical physics should be the calculation of thermodynamic potentials, rather than just a relation between $P$, $V$, and $T$. (Such relation is called the equation of state of the system.) Let us explore this issue on the example of an ideal classical gas in thermodynamic equilibrium, for which the equation of state should be well known to the reader from undergraduate physics (in Chapter 3, we will be derived from statistics):

$$PV = NT,$$  \hspace{1cm} (1.44)

where $N$ is the number of particles in volume $V$.\(^{31}\) Let us try to use it for the calculation of all thermodynamic potentials, and all other thermodynamic variables discussed above. We may start, for example, from the calculation of the free energy $F$. Indeed, solving Eq. (44) for pressure, $P = NT/V$, and integrating the second of Eqs. (35), we get

$$F = -\int PdV|_T = -NT\int \frac{dV}{V} = -NT\int \frac{d(V/N)}{(V/N)} = -NT \ln \frac{V}{N} + Nf(T),$$  \hspace{1cm} (1.45)

where I have divided $V$ by $N$ in both instances just to present $F$ as a manifestly extensive variable, in this uniform system proportional to $N$. The integration “constant” $f(T)$ is some function of temperature that cannot be recovered from the equation of state. This function also affects all other thermodynamic potentials, and entropy. Indeed, using the first of Eqs. (35) together with Eq. (45), we get

\(^{29}\) See, e.g., CM Sec. 1.5.

\(^{30}\) There are a few practical systems, notably including the so-called magnetic refrigerators (to be discussed in Chapter 4), when the natural growth of $S$ is so slow that the condition $S = \text{const}$ may be closely approached.

\(^{31}\) This equation was first derived from experimental data by E. Clapeyron (in 1834) in the form $PV = nRT_k$, where $n$ is the number of moles in the gas sample, and $R \approx 8.31$ J/mole-K is the so-called gas constant. This form is equivalent to Eq. (44), taking into account that $R \approx k_B N_a$, where $N_a \approx 6.02 \times 10^{23}$ mole\(^{-1}\) is the so-called Avogadro number, i.e. the number of molecules per mole. (By definition of the mole, $N_a$ is just the reciprocal mass, in grams, of a baryon - more exactly, by convention, of a 1/12\(^{th}\) part of the carbon-12 atom.)
and now can combine Eqs. (33) and (46) to calculate the (internal) energy,

\[ E = F + TS = \left( -NT \ln \frac{V}{N} + Nf \right) + T \left( N \ln \frac{V}{N} - N \frac{df}{dT} \right) = N \left( f - T \frac{df}{dT} \right), \]  

\[(1.47)\]

then use Eqs. (27), (44) and (47) to calculate enthalpy,

\[ H = E + PV = E + NT = N \left( f - T \frac{df}{dT} + T \right), \]  

\[(1.48)\]

and, finally, plug Eqs. (44), and (45) into Eq. (37) to calculate the Gibbs energy

\[ G = F + PV = N \left( -T \ln \frac{V}{N} + f + T \right), \]  

\[(1.49)\]

In particular, Eq. (47) describes a very important property of the ideal classical gas: its energy depends only on temperature, but not on volume or pressure. One might question whether function \( f(T) \) may be physically insignificant, just like the arbitrary constant that may be always added to the potential energy in nonrelativistic mechanics. In order to address this concern, let us calculate, from Eqs. (24) and (28), both heat capacities, that are readily measurable quantities:

\[ C_v = \left( \frac{\partial E}{\partial T} \right)_v = -NT \frac{d^2 f}{dT^2}, \]  

\[(1.50)\]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p = N \left( -T \frac{d^2 f}{dT^2} + 1 \right) = C_v + N, \]  

\[(1.51)\]

We see that function \( f(T) \), or at least its second derivative, is measurable.\(^{32}\) (In Chapter 3, we will calculate this function for two simple “microscopic” models of the ideal classical gas.) The meaning of this function is evident from the physical picture of the ideal gas: pressure \( P \) exerted on the walls of the containing volume is produced only by the translational motion of the gas molecules, while their internal energy \( E \) (and hence other thermodynamic potentials) may be also contributed by the internal motion of the molecules – their rotations, vibrations, etc. Thus, the equation of state does not give the full thermodynamic description of a system, while the thermodynamic potentials do.

### 1.5. Systems with variable number of particles

Now we have to consider one more important case when the number \( N \) of particles in a system is not rigidly fixed, but may change as a result of a thermodynamic process. Typical examples of such a system is a gas sample separated from the environment by a penetrable partition (Fig. 7), and a gas in a contact with the liquid of the same molecules.

\(^{32}\) Note, however, that the difference \( C_p - C_v = N \) (if temperature is measured in kelvins, \( C_p - C_v = nR \)) is independent of \( f(T) \). (It is possible to show that the difference \( C_p - C_v \) is fully determined by the equation of state for any medium.)
Let us analyze this situation for the simplest case when all the particles are similar (though the analysis may be readily extended to systems with particle of several sorts). In this case we can consider \( N \) as an independent thermodynamic variable whose variation may change energy \( E \) of the system, so that (for a slow, reversible process) Eq. (17) should be now generalized as

\[
dE = TdS - PdV + \mu dN,
\]

(1.52)

where \( \mu \) is a new function of state, called the chemical potential.\(^{33}\) Keeping the definitions of other thermodynamic potentials, given by Eqs. (27), (33), and (37) intact, we see that expressions for their differentials should be generalized as

\[
dH = TdS + VdP + \mu dN, \tag{1.53a}
\]

\[
dF = -SdT - PdV + \mu dN, \tag{1.53b}
\]

\[
dG = -SdT + VdP + \mu dN, \tag{1.53c}
\]

so that the chemical potential may be calculated as either of the following derivatives:\(^{34}\)

\[
\mu = \frac{\partial E}{\partial N}_{S,V} = \frac{\partial H}{\partial N}_{S,P} = \frac{\partial F}{\partial N}_{T,Y} = \frac{\partial G}{\partial N}_{T,P}. \tag{1.54}
\]

Despite their similarity, one of Eqs. (53)-(54) is more consequential than the others. Indeed, the Gibbs energy \( G \) is the only thermodynamic potential that is a function of two intensive parameters, \( T \) and \( P \). However, as all thermodynamic potentials, \( G \) has to be extensive, so that in a system of similar particles it has to be proportional to \( N \):

\[
G = Nf(T,P). \tag{1.55}
\]

Plugging this expression into the last of Eqs. (54), we see that \( \mu \) equals \( f(T,P) \). In other words,

\[
\mu = \frac{G}{N}, \tag{1.56}
\]

so that the chemical potential is just the Gibbs energy per particle.

\(^{33}\) This name, of a historic origin, is a bit misleading: as evident from Eq. (52), \( \mu \) has a clear physical sense of the average energy cost of adding one more particle to the system of \( N \gg 1 \) particles.

\(^{34}\) Note that strictly speaking, Eqs. (9), (15), (31), (35) and (39) should be now generalized by adding one more lower index, \( N \), to the corresponding derivatives.
In order to demonstrate how vital the notion of chemical potential may be, let us consider the situation (parallel to that shown in Fig. 2) when a system consists of two parts, with equal pressure and temperature, that can exchange particles at a relatively slow rate (much slower than the speed of internal relaxation inside each of the parts). Then we can write two equations similar to Eq. (5):

\[ N = N_1 + N_2, \quad G = G_1 + G_2, \]  

where \( N \) = const, and Eq. (56) may be used to describe each component of \( G \):

\[ G = \mu_1 N_1 + \mu_2 N_2. \]  

Plugging \( N_2 \) expressed from the first of Eqs. (57), \( N_2 = N - N_1 \), into Eq. (58), we see that

\[ \frac{dG}{dN_1} = \mu_1 - \mu_2, \]  

so that the minimum of \( G \) is achieved at \( \mu_1 = \mu_2 \). Hence, in the conditions of fixed temperature and pressure, i.e. when \( G \) is the appropriate thermodynamic potential, the chemical potentials of the system parts should be equal - the so-called chemical equilibrium.

Later we will also run into cases when volume \( V \) of a system, its temperature \( T \), and the chemical potential \( \mu \) are all fixed. (The last condition may be readily implemented by allowing the system of interest to exchange particles with a reservoir so large that its \( \mu \) stays constant.) A thermodynamic potential appropriate for this case may be obtained from the free energy \( F \) by subtraction of the product \( \mu N \), resulting is the so-called grand thermodynamic potential (or the “Landau potential”)

\[ \Omega \equiv F - \mu N = F - \frac{G}{N} N = F - G = -PV. \]  

Indeed, for a reversible process, the full differential of this potential is

\[ d\Omega = dF - d(\mu N) = (-SdT - PdV + \mu dN) - (\mu dN + N d\mu) = -SdT - PdV - N d\mu, \]  

so that if \( \Omega \) has been calculated as a function of \( T, V \) and \( \mu \), other thermodynamic variables may be found as

\[ S = -\left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu}, \quad P = -\left( \frac{\partial \Omega}{\partial V} \right)_{T,\mu}, \quad N = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V}. \]  

For an irreversible process, acting exactly as we have done with other potentials, it is straightforward to prove that in the conditions of fixed \( T, V, \) and \( \mu, \) \( d\Omega/dt \leq 0, \) so that system’s equilibrium indeed corresponds to the minimum of the grand potential \( \Omega. \)

### 1.6. Thermal machines

In order to complete this brief review of thermodynamics, I cannot pass the topic of thermal machines – not because it will be used much in this course, but mostly because of its practical and historic significance. (Indeed, the whole field of thermodynamics was spurred by the famous 1824 work by S. Carnot, which in particular gave an alternative, indirect form of the 2nd law of thermodynamics – see below.)
Figure 8a shows the generic scheme of a thermal machine that may perform mechanical work on the environment (in the notation of Eq. (1), equal to $-\mathcal{W}$ during each cycle of the expansion/compression of the “working gas”, by transferring different amounts of heat from a high-temperature heat bath ($Q_H$) and to the low-temperature bath ($Q_L$). One relation between three amounts $Q_H$, $Q_L$, and $\mathcal{W}$ is immediately given by the energy conservation (i.e. by “the 1st law of thermodynamics”):

$$Q_H - Q_L = -\mathcal{W}.$$  \hspace{1cm} (1.63)

From Eq. (1), the mechanical work during the cycle may be calculated as

$$-\mathcal{W} = \oint PdV,$$  \hspace{1cm} (1.64)

i.e. equals the area circumvented by the representing point on the $[P, V]$ plane – see Fig. 8b.\(^{35}\) Hence, the work depends on the exact form of the cycle, which in turn depends not only on $T_H$ and $T_L$, but also on working gas’ properties.

An exception from this rule is the famous Carnot cycle, consisting of two isothermal and two adiabatic processes (all reversible!). In its heat engine’s form, the cycle starts from an isothermic expansion of the gas in contact with the hot bath (i.e. at $T = T_H$), followed by its additional adiabatic expansion until $T$ drops to $T_L$. Then an isothermal compression of the gas is performed in its contact with the cold bath (at $T = T_L$), followed by its additional adiabatic compression to raise its temperature to $T_H$ again, after which the cycle is repeated again and again. (Note that during this cycle the working gas is never in contact with both heat baths simultaneously, thus avoiding the irreversible heat transfer between them.) The cycle’s shape on the $[V, P]$ plane depends on exact properties of the working gas and may be rather complicated. However, since the entropy is constant at any adiabatic process, the Carnot cycle shape on the $[S, T]$ plane is always rectangular – see Fig. 9.\(^{36}\)

---

\(^{35}\) Note that positive sign of the circular integral corresponds to the clockwise rotation of the point, so that work ($-\mathcal{W}$ done by the working gas is positive at the clockwise rotation (pertinent to heat engines) and negative in the opposite case (implemented in refrigerators and heat pumps).

\(^{36}\) A cycle with an $[S, T]$ shape very close to the Carnot (rectangular) one may be implemented at the already mentioned magnetic (or “adiabatic-demagnetization”) refrigeration, using the alignment of either atomic or
Since during each isotherm, the working gas is brought into thermal contact only with the corresponding heat bath, Eq. (19), \(dQ = TdS\) may be immediately integrated to yield

\[
Q_H = T_H (S_2 - S_1), \quad Q_L = T_L (S_2 - S_1).
\]

Hence the ratio of these two heat flows is completely determined by their temperature ratio:

\[
\frac{Q_H}{Q_L} = \frac{T_H}{T_L}, \quad (1.66)
\]

regardless of the working gas properties. Equations (63) and (66) are sufficient to find the ratio of work \(-\mathcal{W}\) to any of \(Q_H\) and \(Q_L\). For example, the main figure-of-merit of a thermal machine used as a heat engine (\(Q_H > 0, Q_L > 0, -\mathcal{W} = |\mathcal{W}| > 0\)), is its efficiency

\[
\eta = \frac{|\mathcal{W}|}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \leq 1.
\]

(1.67)

For the Carnot cycle, Eq. (66) immediately yields the famous relation,

\[
\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}, \quad (1.68)
\]

which shows that at given \(T_L\) (that is typically the ambient temperature \(\sim 300\) K), the efficiency may be increased, ultimately to 1, by raising temperature of the heat source.

On the other hand, if the cycle is reversed (see the dashed arrows in Figs. 8 and 9), the same thermal machine may serve as a refrigerator, providing the heat removal from the low-temperature bath \((Q_L < 0)\) for the cost of consuming external work: \(\mathcal{W} > 0\). This reversal does not affect the basic relation (63) that may be used to calculate the relevant figure-of-merit, called the cooling coefficient of performance \((\text{COP}_{\text{cooling}})\)

\[
\text{COP}_{\text{cooling}} \equiv \frac{|Q_L|}{\mathcal{W}} = \frac{Q_L}{Q_H - Q_L}.
\]

(1.69)

Notice that this coefficient may readily be above unity; in particular, for the Carnot cycle we may use Eq. (66) (which is also unaffected by the cycle reversal) to get

nuclear spins by external magnetic field. In such refrigerators (to be further discussed in the next chapter), the role of the \{-\(P, V\}\) pair of variables is played by the \{\(\mathcal{H}, B\}\) pair – see Eq. (3).
so that the COP_{cooling} is larger than 1 at \( T_H < 2T_L \), and even may be very large when the temperature difference \( (T_H - T_L) \), sustained by the refrigerator, tends to zero. For example, in a typical air-conditioning system, \( T_H - T_L \sim T_L/30 \), so that the Carnot value of COP_{cooling} is as high as \(~30\), while in the state-of-the-art commercial HVAC systems it is the range for 3 to 4. This is why the term “cooling efficiency”, used in some textbooks instead of (COP)_{cooling}, may be misleading.

Since in the reversed cycle \( Q_H = -w + Q_L < 0 \), the system also provides heat flow into the hotter heat bath, and thus may be used as a heat pump. However, the figure-of-merit appropriate for this application is different:

\[
\text{COP}_{\text{heating}} = \frac{|Q_H|}{w} = \frac{Q_H}{Q_H - Q_L},
\]

so that for the Carnot cycle

\[
(\text{COP}_{\text{heating}})_{\text{Carnot}} = \frac{T_H}{T_H - T_L}.
\]

Note that this COP is always larger than 1, meaning that the Carnot heat pump is always more efficient than the direct conversion of work into heat (where \( Q_H = -w \) and \( \text{COP}_{\text{heating}} = 1 \)), though practical electricity-driven heat pumps are substantially more complex (and hence more expensive) than, say, simple electric heaters. Such heat pumps, with typical \( \text{COP}_{\text{heating}} \) values around 4 in summer and 2 in winter, are frequently used for heating large buildings.

I have dwelled so long on the Carnot cycle, because it has a remarkable property: the highest possible efficiency of all heat-engine cycles. Indeed, in the Carnot cycle the transfer of heat between any heat bath and the working gas is performed reversibly, when their temperatures are equal. If this is not so, heat might flow from a hotter to colder system without performing any work. Hence the result (68) also yields the maximum efficiency of any heat engine. In particular, it shows that \( \eta_{\text{max}} = 0 \) at \( T_H = T_L \), i.e., no heat engine can perform any mechanical work in the absence of temperature gradients.\(^37\) In some alternative axiomatic systems of thermodynamics, this fact, i.e. the impossibility of the direct conversion of heat to work, is postulated, and serves the role of the 2nd law.

Note also that according to Eq. (71), COP_{cooling} of the Carnot cycle tends to zero at \( T_L \to 0 \), making it impossible to reach the absolute zero of temperature, and hence illustrating the meaningful (Nernst’s) formulation of the 3rd law of thermodynamics. Indeed, let us prescribe a certain (but very large) heat capacity \( C(T) \) to the low-temperature bath, and use the definition of this variable to write the following evident expression for the (very small) change of its temperature as a result of a relatively number \( dn \) of similar refrigeration cycles:

\[
C(T_L) dT_L = Q_L dn.
\]

\(^{37}\) Such a hypothetical (and impossible!) heat engine, which would violate the 2nd law of thermodynamics, is called the “perpetual motion machine of the 2nd kind” - in contrast to the “perpetual motion machine of the 1st kind” with would violate the 1st law, i.e., the energy conservation.
Together with Eq. (66), this relation yields

\[ C(T_L) dT_L = -\frac{|Q_H|}{T_H} T_L dT, \]  

(1.74)

so that if we perform many \( n \) cycles (with constant \( Q_H \) and \( T_H \)), the initial and final values of \( T_L \) obey the following equation

\[ \int_{T_{in}}^{T_{fin}} \frac{C(T) dT}{T} = -\frac{|Q_H|}{T_H} n. \]  

(1.75)

For example, if \( C(T) \) is a constant, Eq. (75) yields an exponential law,

\[ T_{fin} = T_{ini} \exp \left\{ -\frac{|Q_H|}{CT_H} n \right\}, \]  

(1.76)

with the absolute zero not reached as any finite \( n \). Relation (75) proves the Nernst theorem if \( C(T) \) does not vanish at \( T \to 0 \), but for such metastable systems as glasses the situation is more complicated.\(^{38}\) Fortunately, this issue does not affect other aspects of statistical physics – at least those to be discussed in this course.

1.7. Exercise problems

1.1. A gas has the following properties:
   (i) \( C_V = aT^b \), and
   (ii) the work \( W_t \) needed for its isothermal compression from \( V_2 \) to \( V_1 \) equals \( cT \ln(V_2/V_1) \),
   where \( a, b, \) and \( c \) are constants. Find the equation of state of the gas, and calculate the temperature dependences of its entropy \( S \), and thermodynamic potentials \( E, H, F, G \) and \( \Omega \).

1.2. A vessel with an ideal classical gas of indistinguishable molecules is separated by a partition so that the number \( N \) of molecules in both parts is the same but their volumes are different. The gas is in thermal equilibrium, and its pressure in one part is \( P_1 \), and in another, \( P_2 \). Calculate the change of entropy caused by a fast removal of the partition. Analyze the result.

1.3. For an ideal classical gas with temperature-independent specific heat, derive the relation between \( P \) and \( V \) at the adiabatic expansion/compression.

1.4. As will be discussed in Sec. 3.5, hard-core models of classical particle interaction yield the following equation of state of a gas of such particles:

\[ P = T \varphi(n), \]

where \( n = N/V \) is the particle density, and function \( \varphi(n) \) is generally different from that \( (\varphi_{\text{ideal}}(n) = n) \) of the ideal gas. For such a gas, with temperature-independent \( c_V \), calculate \( P \) as a function of \( n \) at adiabatic compression.

1.5. Two bodies, with negligible thermal expansion coefficients and constant heat capacities \( C_1 \) and \( C_2 \), are placed into a weak thermal contact, at different initial temperatures \( T_1 \) and \( T_2 \). Calculate the full change of entropy of the system before it reaches the full thermal equilibrium.

1.6. For an arbitrary thermodynamic system with a fixed number of particles, prove the following Maxwell relations (already mentioned in Sec. 1.4):

\[
\begin{align*}
\text{(i): } & \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V, \\
\text{(ii): } & \left( \frac{\partial V}{\partial S} \right)_p = \left( \frac{\partial T}{\partial S} \right)_p, \\
\text{(iii): } & \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial P} \right)_T, \\
\text{(iv): } & \left( \frac{\partial P}{\partial S} \right)_V = -\left( \frac{\partial T}{\partial V} \right)_S.
\end{align*}
\]

1.7. Two bodies have equal and constant heat capacities \( C \), but different temperatures, \( T_1 \) and \( T_2 \). Calculate the maximum mechanical work obtainable from this system, using a heat engine.

1.8. A process, performed with a fixed portion of an ideal gas, may be represented with a straight line on the \( [P, V] \) plane – see Fig. on the right. Find the point at which the heat flow into/out of the gas changes its direction.

1.9. Express the efficiency of a heat engine that uses the “Joule cycle” consisting of two adiabatic and two isobaric processes (see Fig. on the right), via the minimum and maximum values of pressure, and compare the result with that for the Carnot cycle. Assume an ideal classical working gas with constant \( C_P \) and \( C_V \).

1.10. Calculate the efficiency of a heat engine using the “Otto cycle”, which consists of two adiabatic and two isochoric (constant-volume) processes – see Fig. on the right. Explore how does the efficiency depend on the ratio \( r \equiv V_{\text{max}}/V_{\text{min}} \), and compare it with Carnot cycle’s efficiency. Assume an ideal working gas with temperature-independent specific heat.

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39 This name stems from the fact that the cycle is an approximate model of operation of the four-stroke internal-combustion engine, which was improved and made practicable (though not invented!) by N. Otto in 1876.
1.11. A heat engine’s cycle consists of two isothermal \((T = \text{const})\) and two isochoric \((V = \text{const})\) reversible processes - see Fig. on the right.

(i) Assuming that the working gas is an ideal classical gas of \(N\) particles, calculate the mechanical work performed by the engine during one cycle.

(ii) Are the specified conditions sufficient to calculate engine’s efficiency?