Chapter 1. Review of Thermodynamics

This chapter reviews the basic ideas of thermodynamics which are supposed to be known to students from their undergraduate studies. Due to this reason, the discussion is rather concise.

1.1. Why thermodynamics?

Thermodynamics may be considered as a phenomenological part of statistical physics and shares its goal of study of *statistical* laws governing large physical systems, in particular those consisting of many identical components. (Think of a gas or a fluid, with $N \sim 10^{20}$ to 10^{23} atoms or molecules in each cm^3.) Indeed, even if the laws governing the dynamics of each component of such systems are exactly known, they do not allow one to find the exact evolution of the system because of the simple reason that it is impracticable to measure the initial state of all the components. The situation is only exacerbated by the phenomena of chaos and turbulence (CM,[1] Ch. 7 and 8) and the quantum-mechanical uncertainty (QM, Ch. 1). As a result, in most situations only statistical predictions about behavior of such systems may be made, with the main mathematical tool being the *probability theory*. An introduction into a statistical description of physical systems will be the main task of this course.

However, the fact that the number N of particles in a typical physical system is so large brings some relief as well. Indeed, it is almost self-evident that any physical function of the motion of all particles of a stationary system (think, e.g., about pressure p of a gas) is almost constant in time. (In Ch. 6, we will show that in most cases the relative fluctuations of such variable are of the order of $N^{-1/2}$, i.e. extremely small.) As a result, the average value of such *macroscopic variable* may characterize the state of the system very well, and the calculation of such averages is the main task of statistical physics, though the analysis of fluctuations is also an important task (see Ch. 6 below).

It would be very sad, however, if such calculations had to be repeated for each of the macroscopic variables characterizing the system, because there are quite a few of them:

- Even disregarding the motion of the system as a whole (as studied, e.g., in classical mechanics), moving and interacting components of the system provide it with some *internal energy E.*

- As will be shown below, in various situations other variables with the dimension of energy are very useful including *free energy F*, *Gibbs energy G*, and *enthalpy W*. (The collective name for these variables is "*thermodynamic potentials*".)

- A very special role in statistical physics and thermodynamics is played by *entropy S* which characterizes the degree of *disorder* of the system and is closely related to the notion of *information*. The sister variable to entropy is *temperature T* of which we all have some intuitive notion but which will be defined exactly below. Note that the internal energy, as well as all other

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[1] Such abbreviations refer to other parts of these lecture notes: CM = Classical Mechanics, QM = Quantum Mechanics, EM = Electricity and Magnetism. In those parts, this Statistical Mechanics notes are referred as SM.

thermodynamic potentials and entropy, are examples of the so-called *extensive variables* proportional to the size N of a (uniform) system, while T is an example of an *intensive variable* which does not depend on the size.

- We will see that temperature and entropy may be defined as first derivatives of thermodynamic potentials. Several other important variables may be also derived as such first derivatives, notably including *pressure p, specific heats C_V and C_P* (intensive variables) and *volume V* (extensive variable). A little bit counter-intuitive, the number of particles N may be also considered one of such (extensive) variables.[2]

- One more slate of thermodynamic variables may be obtained from thermodynamic potentials by second differentiation. An example is the compressibility $K = 1/B$ (where B is the bulk modulus) which has been already introduced in the elasticity theory. This list might be extended to the magnetic permeability μ, etc.

The main role of thermodynamics is to derive general relations between all these variables, which do not depend on the specific system, and allow one to calculate from statistics only few of them, for example only energy E and entropy S.

1.2. Entropy and temperature

While the exact ("microscopic") definition of entropy S is given by statistical physics (see Ch. 2 below), thermodynamics takes a phenomenological approach to this extensive variable, postulating that in a thermally insulated system S may only grow, reaching its constant (maximum) value at equilibrium.[3] This corresponds well to our intuitive notion of the spontaneously growing disorder. (Think, e.g., about the diffusion of an ink drop in a glass of water.)

Surprisingly, this postulate,[4] together with additivity of S in composite systems of non-interacting parts, is sufficient for the definition of the arguably the most important thermodynamic notion, the temperature. Indeed, let us consider a "*closed*" system (defined as a thermally insulated system, with volume and all other external conditions fixed) consisting of two subsystems (Fig. 1) whose internal relaxation is relatively fast. In this case each of the parts is always in some quasi-equilibrium state which may be characterized by a stationary relation between its energy and entropy: $E_1 = E_1(S_1)$, $E_2 = E_2(S_2)$. On the contrary, let the coupling between the two parts be sufficiently small to neglect the interaction terms in the expressions

$$E = E_1 + E_2, \quad S = S_1 + S_2, \tag{1.1}$$

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[2] This list is by no means exhaustive; for example, the (average) electric and magnetic fields produced by a system of charged and/or magnetic particles may be in some situations considered as intensive thermodynamic variables.

[3] Implicitly, this statement also postulates the existence of *thermodynamic equilibrium* in a system under constant external conditions, as an asymptotically reached state in which all thermodynamic variables, including entropy, remain constant.

[4] This postulate, or any of its equivalent formulations, is sometimes being called the 2nd Law of thermodynamics, the 1st Law being the energy conservation – see the next section.

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for the full energy and entropy of the system, but still allowing a slow exchange by energy and entropy. (Such a weak coupling description is valid for a broad variety of systems; for example in systems of many particles with short-range interactions, the interaction between the subsystems is proportional to the interface area while the internal energy is proportional to volume. As the system size N grows, the volume-to-area ratio increases infinitely.)
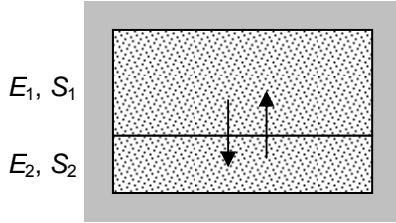

Fig. 1. A composite thermodynamic system.

Now we can calculate the derivative

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2}\frac{dE_2}{dE_1} = \frac{dS_1}{dE_1} + \frac{dS_2}{dE_2}\frac{d(E - E_1)}{dE_1}. \qquad (1.2)$$

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

$$\frac{dS}{dE_1} = \frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}. \qquad (1.3)$$

When the two parts reach the thermodynamic equilibrium, the total entropy S shall reach its maximum, so that $dS/dE_1 = 0$, and

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2}. \qquad (1.4)$$

Thus we see that if a thermodynamic system can be partitioned into weakly interacting sub-systems, their derivatives dS/dE should be equal in thermal equilibrium. The reciprocal of such derivative is called *temperature*:[5]

$$\frac{dE}{dS} \equiv T. \qquad (1.5)$$

Please note that this definition is rather different from, and only in some cases may be reduced to the popular understanding of temperature as a measure of (average) energy per particle; in our course we will repeatedly return to discussion of this issue.

Since temperature is the key notion of thermodynamics, let list its main properties, all of them corresponding to our everyday notion of this variable:

- temperature is an intensive variable (since both E and S are extensive);

- temperatures of all parts of a system are equal at equilibrium (see Eq. (4));

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[5] If temperature is measured in energy units (as we will do in this course), S is dimensionless. The transfer to the traditional units (Kelvins) may be always obtained by dividing such temperature by the Boltzmann constant $k_B \approx 1.38 \times 10^{-23}$ Joule $= 1.38 \times 10^{-16}$ erg; simultaneously S has to be multiplied by k_B.

- in a closed system, 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. 1 and consider the derivative

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{dS_1}{dE_1}\frac{dE_1}{dt} + \frac{dS_2}{dE_2}\frac{dE_2}{dt} \cdot = \frac{1}{T_1}\frac{dE_1}{dt} + \frac{1}{T_2}\frac{dE_2}{dt}. \qquad (1.6)$$

Since in a closed system $E = E_1 + E_2 = $ const, $dE_2/dt = -dE_1/dt$, and we get

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt}. \qquad (1.7)$$

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

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} \geq 0. \qquad (1.8)$$

For example, if $T_1 > T_2$ (i.e. $1/T_1 < 1/T_2$), then $dE_1/dt \leq 0$, i.e. the warmer part gives energy to the colder part.

1.3. Pressure, the 1st and 3rd Laws, and Specific Heat

Before proceeding to the definition of other thermodynamic variables, let us consider a thermally insulated system whose volume V (or other any other external parameter q) may be changed – see Fig. 2. Now let the change be so slow ($dV/dt \rightarrow 0$) that the system may be considered to be in an equilibrium state at any instant. (Such a slow process in thermally insulated system is called *adiabatic*.) Let us consider an adiabatic increase of V, starting from some value V_0 (at which entropy S has already reached its maximum value S_0), and then its adiabatic decrease eventually returning to the initial value V_0. According to the 2nd Law, during this process the entropy cannot decrease. But it cannot increase either, because otherwise in the end of the process it would reach a value larger than S_0 which is, by definition, in already the maximum value of entropy for V_0. Thus we arrive to an important conclusion that entropy of a thermally-insulated system cannot change at all this (or any other) adiabatic process and hence its value cannot depend on V (or any external parameter q).
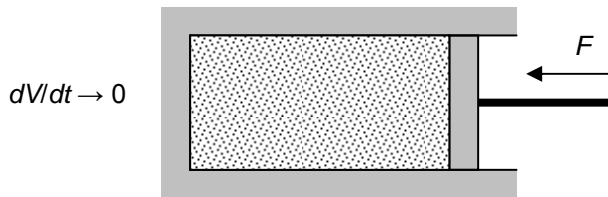

$dV/dt \rightarrow 0$

F

Fig. 2. An example of an adiabatic process.

Now if we define *pressure p* as the derivative $-dE/dV$ for the adiabatic process, the constancy of entropy allows us to rewrite this definition as

$$p \equiv -\left(\frac{\partial E}{\partial V}\right)_S. \tag{1.9}$$

Such notation, in this particular case meaning that the derivative has to be taken at constant entropy S, is very useful in thermodynamics with its broad range of thermodynamic variables. In this notation, Eq. (5), which gives the definition of temperature T in the conditions of constant volume, may be rewritten as

$$T = \left(\frac{\partial E}{\partial S}\right)_V. \tag{1.10}$$

Now let us check that Eq. (9) is equivalent to the general notion of pressure accepted in physics, in particular to its definition accepted in the elasticity theory (CM, Ch. 6). If the system is thermally insulated, the only change of the internal energy E may come from the work A of external forces acting on the system,[6] for example the mechanical force F changing its volume (Fig. 2): $dE = dA$. Evidently the work at the small change of volume is $dA = -Fdx = -pdV$, so that we come back to Eq. (9).

In the more general case when there are several external parameters q_j changing simultaneously, equation $dA = -pdV$ should be generalized as

$$dA = \sum_j Q_j dq_j, \quad Q_j = \left(\frac{\partial E}{\partial q_j}\right)_{S,q_{k \neq j}}, \tag{1.11}$$

where Q_j may be interpreted as the generalized force corresponding to parameter q_j considered as a generalized coordinate of the system, very much in the spirit of the Lagrangian approach in analytical mechanics (CM, Ch. 2). Important examples of such generalized force-coordinate pairs are given by well-known expressions for a unit volume of a media in the electromagnetic field:[7]

$$dA = \frac{1}{4\pi}\left(\vec{E}d\vec{D} + \vec{B}d\vec{H}\right) = \frac{1}{4\pi}\sum_{j=1}^{3}\left(E_j dD_j + B_j dH_j\right), \tag{1.12}$$

where (in this particular equation only) $\vec{E}$ is the (average) electric field, $\vec{D}$ is the electric displacement vector, $\vec{B}$ is the (average) magnetic induction and $\vec{H}$ the magnetic field. In quasi-stationary electric circuits, Eq. (12) may be recast into the form

$$dA = VdQ + \frac{1}{c}Id\Phi, \tag{1.13}$$

where (here only) I is current, Φ the magnetic flux, V is the voltage, and Q the electric charge. Similar pairs $\{Q_j, q_j\}$ may be found in other areas of physics (say, gravitation or surface tension).

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[6] With all my desire to keep notation the same in all parts of the notes, I have to comply with the general use of symbol W for enthalpy, and hence denote work by another letter. Most textbooks on thermodynamics and statistical physics use A for work, and I will follow this convention.

[7] Equations (12), (13) are in the Gaussian units.

I will write all the following formulas for the traditional pair $\{-p, V\}$, but all of them are open for the replacement $-p \rightarrow Q_j$, $V \rightarrow q_j$, with the corresponding name change. For example, the bulk modulus $\partial p / \partial V$ (per unit volume) may be paralleled with the magnetic permeability $\partial B / \partial H$, etc.

Let us now consider a more general thermodynamic system which may exchange thermal energy ("*heat*") with the environment (Fig. 3). For it, 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 find a change of E at arbitrary but small changes of S and V:

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV. \tag{1.14}$$
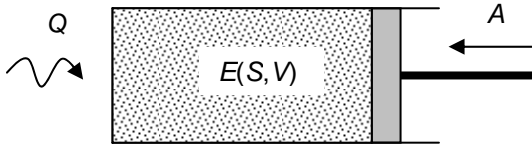

Fig. 3. A more general thermodynamic process involving heat exchange with the environment.

This formula, based on the stationary relation $E(S, V)$ is only valid for processes as slow as those giving an adiabatic process in a thermally-insulated system. (Such slow processes in a general system are called *reversible*, because any process returning the system to the initial point on the $[S, V]$ plane returns E to its initial value. Let us emphasize that each adiabatic process is reversible, but not vice versa.) Now, using Eqs.(9) and (10), we may rewrite Eq. (14) as

$$dE = TdS - pdV. \tag{1.15}$$

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,[8] the first term has to be equal to the *heat dQ* transferred from the environment to the system:

$$dE = dQ + dA, \tag{1.16}$$

$$dQ = TdS . \tag{1.17}$$

The last relation, divided by T and integrated along then some process,

$$S = \int \frac{dQ}{T} + \text{const}, \tag{1.18}$$

is frequently used as an alternative definition of entropy S. It is useful to recognize that entropy (like energy) may be defined to an arbitrary constant which does not affect any other thermodynamic observables, though the common convention is to take

$$S \rightarrow 0 \text{ at } T \rightarrow 0. \tag{1.19}$$

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[8] Such conservation, expressed by Eq. (16), is sometimes called the 1st Law of thermodynamics. While it (in contrast with the 2nd Law) does not present any new law of nature on the top of classical mechanics, such grand name was quite justified at the moment of its discovery in the 1850s when the mechanical nature of the internal energy was not at all clear.

This condition is known under one more grand name of the 3rd Law of thermodynamics. Though just a convention, it corresponds well to the notion of zero disorder (full order) in some systems (e.g. perfect crystals) at $T = 0$.

Now let us discuss specific heat which, by definition, is the amount of heat (dQ) which can be given to a system to raise its temperature by a fixed amount dT. The specific heat depends, naturally, on whether the heat dQ goes only to an increase of the internal energy dE of the system (as it does when the volume V is constant), or also to the system expansion and the corresponding mechanical work dA (as it happens, for example, if pressure p, rather than volume V, is fixed). Hence we should discuss at least two different quantities:

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V \quad \text{and} \quad C_p \equiv \left(\frac{\partial Q}{\partial T}\right)_p ; \qquad (1.20)$$

we may expect that for all "normal" (stable) systems, $C_p \geq C_V$.

A disadvantage of Eqs. (20) is that Q is not a function of state of the system, and hence (in contrast with temperature and pressure) does not allow an immediate calculation of specific heat if, say, the relation between E, S, and V is known. For C_V the situation is immediately correctable, because at fixed volume, $dA = -pdV = 0$ and hence $dQ = dE$ – see Eq. (16). Hence we may write

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V , \qquad (1.21)$$

or otherwise use Eq. (17) to get a relation

$$C_V \equiv T\left(\frac{\partial S}{\partial T}\right)_V \qquad (1.22)$$

which solves the problem.

However, if we want to write similarly simple expressions for C_p, we need to introduce new notion of enthalpy, which is the first of

1.4. Thermodynamic Potentials

Let us rewrite Eq. (16) as

$$dQ = dE + pdV. \qquad (1.23)$$

If pressure is kept constant, this expression is equivalent to

$$dQ = dE + d(pV) = d(E + pV). \qquad (1.24)$$

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

$$W \equiv E + pV, \qquad (1.25)$$

called *enthalpy* (or "heat function"), we may use the second of Eqs.(20) to write

$$C_p = \left(\frac{\partial W}{\partial T}\right)_p. \tag{1.26}$$

Now let us explore properties of enthalpy for an arbitrary reversible process (lifting the restriction $p = $ const). Differentiating Eq. (1.25), we have

$$dW = dE + pdV + Vdp, \tag{1.27}$$

so that plugging in Eq. (15) for dE, we get

$$dW = TdS + Vdp. \tag{1.28}$$

This equation shows that if W has been found (say, experimentally or by the means of statistical physics) as a function of entropy S and volume p, we can find temperature T and volume V by dimple differentiation:

$$T = \left(\frac{\partial W}{\partial S}\right)_p, \quad V = \left(\frac{\partial W}{\partial p}\right)_S. \tag{1.29}$$

Comparing Eq. (21) with (26) we see that enthalpy W plays the same role at fixed pressure as internal energy E plays at fixed volume, while the comparison of Eq. (15) with Eq. (29) shows that the transfer from E to W leads to a simple swap of p and V in the expressions for the differentials of these variables. This immediately raises the question whether we could define another useful variable with the dimensionality of energy if make a similar swap of T and S. We already know that the adiabatic processes (Fig. 2) conserves entropy, so that now we should define a reversible process with fixed temperature. Such *isothermal* process may be obtained by placing the system under consideration into a good thermal contact with a much larger system called either "*heat bath*" or "*heat reservoir*", or "*thermostat*" (Fig. 4) in thermodynamic equilibrium.
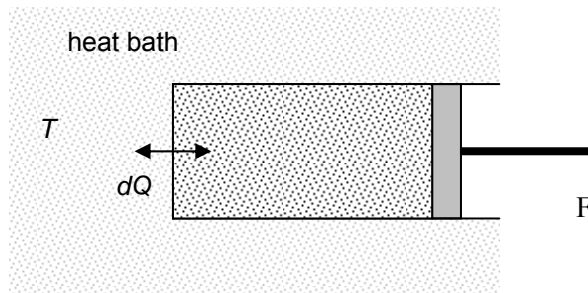

Fig. 4. Isothermal process.

Let us calculate elementary work dA for such a process. According to the general Eq. (16), $dA = dE - dQ$. Plugging in dQ from Eq. (17), for $T = $ const we get

$$dA = dE - TdS = d(E - TS) = dF, \tag{1.30}$$

where the combination

$$F \equiv E - TS \tag{1.31}$$

is called "*free energy*" (or sometimes "Helmholtz free energy"). Just as we have done for the enthalpy, let us establish properties of this new thermodynamic function for an arbitrary (not

necessarily isothermal) small reversible variation of variables. Differentiating Eq. (31) and using Eq. (15), we get

$$dF = -SdT - pdV. \tag{1.32}$$

So we know the function $F(T, V)$, we can get S and p by simple differentiation:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{1.33}$$

It is easy to see that we can make the situation symmetric if we need to introduce of one more function ("*thermodynamic potential*") of this type. Indeed, we have shown that three already introduced thermodynamic potentials give especially easy results if each of them is considered a function of a specific "thermal variable" (either S or T) and a specific "mechanical variable" (either p or V):

$$E = E(S,V), \quad W = W(S,p), \quad \text{and} \quad F = F(T,V). \tag{1.34}$$

In this list of 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 "Gibbs free energy") G. The way to define it is evident from the "circular diagram" shown in Fig. 5a.
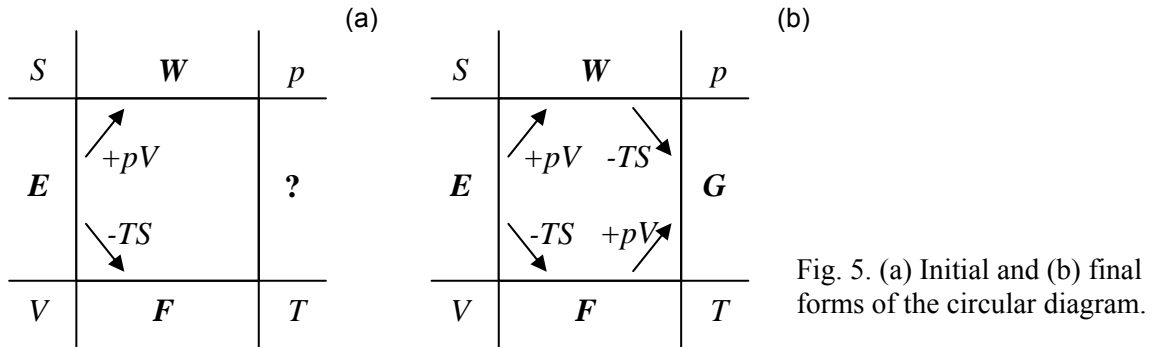

Fig. 5. (a) Initial and (b) final forms of the circular diagram.

In this diagram, each thermodynamic potential (shown in boldface) is located between two appropriate arguments (cf. Eq. (34)), while arrows show the way the potentials W and F have been obtained from energy E – cf. Eqs. (25) and (31). It is almost obvious from this diagram that the last potential G has to be defined as (Fig. 5b)

$$G \equiv E - TS + pV = W - TS = F + pV. \tag{1.35}$$

Indeed, let us calculate the differential of this potential, using, e.g., from Eq. (1.32):

$$dG = dF + d(pV) = (-SdT - pdV) + (pdV + Vdp) = -SdT + Vdp, \tag{1.36}$$

so that if we know the function $G(T, p)$, we can readily calculate entropy and volume:[9]

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[9] It is curious that the circular diagram shown in Fig. 5b may be used even for the fast determination of proper signs before the derivatives in Eqs. (9), (10), (29), (33), and (37). Indeed, the derivatives defining variables of the upper row (S and p) are always taken with negative signs, while those giving the variables of the bottom row (V and T), with positive signs.

$$S = -\left(\frac{\partial G}{\partial T}\right)_p, \quad V = \left(\frac{\partial G}{\partial p}\right)_T. \tag{1.37}$$

Now I have to justify the term "thermodynamic potentials"; unfortunately destroying in part the beautiful symmetry of the circular diagram in the process. For that, let us consider an *irreversible* process. (Classical examples of such processes are a fast compression of a gas, or its rapid expansion from one part of a volume into the other part.) At such process the entropy may grow faster than predicted by Eq. (17) which has been derived for a reversible process:

$$dS \geq \frac{dQ}{T}. \tag{1.38}$$

Plugging this inequality into Eq. (16) (which, being just the energy conservation law, remains valid for irreversible processes), we get

$$dE \leq TdS - pdV. \tag{1.39}$$

We may now can use this relation to have a look at the behavior of thermodynamic potentials in the irreversible situation, keeping their definitions (25), (31), and (35) intact.

Let us start from the (very common) case when both temperature T and volume V are kept constant. If the process was reversible, entropy S and hence the free energy $F(T, S)$ would be fixed, and its time derivative would equal zero. Equations (39) says that at the irreversible process it is not necessarily so:

$$\frac{dF}{dt} = \frac{d}{dt}(E - TS) = \frac{dE}{dt} - TdS \leq (TdS - pdV) - TdS = 0. \tag{1.40}$$

Hence, in a general (irreversible) situation F can decrease in time, but not decrease. This means that F approaches it minimum value $F(T, S)$ which is given by the equations of reversible thermodynamics. Thus in the case $T = $ const, $V = $ const, the free energy plays the role of the potential energy in the classical mechanics of dissipative processes (CM, Ch. 3): its minimum corresponds to the (in the case of F, thermodynamic) equilibrium of the system.

It is easy to get convinced that in the case $T = $ const, $p = $ const, the same role is played by the Gibbs energy:

$$\frac{dG}{dt} = \frac{d}{dt}(E - TS + pV) = \frac{dE}{dt} - TdS + pdV \leq (TdS - pdV) - TdS + pdV = 0, \tag{1.41}$$

so that the thermal equilibrium now corresponds to the minimum of G rather than F. By the way, one can argue that the difference between F and G has nothing to do with thermodynamics, because these notions exist (although are not much advertised) in classical mechanics as well. Indeed, the difference between F and $G = F + pV$ may be generalized as $G = F - fx$, where x is any generalized coordinate and f any generalized force - see Eq. (10) and its discussion. In this case the minimum of F corresponds to the equilibrium of an isolated system (with $f = 0$), while the equilibrium position of the same system under the action of external force f is given by the minimum of G. For example, in order to find an equilibrium position of a spring left alone, one may minimize its potential energy $kx^2/2$, while finding the fixed point of a spring compressed by force f requires the minimization of the Gibbs energy $kx^2/2 - fx$.

Let us now return to two remaining thermodynamic potentials, E and W. For them, one cannot make the calculations similar to Eq. (40) and (41), because that would require $S = $ const

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(with V = const for E, and p = const for W), but there is no practicable way to prevent the entropy growth if initially S was lower than its equilibrium value. As a result, while being an important variable for thermal engineering, enthalpy W remains an "orphan" of statistical physics and is being used for practical calculations much more rarely than F and G. (The internal energy E escapes this fate by being used as the entry point for the calculations of both F and G.)

1.5. Why Not the Equation of State?

One may ask why the main task of statistical physics is 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 is well known from undergraduate physics (we will derive it in the beginning of Ch. 3):

$$pV = NT, \qquad (1.42)$$

where N is the number of particles in the gas sample.[10] Let us try to use it for the calculation of all the thermodynamic potentials, and all other thermodynamic variables discussed above. We may start, e.g., from the calculation of the free energy F. Indeed, solving Eq. (42) for p and using the second of Eqs. (33), we get

$$F = -\int pdV_{|T=\text{const}} = -NT\int \frac{dV}{V} = -NT \ln V + f(T), \qquad (1.43)$$

where $f(T)$ is some function of temperature which cannot be recovered from the equation of state. This function also affects all other thermodynamic potentials, and entropy. Indeed, using the first of Eqs. (33), we get

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N \ln V - f'(T), \qquad (1.44)$$

and now can combine Eqs. (31) and (44) to calculate the internal energy

$$E = F + TS = (-NT \ln V + f) + T(N \ln V - f') = f - Tf', \qquad (1.45)$$

Eqs. (25) and (42) to calculate enthalpy

$$W = E + pV = E + NT = f - Tf' + NT, \qquad (1.46)$$

and Eq. (35) and (42) to calculate the Gibbs energy

$$G = F + pV = -NT \ln V + f + NT. \qquad (1.47)$$

One might question whether all these undetermined functions of temperature are physically significant, or may be ignored, just like the arbitrary constant which may be always

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[10] Using the notion of gas constant $R \equiv N_A k_B$, where $N_A \approx 6.02 \times 10^{23}$ mole^{-1} is the so-called *Avogadro number* (the number of molecules per mole, which is, crudely, just the reciprocal weight of a proton or neutron, expressed in grams), Eq. (42) may be presented in the more familiar form $pV = nRT_K$, where $n = N/N_A$ is the number of moles in the gas sample, and $T_K = T/k_B$ is the temperature expressed in Kelvins (see Footnote 5 above).

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added to the potential energy in classical mechanics. The answer is however *no*, because, for example, Eqs. (23) and (26) show that both values of specific heat, which are explicitly measurable quantities, do depend on the undetermined function $f(T)$[11]

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = (f - Tf')',$$ (1.48)

$$C_p = \left(\frac{\partial W}{\partial T}\right)_p = (f - Tf')' + N.$$ (1.49)

The reason of this problem is evident from the physical picture of the ideal gas: pressure p is produced only by the translational thermal motion of the atoms or molecules of the gas, while their internal energy E (and hence all other thermodynamic potentials) may be also contributed by the thermal excitation of their internal degrees of freedom (rotation, vibrations, etc.). Hence, the equation of state does not give a full thermodynamic description of an equilibrium system, while the thermodynamic potentials do.

1.6. Systems with Variable Number of Particles

In order to complete our brief review of thermodynamics, 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 include a gas volume separated from the environment by a penetrable partition (Fig. 6) or a gas in contact with the liquid of the same molecules.
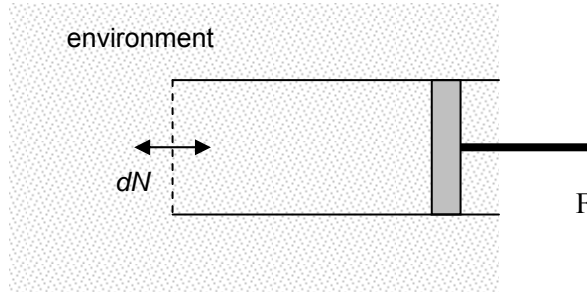

Fig. 6. Example of a system with variable N.

Let us analyze this situation for the simplest case when all the particles are similar (though the analysis may be extended to systems with particle of several sorts). In this case we can consider N as independent thermodynamic variable whose variation may change energy E of the system, so that (for a slow, reversible process) Eq. (15) should be generalized as

$$dE = TdS - pdV + \mu dN,$$ (1.50)

where μ is a function of state, called the *chemical potential*. As evident from Eq. (50), its physical sense is the *average* energy cost of adding one particle to the system. Keeping the

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[11] Note, however, that according to Eqs. (48) and (49), the difference $C_p - C_V = N$ (if temperature is measured Kelvins, $C_p - C_V = nR$) is independent of $f(T)$. It is easy to show that this fact (though not the exact value of the difference) is general: the difference $C_p - C_V$ is always fully determined by the equation of state.

definitions of other thermodynamic potentials, given by Eqs. (25), (31), and (35) intact, we see that their differentials should be generalized as

$$dW = TdS + Vdp + \mu dN, \tag{1.51}$$

$$dF = -SdT - pdV + \mu dN, \tag{1.52}$$

$$dG = -SdT + Vdp + \mu dN, \tag{1.53}$$

so that the chemical potential may be calculated as either of the derivatives

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = \left(\frac{\partial W}{\partial N} \right)_{S,p} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,p}. \tag{1.54}$$

Despite their similarity, one of Eqs. (50)-(54) is more consequential than others. Indeed, Gibbs energy G is the only thermodynamic potential which is a function of two *intensive* parameters, T and p. However, as all 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 μ equals the function $f(T,p)$. In other words,

$$\mu = \frac{G}{N}, \tag{1.56}$$

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

How can be the notion of chemical potential useful? Let us consider the situation (parallel to that shown in Fig. 1) when a system consists of two parts which can exchange particles at a relatively slow rate (much slower than the speed of internal relaxation inside each of the parts). Than we can write two equations similar to Eq. (1):

$$N = N_1 + N_2, \quad G = G_1 + G_2, \tag{1.57}$$

where $N = \text{const}$, and Eq. (56) may be used to describe the components of G:

$$G = \mu_1 N_1 + \mu_2 N_2. \tag{1.58}$$

Plugging into this expression N_2 expressed from the first of Eqs. (57), we see that

$$\frac{dG}{dN_1} = \mu_1 - \mu_2, \tag{1.59}$$

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

In statistical physics, we will run into a situation when the volume of a system, its temperature, and the chemical potential are fixed. A thermodynamic potential appropriate for this case may be obtained from free energy F by subtraction of the product μN. The resulting potential is just

$$\Omega \equiv F - \mu N = F - \frac{G}{N} N = F - G = -pV. \tag{1.60}$$

For a reversible process, its differential is

$$d\Omega = dF - d(\mu N) = (-SdT - pdV - \mu dN) - (\mu dN + Nd\mu) = -SdT - pdV - Nd\mu, \tag{1.61}$$

while for an irreversible process this relation turns in an inequality:

$$d\Omega \leq -SdT - pdV - Nd\mu, \tag{1.62}$$

In the conditions of fixed T, V, and μ, the right hand part of this equation vanishes, so that the equilibrium indeed corresponds to the minimum of $\Omega = -pV$.

1.7. What Has Not Been Covered

Finishing here our brief review of thermodynamics,[12] I would like to emphasize that there are other important parts of this discipline which the students should know, despite we will not run into them in our course of statistical mechanics.

Most importantly, thermodynamics allows one to analyze the work of thermal machines: the thermal engine turning heat flow into mechanical work, and refrigerators and heat pumps, tuning work into heat flow. In particular, it allows the calculation of the figures-of-merit of the thermal machines and their ultimate values (most famously, the ultimate efficiency of the heat engine, which may be achieved using the Carnot cycle consisting of two adiabatic and two reversible isothermal stages.) A famous example of the opposite, ultimately irreversible process is the Joule-Thompson expansion of a gas into vacuum.

Other prominent uncovered topics include the conditions of stability of thermodynamic systems, and the Le Chatelier's principle describing the sign of a system reaction to the external perturbation.

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[12] Actually we will return to this phenomenological approach now and then through the course. In particular, our treatment of non-ideal classical gases in Ch. 4 will be mostly phenomenological.