Statistical Thermodynamics - Fall 2009

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Thermodynamics

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I. PREFACE

The course of Statistical Thermodynamics consist of two parts: Thermodynamics and Statistical Physics. These both branches of physics deal with systems of a large number of particles (atoms, molecules, etc.) at *equilibrium.*

One cm^3 of an ideal gas under normal conditions contains $N_L = 2.69 \times 10^{19}$ atoms, the so-called Loschmidt number. Although one may describe the motion of the atoms with the help of Newton's equations, direct solution of such a large number of differential equations is impossible. On the other hand, one does not need the too detailed information about the motion of the individual particles, the *microscopic* behavior of the system. One is rather interested in the *macroscopic* quantities, such as the pressure P. Pressure in gases is due to the bombardment of the walls of the container by the flying atoms of the contained gas. It does not exist if there are only a few gas molecules. Macroscopic quantities such as pressure arise only in systems of a large number of particles. Both thermodynamics and statistical physics study macroscopic quantities and relations between them. Some macroscopics quantities, such as temperature and *entropy*, are non-mechanical.

Equilibruim, or thermodynamic equilibrium, is the state of the system that is achieved after some time after time-dependent forces acting on the system have been switched off. One can say that the system approaches the equilibrium, if undisturbed. Again, thermodynamic equilibrium arises solely in macroscopic systems. There is no thermodynamic equilibrium in a system of a few particles that are moving according to the Newton's law. One should not confuse thermodynamic equilibrium with mechanical equilibrium achieved at a local or global energy minimum. The microstate of a macroscopic system at thermodynamic equilibrium is permanently changing. However, these changes are irrelevant, whereas the important macroscopic state of the system does not change. At equilibrium the behavior of the system strongly simplifies. Typically, pressure and temperature become the same across the system. Both thermodynamics and statistical physics lead to a number of results at equilibrium that do not depend on the exact nature of the system and thus are universal. To the contrary, nonequilibrium processes (such as *relaxation*, the process of approaching the equilibrium) are much less universal and therefore much more difficult to describe.

Thermodynamics uses the *phenomenological* approach that consists in working with macroscopic quantities only and not going down to the micro-level of description. Since macroscopic quantities are what is directly of indirectly observed in the experiment, one can say that thermodynamics concentrates on the phenomena leaving out the question of how they are exactly formed. This is the ethymology of the word ,,phenomenological". It turns out that one can formulate a number of principles taken from observations (energy is conserved, temperatures of two bodies in contact tend to equilibrate, etc.) basing on which one can arrive at many important conclusions. Thermodynamics emerged in XIX century in the course of industrialization and it is the basis of understanding steam engines, refrigerators, and other machines. Thermodynamics studies relations between different macroscopic quantities taking many inputs from the experiment.

Statistical physics, to the contrary, uses the microscopic approach to calculate macroscopic quantities that thermodynamics has to take from the experiment. The microscopic approach of the statistical physics is still much less detailed than the full dynamical description based on Newton's equations. Instead of finding trajectories of the particles, statistical physics operates with the *probability* for the system to be in a certain microscopic state. At equilibrium, the probabilities of microstates turn out to be given by a universal formula, the so-called Gibbs distribution. Using the latter, one can calculate macroscopic quantities.

All thermodynamic relations can be obtained from statistical physics. However, one cannot consider statistical physics as superior to thermodynamics. The point is that thermodynamic relations are universal because they are model-independent. To the contrast, results of statistical physics for macroscopic quantities are always based on a particular model and thus are less general.

II. DEFINITIONS OF THERMODYNAMICS

A. System and environment

Thermodynamics studies a macroscopic system that can be in contact with other macroscopic systems and *environment.* Environment (or *surrounding*, or *bath,* or *heat reservoir*) is a special type of a system that has a very large size. The system under consideration can change its state as a result of its contact to the bath but the state of the bath does not change due to the interaction with a much smaller system. For instance, the thermometer measuring the temperature of a body can be considered as the system, whereas the body itself plays the role of the bath.

B. Open, close, adiabatic, and isolated systems

Systems can be *open*, *closed*, *adiabatic*, and *isolated.* An open system can exchange mass and energy with the environment.

A closed system cannot exchange the mass but it can receive or lose energy in the form of heat due to the thermal contact with the bath or through the work done on the system.

An adiabatic system is thermally isolated so that it cannot receive or lose heat, although work can be done on this system. The corresponding processes (such as compression/expansion) are called *adiabatic processes.* Fast processes are adiabatic, too, because the heat exchange through the surface requires a too long time and becomes inefficient during the time of the process.

An isolated system cannot exchange neither mass nor energy, there is no contact between the system and the environment.

C. Extensive, intensive, and specific quantities

Macroscopic physical quantities can be *intensive* and *extensive.* Intensive quantities (pressure P, temperature T) do not depend on the size (mass) of the system, while the extensive quantities (mass M, volume V, energy E or U) scale with the system size. To make this definition more precise, one can split the system into two equal parts by an imaginary membrane. The intensive quantities of the two resulting systems will remain the same while the extensive quantities of each subsystem will be half of that for the whole system.

Specific quantities is the third type of quantities that can be obtained from an extensive quantity by division by another extensive quantity. By this definition, specific quantities do not depend on the system size. An example of specific quantity is the mass density

$$\rho = \frac{M}{V}. \tag{1}$$

D. Quasi-static, reversible and irreversible processes

In the preface it is written that thermodynamics studies macroscopic systems at equilibrium, while equilibrium is a time-independent state reached as a result of relaxation under time-independent conditions. On the other hand, thermodynamic considers processes such as compression/expansion or heating that evolve in time. Isn't here a contradiction with the equilibrium nature of thermodynamics? The solution of this paradox is that ,,good" thermodynamic processes must be *quasi-static* or *quasi-equilibrium.* This means that the external parameters that control the system change with time so slowly that the system at any moment of time is very close to the equilibrium, corresponding to the instantaneous values of the control parameters. These external parameters define the macroscopic quantities of the system at any stage of the process that can be represented as a continuous line in the space of these quantities, such as (P, V). Such space can be called *configurational space.* If the external parameters change fast, the system deviates from the equilibrium and, in most cases, its macroscopic quantities become undefined. In this case the process cannot be represented as a line in the (P, V) or other diagram. For instance, fast compression of a gas creates sound waves or even shock waves that travel through the system making density, pressure, and temperature non-uniform, so that there are no unique values of these quantities. In this case, only the initial and final states of the system are equilibrium states but there is no line connecting them.

Reversible processes are quasi-static processes that can go in both directions along the same line in the space of thermodynamic quantities. Most quasi-static processes are reversible. An exclusion is the slow stirring process of a liquid or gas that cannot be inverted. In this process, the stirring wheel produces work on the system so that the system warms up. However, from the point of view of the system, this process is equivalent to heating and it does not matter how exactly the heat is being delivered. By subsequent taking out the heat through the thermal contact with the bath one can let the system go the same path in the opposite direction in the configurational space, that is, invert this process. On the other hand, all non-quasi-static processes are *irreversible.*

III. TEMPERATURE

On the intuitive level, temperature is associated with notions ,,hot" and ,,cold". The experience shows that if hot and cold bodies are brought in contact, their temperatures would eventually equilibrate. Consider a system in a thermal contact with the bath and make a quasi-static compression or expansion of the system plotting its states in the (P, V) diagram. As the bath is large, its temperature remains unchanged and as the process is slow, the temperature of the system will have the same unchanged value. In this way one obtains the isothermal curve, or *isotherm*, in the (P, V) plot. Repeating this with different temperatures of the bath, one obtains many isotherms. For most of substances (except water near 4° C) isotherms corresponding to different temperatures do not cross. This allows to define the *empirical temperature* T as a parameter labeling isotherms:

$$\phi(P, V) = T. \tag{2}$$

Indeed, if $T = \text{const}$, P and V are related and belong to a particular isotherm. Note that any monotonic function of the empirical temperature (e.g., $\sqrt{T}$ or T^2) can serve as empirical temperature as well, so that the choice of the latter is not unique. Eq. (2) is the basis of thermometers using different substances such as alcohol, mercury, ideal gas, etc. One can, say, fix P to the athmospheric pressure and measure V (or the hight of the alcohol or mercury column) that changes with temperature. It is convenient to choose the empirical temperature in the way that the changes of the volume and temperature are proportional to each other, $\Delta T \propto \Delta V$. Alternatively, one can fix V and use P to define the temperature changes as $\Delta T \propto \Delta P$. This makes the empirical temperature proportional to the actual temperature that we deal with in our life. What remains is to choose the proportionality coefficient in the above formula and the additive constant (offset) in T. This has been done historically in a number of different ways, resulting in the Fahrenheit, Celsius, Kelvin, and many other defunct temperature scales.

The advantage of the Celsius scale is using very natural events, melting of ice and boiling of water (at normal conditions), to define the basic temperature points 0°C and 100°C. Physicists use the Kelvin scale in which the temperature, corresponding to the extrapolated point, where the volume (or pressure) of the ideal gas vanishes, is set to zero and one degree of temperature difference is the same as in the Celsius scale. The relation between the two scales is

$$T(^\circ\mathrm{C}) = T(^\circ\mathrm{K}) + 273.15. \tag{3}$$

Existence of the temperature as the new (non-mechanical) quantity that equilibrates in the case of systems in thermal contact, is called the *zeroth law of thermodynamics.*

IV. EQUATION OF STATE

One can rewrite Eq. (2) in the form symmetric with respect to the thermodynamic quantities P, V, T

$$f(P, V, T) = 0. \tag{4}$$

This relation between the three quantities is called *equation of state.* If two of the quantities are known, the third can be found from Eq. (4). If $T = \text{const}$, P and V lie on the curve called *isotherm.* If $P = \text{const}$, V and T lie on the curve called *isobar.* If $V = \text{const}$, P and T lie on the curve called *isochore.*

Equation (4) is written for a fixed amount of substance in a closed system. As the dependence on the latter is trivial (at fixed P and T the volume scales with the amount of the substance), this is not included in the equation of state.

Considerations above, including the definition of temperature, pertain to the simplest thermodynamic systems such as gas or liquid that are characterized by pressure and volume. There are many other systems described by other macroscopic quantities. For instance, magnetic systems are additionally described by the magnetic induction B (intensive quantity) and the magnetic moment $\mathcal{M}$ (extensive quantity). Usually magnetic systems are solid and their volume and pressure do not change. Thus the equation of state for magnetic systems has the form $f(B, \mathcal{M}, T) = 0$.

The simplest equation of state is that of the ideal gas that is written in the form

$$PV = \nu RT, \tag{5}$$

where ν is the number of kilomoles of the gas and $R = 8.314 \times 10^3$ J/(kilomole K) is the universal gas constant. The number of kilomoles is defined by $\nu \equiv M/M_{KM}$, where M is the mass of the gas and M_{KM} is the mass of one kilomole of this gas (in kg), numerically equal to its atomic weight (approximately the combined number of protons and neutrons in the nucleous).

Writing the equation of state in the above form contradicts the spirit of thermodynamics that generally neglects the internal structure of the matter. One could rewrite the equation of state in the completely thermodynamic form as $PV = M\bar{R}T$, where $\bar{R} \equiv R/M_{KM}$. The downside of this equation is that $\bar{R}$ is not universal and depends on the particular gas. This is why Eq. (5) is still preferred.

From the point of view of physics, a more useful form of the equation of state of the ideal gas making connection to the molecular theory is

$$PV = Nk_BT, \tag{6}$$

where N is the number of particles (atoms or molecules) in the gas and $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. Using the definition of the atomic weight, one can establish the relation between the two forms of the equation of state.

The isotherm of the ideal gas is a hyperbole, while the isochore and isobar are straight lines.

The temperature in Eqs. (5) and (6) is in Kelvin. One can see, as was said above, that at least one of P and V turns to zero at $T = 0$. The beginning of the Kelvin temperature scale has a deep physical meaning: At the absolute zero $T = 0$ the molecules of the ideal gas freeze and stop to fly inside the container, falling down into their state of the lowest energy. As the pressure is due to the impact of the molecules onto the walls, it vanishes at $T = 0$. Of course, the equation of state of the ideal gas loses its applicability at temperatures low enough because any actual gas becomes non-ideal and condenses at low T. Nevertheless, one can extrapolate the isochore or isobar to the left and find the intercept with the T-axis that is located at -273°C, the absolute zero in the Kelvin scale.

V. THERMODYNAMIC COEFFICIENTS

As thermodynamic quantities are related by the equation of state, changing some quantities causes changing the others. In particular, writing $V = V(P, T)$ one obtains for the infinitesimal changes the full differential

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT. \tag{7}$$

Here the subscripts T and P mean that these quantities are held constant in the differentiation. The partial derivatives above enter the thermodynamic coefficients isothermal compressibility $\varkappa_T$ and thermal expansivity β, defined as specific quantities

$$\varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{8}$$

As $\varkappa_T < 0$ contradicts mechanical stability, all materials have

$$\varkappa_T > 0. \tag{9}$$

There is no general principle that could limit the range of β. Most materials expand upon heating, $\beta > 0$. However, materials that consist of long polymer molecules such as rubber contract upon heating, $\beta < 0$, that can be explained by their molecular motion.

Using $P = P(V, T)$, one obtains the differential

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT. \tag{10}$$

Both partial derivatives here can be reduced to those considered above with the help of two formulas from the calculus. First, one has simply

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{(\partial V/\partial P)_T} \tag{11}$$

that is an obvious relation. Next, with the help of the triple product rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \tag{12}$$

one obtains

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\beta}{\varkappa_T}. \tag{13}$$

Let us calculate thermodynamic coefficients for an ideal gas, Eq. (5). Using $V = \nu RT/P$, in Eq. (8) one obtains

$$\varkappa_T = -\frac{P}{\nu RT}\left(-\frac{\nu RT}{P^2}\right) = \frac{1}{P} \tag{14}$$

and

$$\beta = \frac{P}{\nu RT}\left(\frac{\nu R}{P}\right) = \frac{1}{T}. \tag{15}$$

Now Eq. (13) yields

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}. \tag{16}$$

VI. WORK AND INTERNAL ENERGY

The system and environment can exchange energy with each other. One of the ways to exchange energy is doing work that can be understood in mechanical terms. According to the Newton's third law, the work done on the system by the environment and the work done by the system on the environment differ by the sign. In the general formulation of thermodynamics, we consider the former. For the basic thermodynamic system characterized by $P, V, T,$ the infinitesimal work is given by

$$\delta W = -PdV. \tag{17}$$

That is, when the system is compressed, $\delta W > 0$ and the system receives energy. We write δW instead of dW to emphesize that work is not a *state variable,* thus δW is a small increment but not a differential. State variable is any thermodynamic quantity that has a well-defined value in any particular state of the system. In particular, for *cyclic process*es the system returns to the same state at the end of the cycle, so that all state variables assume their initial values. However, nonzero work can be done in cyclic processes (the area circomscribed by the cycle in the P, V diagram), so that one cannot ascribe an ,,amount of work" to any particular state of the system. The finite work

$$W_{12} = -\int_1^2 PdV \tag{18}$$

done on the way from the initial state 2 to the final state 1 depends on the whole way from the initial to the final states. That is, work is a *way function* rather than a state function.

Equation (17) can be easily obtained considering a cylinder with a moving piston of the area S. Indeed, with the position of the piston l one obtains $\delta W = -Fdl = -PSdl = -PdV$. In fact, Eq. (17) is general and it can be obtained for any type of deformations of the system's surface.

Other thermodynamic systems characterized by other macroscopic variables, such as magnetic systems, have their own expressions for the infinitesimal work that we do not consider at the moment.

Let us calculate the work W_{12} for typical processes of the ideal gas. For the isochoric process obviously $W_{12} = 0$ because the volume does not change.

For the isobaric process, the integrand P in Eq. (18) is constant, so that the integral is trivial:

$$W_{12} = -P\int_1^2 dV = P(V_1 - V_2). \tag{19}$$

For the isothermal process with the help of the equation of state (5) one obtains

$$W_{12} = -nRT\int_1^2 \frac{dV}{V} = nRT\ln\frac{V_1}{V_2}. \tag{20}$$

One can see that positive work is done on the system in both isobaric and isothermal compression.

The work due to the change of externally controlled parameters, such as V, is sometimes called c*onfigurational work*, to distinguish it from the *dissipative work*. Examples of the latter are work done on a liquid by stirring or work on a hard surface by rubbing. It is understood that the dissipative work cannot be described by Eqs. (17) and (18). While the configurational work is reversible, dissipative work is irreversible. The total work is the sum of both:

$$\delta W=\delta W_{\mathrm{configurational}}+\delta W_{\mathrm{dissipative}} \tag{21}$$

while

$$\delta W_{\mathrm{dissipative}}\geq 0. \tag{22}$$

This nearly evident inequality follows from Eqs. (89) and (82).

Similarly to mechanics, one can define the *internal energy* U of the system through the work on the way from 1 to 2. Do do this, one has to thermally insulate the system from the environment. The experiment shows that the total amount of work (configurational + dissipative) W_{12} on the *adiabatic* system is entirely determined by the initial and final states 1 and 2. This allows one to define the internal energy for any state 2 of the system as

$$U_2=U_1+W_{12}, \tag{23}$$

where U_1 is an irrelevant additive constant.

To reach the state 2 from the state 1, one has to make, in general, both configurational and dissipative work. The order in which these works are done is arbitrary, so that there are many paths leading from 1 to 2. Still the work W_{12} is the same for all these paths, thus U_2, or simply U, is a state quantity. This statement, following from the experiment, can be considered as the foundation of the First Law of thermodynamics.

Since the internal energy is a state quantity, one can express it as a function of two basic quantities, say

$$U=U(T,V). \tag{24}$$

This is the so-called caloric equation of state. Within the thermodynamics, the only way to obtain the latter is to take it from the experiment, as described above. Statistical physics provides the caloric equation of state in the analytical form in many cases. For ideal gases, the internal energy depends only on the temperature, $U=U(T)$. This is the consequence of the negligibly weak interaction between the particles. For some ideal gases $U=aT$ with $a=\mathrm{const}$ in a wide range of temperatures. Such an ideal gas is called *perfect gas.* As the constant a turns out to be the heat capacity of the system at a constant volume, we will discuss the later before considering examples of the heat received in a process.

VII. HEAT AND THE FIRST LAW OF THERMODYNAMICS

Having defined the internal energy U for any state P,V of the system, one can relax the condition that the system is adiabatic. As soon as one allows thermal contact between the system and the environment, it turns out that the energy balance in the mechanical form, $dU=\delta W$, is no longer satisfied. To restore the energy conservation, one has to include the heat Q received by the system from the environment. In the infinitesimal form the energy conservation reads

$$dU=\delta Q+\delta W, \tag{25}$$

that is, the change of the internal energy is work done on the system plus the heat received by the system. Similarly to work, heat is not a state function, thus we use δQ instead of dQ. The energy conservation law written in the form of Eq. (25) constitutes the first law of thermodynamics.

Before the major advances of thermodynamics in the XIX century, the dominant idea of the heat was that heat is a kind of a special substance that can enter or exit the system. If it were true, one could speak of the heat contained in the system, thus the heat were a state function. However, this interpretation turned out to be erroneous, as follows from Joule's experiment proving that the heat is just a form of energy. In this experiment a stirring wheel makes a dissipative work on a liquid that leads to warming up the system. The result of this process is identical to that of adding heat through the walls of the container. This is incompatible with the model of heat as a special substance. Moreover, one can show that the total heat received in cyclic processes is usually non-zero, so that heat is not a state function.

Before the Joule's experiment, the unit of heat, the calory, was introduced as the amount of heat needed to increase the temperature of 1 g water by 1°C. Joule's experiment determined the mechanical equivalent of the calory,

$$1\ \mathrm{cal}=4.19\ \mathrm{J}. \tag{26}$$

The heat received in a finite process is given by

$$Q_{12} = \int_1^2 (dU - \delta W) = U_2 - U_1 - W_{12}. \tag{27}$$

Since W_{12} depends on the path between 1 and 2, Q_{12} also depends on this path. Thus the heat is a path function rather than a state function.

From the point of view of the system, dissipative work on it amounts to adding heat. As the system then can give away this amount of heat (as a real heat, not a dissipative work), it is convenient to count dissipative work as heat, so that these processes become reversible. In the sequel, dissipative work will always be included in heat.

VIII. HEAT CAPACITY

In most cases adding heat to the system leads to increase its temperature. One can define the heat capacity as

$$C = \frac{\delta Q}{dT}. \tag{28}$$

C is large if large amounts of heat cause only insignificant temperature increase. The heat capacity, as defined above, is proportional to the system size and thus is extensive. One can introduce specific quantities, heat and heat capacity per kilomole,

$$q \equiv \frac{Q}{\nu}, \qquad c = \frac{C}{\nu} = \frac{\delta q}{dT}. \tag{29}$$

Heat capacity depends on the type of the process. If the heat is added to the system while the volume is kept constant, $dV = 0$, one obtains the isochoric heat capacity

$$C_V = \left(\frac{\delta Q}{dT}\right)_V. \tag{30}$$

Also one can keep a constant pressure, $dP = 0$, to obtain the isobaric heat capacity

$$C_P = \left(\frac{\delta Q}{dT}\right)_P. \tag{31}$$

In the isochoric case no work is done, so the heat fully converts into the internal energy U and the temperature increases. In the isobaric case, the system usually expands upon heating and a negative work is done on it. This leads to a smaller increase of U and thus smaller increase of the temperature. Consequently, for most materials $C_P > C_V$ should be satisfied. Rigorous consideration at the end of this section shows, however, that $C_P > C_V$ is satisfied for all materials, including rubber that shrinks upon heating.

In the isothermal process, the system receives or lose heat but $dT = 0$, thus $C_T = \pm\infty$.

Finally, in the adiabatic process $\delta Q = 0$ but the temperature changes. Thus in this process $C_S = 0$. The subscript S refers to the *entropy* that is a state function conserved in the reversible adiabatic processes, to be studied later.

Let us rewrite the first law of thermodynamics, Eq. (25) with Eq. (17), in the form

$$\delta Q = dU + PdV. \tag{32}$$

Considering the energy as a function of T and V, as in Eq. (24), one can write

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{33}$$

Combining this with the previous equation, on obtains

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \tag{34}$$

At constant volume this equation yields $\delta Q = (\partial U/\partial T)_V \, dT$ thus

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{35}$$

To find the isobaric heat capacity C_P, one has to take into account that at constant pressure the volume in Eq. (32) changes because of thermal expansion,

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT. \tag{36}$$

Inserting this into Eq. (34) one obtains

$$\delta Q = \left[C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT. \tag{37}$$

This yields

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P. \tag{38}$$

As said above, the energy of the ideal gas depends only on T, so that $(\partial U/\partial V)_T = 0$. Another partial derivative can be obtained from the equation of state (5) and is given by $(\partial V/\partial T)_P = \nu R/P$. The result is the famous Mayer's relation for the ideal gas

$$C_P = C_V + \nu R, \tag{39}$$

or $c_P = c_V + R$ for heat capacities per kilomole. In terms of the number of particles N, see Eq. (6), Mayer's relation becomes

$$C_P = C_V + N k_B \tag{40}$$

or $c_P = c_V + k_B$ for heat capacities per particle.

We have used $(\partial U/\partial V)_T = 0$ for the ideal gas as taken from the experiment and we can explain it within the molecular theory. It turns out, however, that $(\partial U/\partial V)_T$ can be calculated within the thermodynamics and has the form

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{41}$$

Now for the ideal gas from the equation of state follows $(\partial U/\partial V)_T = 0$. In the general case Eqs. (38) and (41) combine to

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P. \tag{42}$$

The last term here can be expressed via the thermodynamic coefficients of Sec. V. Using Eqs. (8) and (13), one obtains

$$C_P = C_V + VT\frac{\beta^2}{\varkappa_T}. \tag{43}$$

Since the compressibility $\varkappa_T > 0$ for all materials, one concludes that always $C_P > C_V$. The derivation of Eq. (41) is based on the concept of *entropy* discussed later in the course.

IX. ADIABATIC PROCESS OF THE IDEAL GAS

For the ideal gas the internal energy is a function of the temperature only, thus one has

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT. \tag{44}$$

In the adiabatic process $\delta Q = 0$. Adopting these two results in Eq. (25) and using Eq. (17), one obtains

$$C_V dT = -P dV. \tag{45}$$

Here one of the quantities P or V can be eliminated with the help of the equation of state (5). Substituting $P = \nu RT/V$, one obtains

$$C_V dT = -\nu RT \frac{dV}{V}. \tag{46}$$

This is equivalent to a differential equation that can be integrated if the temperature dependence $C_V(T)$ is known. For the perfect gas, $C_V = \text{const}$, integrating is easy and yields

$$\ln T = -\frac{\nu R}{C_V} \ln V + \text{const} \tag{47}$$

or, finally, the adiabat equation

$$TV^{\nu R/C_V} = \text{const}. \tag{48}$$

It is convenient to introduce the ratio of heat capacities

$$\gamma \equiv \frac{C_P}{C_V}, \tag{49}$$

so that, with the help of Mayer's equation (39), one has

$$C_V = \frac{\nu R}{\gamma - 1}, \qquad C_P = \frac{\nu R \gamma}{\gamma - 1}. \tag{50}$$

Then the adiabat equation (48) becomes

$$TV^{\gamma - 1} = \text{const}. \tag{51}$$

One also can express the adiabat equation via P, V using the equation of state (5) that yields

$$PV^{\gamma} = \text{const}. \tag{52}$$

The third form of the adiabat equation is

$$TP^{1/\gamma - 1} = \text{const}. \tag{53}$$

Let us calculate the work done in the adiabatic process from 1 to 2. Using Eq. (52), one obtains

$$W_{12} = -\int_{V_1}^{V_2} P dV = -\text{const} \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = -\frac{\text{const}}{1-\gamma} \left(V_2^{1-\gamma} - V_1^{1-\gamma} \right). \tag{54}$$

Here the constant can be eliminated using $\text{const} = P_1 V_1^\gamma = P_2 V_2^\gamma$ for the two terms. One obtains

$$W_{12} = \frac{1}{\gamma - 1} \left(P_2 V_2 - P_1 V_1 \right). \tag{55}$$

With the help of the equation of state and Eq. (50) one can simplify this formula to

$$W_{12} = \frac{\nu R}{\gamma - 1} \left(T_2 - T_1 \right) = C_V \left(T_2 - T_1 \right). \tag{56}$$

Equation (56) is a very simple result that can be obtained by another and simpler method. Indeed, according to the first law of thermodynamics, in the adiabatic process the work is equal to the change of the internal energy, $W_{12} = U_2 - U_1$. For the ideal gas $U = U(T)$ and $dU/dT = C_V$. Thus the internal energy of the ideal gas is given by

$$U(T) = \int C_V(T) dT \tag{57}$$

For the perfect gas, $C_V = \text{const}$, one has

$$U(T) = C_V T + U_0, \qquad U_0 = \text{const}, \tag{58}$$

thus

$$U_2 - U_1 = C_V \left(T_2 - T_1 \right), \tag{59}$$

so that Eq. (56) follows.

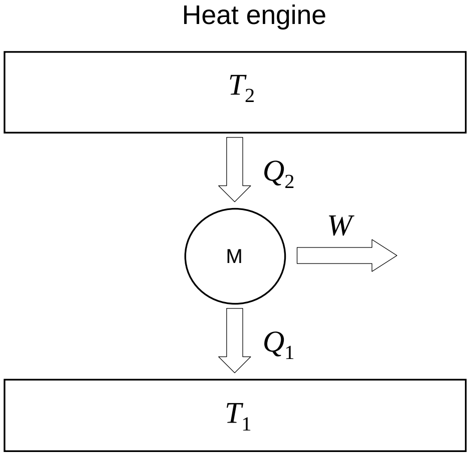

FIG. 1: Schematic representation of a heat engine.

X. HEAT MACHINES

Heat machines was a major application of thermodynamics in the XIX century that greatly contributed to its development. As engines convert energy between different forms, such as work and heat, the basis of their understanding is the first law of thermodynamics, Eq. (25). There are three types of heat machines: Engines, refrigerators, and heat pumps. In all cases a heat machine includes two reservoirs with different temperatures and a system that exchanges heat with the two reservoirs and does work in a cyclic process. Engines of the XIX century used steam as a source of heat, while the steam was obtained by heating water by fire. Contemporary motors use fuel that burns and generates heat directly. Refrigerators and heat pumps also use agents other than water.

A. Heat engine

In engines, during one cycle the system receives the heat Q_2 from the hot reservoir, gives the heat Q_1 to the cold reservoir, and makes the work, see Fig. 1. This work is $-W$, the negative of the work W made on the system that we are using in general formulations. The efficiency of the engine is defined as the ratio of the output energy (work $-W$) to the input energy Q_2,

$$\eta = \frac{-W}{Q_2}, \tag{60}$$

whereas Q_1 is the lost energy. In cyclic processes the internal energy of the system does not change,

$$\Delta U = \oint dU = 0. \tag{61}$$

Thus, integrating Eq. (25) over the cycle, one obtains

$$0 = \oint (\delta Q + \delta W) = Q + W = Q_2 - Q_1 + W, \tag{62}$$

so that the work done by the system is $-W = Q_2 - Q_1$. Inserting this into Eq. (60), one obtains

$$\eta = 1 - \frac{Q_1}{Q_2}. \tag{63}$$

One can see that $\eta < 1$. To make the efficiency η as high as possible, one should minimize Q_1.

Let us consider a particular process, the Carnot cycle, the working body being an ideal gas. The Carnot cycle consists of two isotherms T_1 and T_2 and two adiabats connecting them (see Fig. 2) The cycle goes in the clockwise direction, so that the work done by the system is positive, $-W = \oint PdV > 0$. One can see that the heat Q_2 is received on the isothermal path AB at $T = T_2$, whereas the heat Q_1 is given away on the isothermal path CD at $T = T_1$. There is no heat exchange on the adiabatic paths BC and DA. This is why the Carnot cycle is the most simple and thus

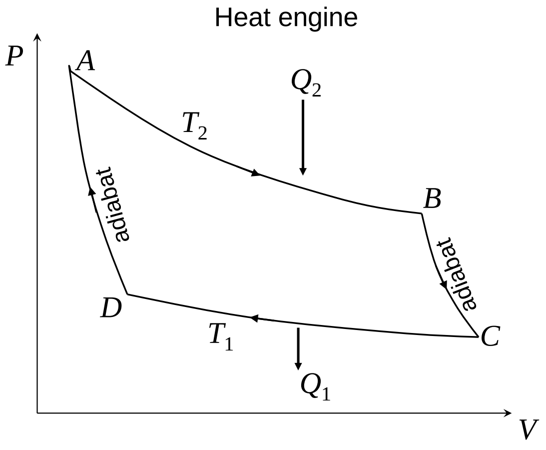

FIG. 2: Carnot cycle of a heat engine

the most fundamental of thermodynamic cycles. To calculate Q_1 and Q_2, one can use the fact that for the ideal gas $U = U(T)$, so that along the isotherms $U = \text{const}$ and thus $dU = \delta Q + \delta W = 0$. The work in the isothermal process has been calculated above. Using Eq. (20), one obtains

$$\begin{aligned} Q_2 &= Q_{AB} = -W_{AB} = -\nu R T_2 \ln \frac{V_A}{V_B} = \nu R T_2 \ln \frac{V_B}{V_A} > 0 \\ Q_1 &= -Q_{CD} = W_{CD} = \nu R T_1 \ln \frac{V_C}{V_D} > 0. \end{aligned} \tag{64}$$

Now, with the help of the adiabat equations, one can show that the logarithms in these expressions are the same. Indeed, from Eq. (51) follows

$$\begin{aligned} T_2 V_B^{\gamma-1} &= T_1 V_C^{\gamma-1} \\ T_2 V_A^{\gamma-1} &= T_1 V_D^{\gamma-1}. \end{aligned} \tag{65}$$

Dividing these equations by each other, one obtains $V_B/V_A = V_C/V_D$. Thus the ratio Q_1/Q_2 simplifies as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{66}$$

and Eq. (63) gives the famous Carnot formula

$$\eta = 1 - \frac{T_1}{T_2}. \tag{67}$$

One can see that the efficiency η becomes close to 1 if the temperature of the cold reservoir is close to the absolute zero. Practically it is impossible to realize. In standard engines, T_1 is the temperature at nornal conditions, $T_1 = 300$ K. Then the temperature T_2 of the hot reservoir must essentially exceed T_1. In particular, for $T_2 = 600$ K one obtains $\eta = 0.5$. In practice, the processes in heat engines deviate from the Carnot cycle that can be shown to be optimal. This leads to further decrease of the efficiency η.

B. Refrigerator

Refrigerators are inverted heat engines, see Fig. 3. The work is done on the system that extracts the heat Q_1 from the cold reservoir (eventually lowering its temperature) and gives heat Q_2 to the hot reservoir (the environment). The efficiency of the refrigerator is defined as the energy output Q_1 to the energy input, W. As the energy balance of the refrigerator is similar to that of the engine, $W = Q_2 - Q_1$, the efficiency formula becomes

$$c = \frac{Q_1}{W} = \frac{Q_1}{Q_2 - Q_1}. \tag{68}$$

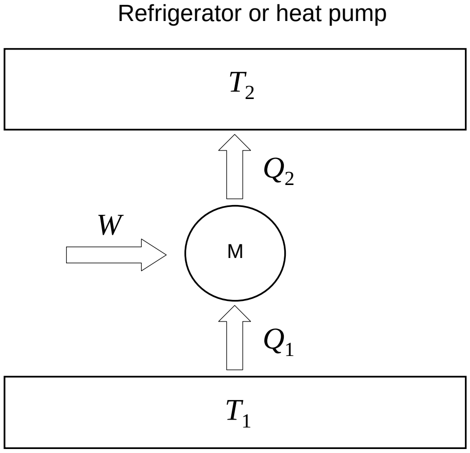

FIG. 3: Schematic representation of a refrigerator (environment at T_2) or heat pump (environment at T_1).

For the Carnot refrigerator with the help of Eq. (66) this transforms to

$$c = \frac{T_1}{T_2 - T_1}. \tag{69}$$

One can see that the efficiency of a refrigerator can be very high if T_1 and T_2 are close. This is the situation when the refrigerator starts to work. However, as T_1 decreases well below T_2 (that is essentially the environmental temperature 300 K), the efficiency becomes small.

C. Heat pump

Heat pump is similar to refrigerator, only the interpretation of reservoirs 1 and 2 changes. Now 1 is the environment from where the heat is being pumped, whereas 2 is the reservoir that is being heated, for instance, a house. The efficiency of the heat pump is defined as the ratio of the output Q_2 to the input $W = Q_2 - Q_1$

$$d = \frac{Q_2}{W} = \frac{Q_2}{Q_2 - Q_1}. \tag{70}$$

For the Carnot heat pump the efficiency becomes

$$d = \frac{T_2}{T_2 - T_1}, \tag{71}$$

the inverse of that of the Carnot engine. One can see that the efficiency of the heat pump is always greater than 1. If the temperatures T_1 and T_2 are close to each other, d becomes large. This characterizes the initial stage of the work of a heat pump. However, after T_2 increases well above T_1, the efficiency becomes close to 1. This is the regime of direct heating in which the energy input W is converted into heat Q_2, while the additional heat Q_1 obtained from the environment is small. Practically, we do not need to warm up our house to the temperatures much greater than T_1. Typically, in winter $T_1 \approx 270$ K while $T_2 \approx 300$ K. In this case $d \approx 10$. One can see that the heat pump is much more efficient than a direct heater. However, in reality there are losses that lower its efficiency.

XI. SECOND LAW OF THERMODYNAMICS; CARNOT'S THEOREM

Experience shows that through a thermal contact between two bodies the heat is always transmitted from the hotter body to the colder body, so that their temperatures equilibrate with time. This process cannot go in the opposite direction, although it would not contradict the first law of termodynamics, the energy conservation. The statement of the impossibility of the heat transfer from the cold to hot reservoir (that is not accompanied by work), or its equivalent forms, constitutes the *second law* of thermodynamics. The consequence of the second law is existence of the *entropy* S, a state function at thermodynamic equilibrium, whose differential is given by

$$dS = \frac{\delta Q}{T}. \tag{72}$$

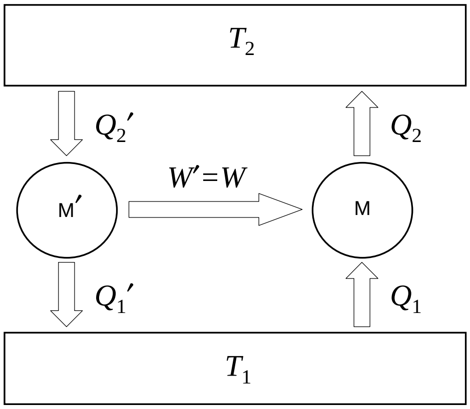

FIG. 4: Coupled engine M′ and Carnot engine M. The former is driving the latter acting as a refrigerator.

S being a state function, it does not change in any reversible cyclic process:

$$\oint \frac{\delta Q}{T} = 0. \tag{73}$$

This result can be checked for particular quasi-static processes, including those of the ideal gas. After one has defined the entropy as a state function, one can look at the change of S in irreversible processes, e.g., processes of relaxation, just comparing the entropies of the initial and final states. It turns out and will be discussed below, as the result of irreversibility the entropy of the system increases. This happens, in particular, in isolated systems, $\delta Q = 0$ and $\delta W = 0$, that approach equilibrium.

Using the second law of thermodynamics, one can prove the famous Carnot's theorem saying that the efficiency of any reversible heat engine operating between the heat reservoirs with temperatures T_1 and T_2 is equal to the efficiency of Carnot engine $\eta = 1 - T_1/T_2$, while the efficiency of any irreversible heat engine is lower than this. It should be noted that "operating beetween the heat reservoires with T_1 and T_2 is a serious limitation on the heat engine that requires that the heat exchange takes place at constant temperates T_1 and T_2 and thus transition between states with these temperatures must be adiabatic. This excludes other types of cycles, e.g., the cycle in which adiabats are replaced by isochores on which the temperature changes. Effectively, the cycle performed by our "any" reversible heat engine is also a Carnot cycle. The only and a very serious difference with the above is that the working body is arbitrary and not necessary an ideal gas.

To prove Carnot's theorem, one can let a general heat engine M′ drive Carnot machine M acting in reverse (i.e., as a refrigerator), see Fig. 4. Our composite machine does not do any work because $W' = W$, thus the only effect is taking heat $Q_2' - Q_2$ from the hot reservoire and giving the same heat $Q_1' - Q_1$ to the cold reservoire. According to *second law* of thermodynamics, $Q_2' - Q_2 \geq 0$. Now the difference of the efficiencies of the ideal Carnot engine M and our engine M′ becomes

$$\eta' - \eta = \frac{W'}{Q_2'} - \frac{W}{Q_2} = \frac{W}{Q_2'} - \frac{W}{Q_2} = \frac{W\left(Q_2 - Q_2'\right)}{Q_2 Q_2'} \leq 0 \tag{74}$$

that proves Carnot's theorem. In the reversible case no heat flow from the hot to cold reservoir is present and thus $\eta' = \eta$.

Now we rewrite the condition above using Eq. (63) for M′ (arbitrary body) and Eq. (67) for M (ideal gas!). Also we drop primes, as we are going to work with the arbitrary body only, and change the sign in front of Q_1, redefining it in the standard way as the heat received. This yields

$$\eta' - \eta = 1 + \frac{Q_1}{Q_2} - 1 + \frac{T_1}{T_2} = \frac{Q_1}{Q_2} + \frac{T_1}{T_2} \leq 0 \tag{75}$$

or, as $Q_2 > 0$,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0. \tag{76}$$

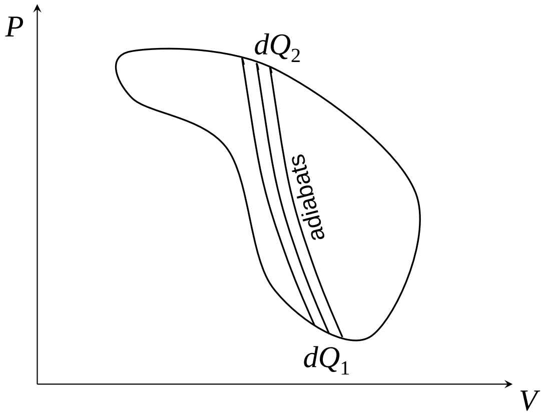

FIG. 5: An arbitrary cycle represented as a series of infinitesimal Carnot cycles.

Next, for an infinitesimally narrow Carnot cycle, made on an arbitrary body, one obtains

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} \leq 0. \tag{77}$$

An infinite number of such Carnot cycles can be used to represent an arbitrary cyclic process with T changing arbitrarily, as the long adiabats cancel each other, see Fig. 5. Thus for an arbitrary reversible cycle one has Eq. (73), that is, there is a state function, entropy, defined by Eq. (72). Then from Eq. (72) follows the important relation

$$\delta Q = T dS. \tag{78}$$

If a cycle includes irreversibility, one obtains

$$\oint \frac{\delta Q}{T} \leq 0, \tag{79}$$

the famous Clausius inequality.

Let us consider the change of entropy in irreversible processes. In nonequilibrium states, the thermodynamic entropy is undefined. If, however, the initial and final states of an irreversible process are equilibrium, the entropy in these states is defined, so one can define the entropy change $\Delta S_{12} = S_2 - S_1$. One always can find a reversible process connecting 1 and 2, the so-called *equivalent reversible process*. Both processes can be joined into an irreversible cyclic process for which Eq. (79) applies and takes the form

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_{\text{reversible}}}{T} \leq 0. \tag{80}$$

Since the reversible integral is related to the change of the entropy, one obtains

$$\int_1^2 \frac{\delta Q_{\text{reversible}}}{T} = \Delta S_{12} \geq \int_1^2 \frac{\delta Q}{T}. \tag{81}$$

The differential form of this inequality reads

$$dS \geq \frac{\delta Q}{T}. \tag{82}$$

If the system is isolated, $\delta Q = \delta W = 0$. Still the entropy of the system can increase, $dS \geq 0$, due to the irreversible processes inside the systems, e.g, relaxation to the equilibrium.

To illustrate the entropy increase in processes of approaching equilibruim, consider an isolated system that consists of two subsystems, each of them at internal equilibrium, whereas there is no equilibruim between the subsystems. Assume that the subsystems do not do work on each other and only can exchange heat. An example is two bodies with different temperatures brought in thermal contact with each other. Since both subsystems are at internal equilibrium, Eq. (72) is valid for both. Then for the whole system follows

$$dS = dS_1 + dS_2 = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = \delta Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \tag{83}$$

According to the second law of thermodynamics, the heat flows from the hot to cold body, $T_1 < T_2$ and $\delta Q_1 > 0$. This yields $dS \geq 0$, although the whole system is isolated, $\delta Q = \delta Q_1 + \delta Q_2 = 0$.

XII. FIRST AND SECOND LAWS COMBINED

Inserting Eqs. (17) and (78) into the first law of thermodynamics, Eq. (25), one obtains the so-called *main thermodynamic identity*

$$dU = TdS - PdV. \tag{84}$$

Eq. (84) is a differential of the internal energy as a function of two variables: $U = U(S, V)$. Correspondingly,

$$T = \left(\frac{\partial U}{\partial S} \right)_V, \qquad -P = \left(\frac{\partial U}{\partial V} \right)_S. \tag{85}$$

The subscript S at the derivative means the adiabatic process. As the second mixed derivative $\partial^2 U / (\partial S \partial V)$ does not depend on the order of differentiation, one obtains the relation

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V. \tag{86}$$

Relations of this type in thermodynamics are called Maxwell relations.

An important comment to Eq. (84) is in order. Since the employed expressions for the heat and work are reversible, one could think that Eq. (84) is valid for reversible processes only. In the literature one can find the inequality $dU \leq TdS - PdV,$ where $<$ is said to be realized for irreversible processes where $\delta Q < TdS$. However, for basic systems that are completely described by the minimal set of thermodynamic variables such as P and V, Eq. (84) is exact and it does not rely on the process being reversible. Since all quantities in this equation are state functions, it simply gives a small difference of the internal energy between two close points on the plot S, V. The inequality sigh in $dU \leq TdS - PdV$ can only be achieved if there are irreversible processes in the system such as dissolution, chemical reactions, phase transformations, etc., that are described by additional parameters.

For the basic thermodynamic system, both Eqs. (25) and (84) are exact. There is no contradiction with $\delta Q < TdS$ for irreversible processes, because in these cases one has $\delta W > -PdV$ as well. An example is free expansion of a gas into vacuum, Sec. XII C, where $\delta Q = \delta W = 0$ but $TdS = PdV > 0$. Generally, for irreversible processes one can write

$$\begin{aligned} \delta Q &= \delta Q_{\text{reversible}} + \delta Q_{\text{dissipative}}, \qquad \delta Q_{\text{reversible}} = TdS \\ \delta W &= \delta W_{\text{reversible}} + \delta W_{\text{dissipative}}, \qquad \delta W_{\text{reversible}} = -PdV. \end{aligned} \tag{87}$$

Then from

$$\delta Q + \delta W = \delta Q_{\text{reversible}} + \delta W_{\text{reversible}} = TdS - PdV \tag{88}$$

follows $\delta Q_{\text{dissipative}} + \delta W_{\text{dissipative}} = 0$ and further

$$\delta Q + \delta W_{\text{dissipative}} = TdS. \tag{89}$$

This shows that the dissipative work is equivalent to heat supply. $\delta W_{\text{dissipative}} \geq 0$ restoring the balance in Eq. (82) can always be found in particular irreversible processes described by a single set of thermodynamic quantities. One example is stirring a liquid. Another example is free expansion of the ideal gas, see comment below Eq. (115).

A. Volume dependence of the entropy and internal energy

Let us now derive Eq. (41). Rewriting Eq. (84) in the form

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \tag{90}$$

and using Eq. (33), one can obtain the differential of the entropy as a function of T and V:

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV. \tag{91}$$

Alternatively, this equation could be obtained from Eq. (34) with $\delta Q = TdS$. Eq. (91) implies

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T} \tag{92}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]. \tag{93}$$

The uniqueness of the second mixed derivative of $S(T,V)$ is expressed as

$$\left[\frac{\partial}{\partial V}\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right]_T = \left\{\frac{\partial}{\partial T}\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\right\}_V. \tag{94}$$

Performing differention, one obtains

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V. \tag{95}$$

Taking into account the uniqueness of the mixed second derivative of $U(T,V)$ and siplifying, one arrives at

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{96}$$

that is Eq. (41). For the ideal gas from this formula and the equation of state follows $(\partial U/\partial V)_T = 0$, that is, $U = U(T)$.

With the help of Eq. (41) one can simplify Eq. (93) to

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \tag{97}$$

This is one of the Maxwell relations, Eq. (129), that easily follow from thermodynamic potentials. Using this equation allows to derive Eq. (96) in a short way. From Eq. (84) follows

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \tag{98}$$

Then using Eq. (97) yields Eq. (96).

B. *Thermodynamic coefficients for adiabatic processes

In Sec. V we considered thermodynamic coefficient relating changes of two thermodynamic quantities with the third quantity fixed. In particular, we discussed the isothermal compressibility $\varkappa_T$. If the system is thermally isolated or compression is so fast so that the heat exchange that requires some time is effectively switched off, the compression process is adiabatic. One can define the adiabatic compressibility similarly to Eq. (8),

$$\varkappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S. \tag{99}$$

To express $\varkappa_S$ through exmerimentally measurable quantities, one can use Eq. (7) in which $dT \neq 0$ since T changes in the adiabatic process. To find dT, one can use

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV. \tag{100}$$

Setting $dS = 0$ and inserting Eqs. (92) and (97), one obtains the relation.

$$0 = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV. \tag{101}$$

Combining this with Eq. (7), one obtains

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP - \left(\frac{\partial V}{\partial T}\right)_P \frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V dV \tag{102}$$

or

$$\left[1 + \left(\frac{\partial V}{\partial T}\right)_P \frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V\right] dV = \left(\frac{\partial V}{\partial P}\right)_T dP. \tag{103}$$

This relation can be simplified with the help of Eq. (42) to

$$\gamma dV = \left(\frac{\partial V}{\partial P}\right)_T dP, \tag{104}$$

where $\gamma = C_P/C_V$. Thus the adiabatic compressibility is given by

$$\varkappa_S = \frac{\varkappa_T}{\gamma}. \tag{105}$$

Since $C_P > C_V$ for all substances, $\varkappa_S < \varkappa_T$ is universally valid.

Adiabatic compression is accompanied by temperature increase that is described by the thermodynamic coefficient $(\partial T/\partial P)_S$. Combining Eqs. (101) and (104), one obtains

$$-\frac{C_V}{T} dT = \left(\frac{\partial P}{\partial T}\right)_V \frac{C_V}{C_P} \left(\frac{\partial V}{\partial P}\right)_T dP. \tag{106}$$

This yields

$$\left(\frac{\partial T}{dP}\right)_S = -\frac{T}{C_P} \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T. \tag{107}$$

With the help of Eq. (13) this simplifies to

$$\left(\frac{\partial T}{dP}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P = \frac{VT\beta}{C_P}. \tag{108}$$

For the ideal gas $T\beta = 1$ and this formula gives

$$\left(\frac{\partial T}{dP}\right)_S = \frac{T}{C_P} \frac{\nu R}{P} = \frac{V}{C_P}. \tag{109}$$

On the other hand, the adiabat equation of the ideal gas in the form of Eq. (53) can be rewritten as

$$T = AP^{1-1/\gamma}, \qquad A = \text{const}. \tag{110}$$

Differentiating this equation, one obtains

$$\left(\frac{\partial T}{dP}\right)_S = A\left(1 - \frac{1}{\gamma}\right) P^{-1/\gamma} = \left(1 - \frac{1}{\gamma}\right) \frac{T}{P} = \left(1 - \frac{1}{\gamma}\right) \frac{V}{\nu R}. \tag{111}$$

Using Mayer's equation (39), one can reduce this result to Eq. (109). This is a check of the general formula (108).

C. Entropy of the ideal gas

As was proven above, the energy of the ideal gas depends on the temperature only, $U = U(T)$. This dependence can be expressed by Eq. (57) or by Eq. (58) for the perfect gas. In the latter case $C_V = \mathrm{const}$ and Eq. (92) can be integrated over T:

$$S(T, V) = C_V \ln T + f(V), \tag{112}$$

where $F(V)$ is the integration constant in the temperature integration that can depend on V. To define the latter, one can use Eq. (97), that becomes

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T} = \frac{\nu R}{V} \tag{113}$$

for the ideal gas. Inserting $S(T, V)$ above into this equation, one obtains $df/dV = \nu R/V$, an ordinary differential equation. Integration yields $f = \nu R \ln V + S_0$. Then with the help of Eq. (50) one obtains

$$S = C_V \ln T + \nu R \ln V + S_0 = C_V \ln \left(T V^{\gamma-1}\right) + S_0. \tag{114}$$

This formula defines the entropy up to an arbitrary constant S_0. In the adiabatic process of a perfect gas $TV^{\gamma-1} = \mathrm{const}$ and the entropy does not change.

If an ideal gas is freely expanding into vacuum after a wall containing it has been suddenly removed, the gas does not do work and it also does not receive heat. Thus in this process its internal energy is conserved. Since $U = U(T)$ for the ideal gas, its temperature does not change as well. Then the entropy increases due to the increase of the volume. For the perfect gas this is described by Eq. (114).

Free expansion of the perfect gas provides an example of the equivalent reversible process introduced above Eq. (82). For the infinitesimal free expansion Eq. (114) with $T = const$ yields

$$dS = \frac{\nu R}{V} dV = \frac{P dV}{T}. \tag{115}$$

The equivalent reversible process includes the same infinitesimal expansion plus receiving the infinitesimal heat $\delta Q_{\mathrm{reversible}} = T dS = -\delta W_{\mathrm{reversible}} = P dV$ that compensates for the work done by the gas and keeps its internal energy unchanged. On the other hand, for the actual irreversible process of free expansion $\delta Q = 0$ that is in accord with Eq. (82). Also for the actual irreversible process $\delta W = \delta W_{\mathrm{reversible}} + \delta W_{\mathrm{dissipative}} = 0$ (dissipative work balances the reversible work) while $\delta W_{\mathrm{dissipative}} = T dS = P dV$, see Eq. (89). Of course, in this case the dissipative work is somewhat formal.

XIII. THIRD LAW OF THERMODYNAMICS

Analyzing experimental data, Nerst has concluded that in the limit $T \to 0$ the entropy becomes a constant independent of other thermodynamic parameters such as volume and pressure,

$$\left(\frac{\partial S}{\partial V}\right)_{T\to 0} = \left(\frac{\partial S}{\partial P}\right)_{T\to 0} = 0. \tag{116}$$

Since in thermodynamics entropy is defined up to a constant, Planck has suggested to define

$$S(T \to 0) = 0. \tag{117}$$

Explanation of these results is possible only within statistical physics. It turms out that statistically defined entropy always satisfies Eq. (116), whereas Eq. (117) holds for most substances. Some materials have a degenerate ground state, and in this case the entropy tends to a finite constant at $T \to 0$.

Let us consider the consequences of the third law. First, integrating Eq. (92) one obtains

$$S = \int_0^T \frac{C_V}{T} dT + S_0. \tag{118}$$

If C_V is finite at $T \to 0$, the entropy logarithmically diverges that contradicts the third law. Thus

$$C_V(T \to 0) = 0. \tag{119}$$

The same condition for C_P can be proven in a similar way. Note that the divergence of the entropy of the ideal gas, Eq. (114), at $T \to 0$ only proves that the concept of the ideal gas breaks down at low temperatures where gases become liquid and solid.

From Eq. (97) follows that the pressure thermal coefficient vanishes at absolute zero:

$$\left.\left(\frac{\partial P}{\partial T}\right)_V\right|_{T\to 0} = 0. \tag{120}$$

From Eq. (133) follows that the thermal expansion coefficient vanishes:

$$\left.\left(\frac{\partial V}{\partial T}\right)_P\right|_{T\to 0} = 0. \tag{121}$$

XIV. THERMODYNAMIC POTENTIALS

Internal energy U expressed via S and V is one of the so-called *thermodynamic potentials*. The differential of a thermodynamic potential yields the first- and second laws of thermodynamics combined. For $U(S,V)$ this is Eq. (84). One can introduce three other thermodynamic potentials making the Legendre transformation with respect to the pairs of variables T,S or P,V.

The enthalpy H is defined by

$$H = U + PV, \tag{122}$$

so that $dH = dU + PdV + VdP$. With the help of Eq. (84) one obtains

$$dH = TdS + VdP. \tag{123}$$

One can see that the enthalpy should be considered as a function of S and P that are its so-called *native variables*. One has

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \qquad V = \left(\frac{\partial H}{\partial P}\right)_S \tag{124}$$

and the Maxwell relation

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{125}$$

The (Helmholtz) free energy F is defined by

$$F = U - TS, \tag{126}$$

so that $dF = dU - TdS - SdT$. With the help of Eq. (84) one obtains

$$dF = -SdT - PdV. \tag{127}$$

The native variables for F are T and V. One has

$$-S = \left(\frac{\partial F}{\partial T}\right)_V, \qquad -P = \left(\frac{\partial F}{\partial V}\right)_T \tag{128}$$

and the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{129}$$

that was already obtained above, Eq. (97).

Finally, the Gibbs free energy is defined by

$$G = U - TS + PV. \tag{130}$$

The differential of G is given by

$$dG=-SdT+VdP, \tag{131}$$

so that $G=G(T,P)$ in native variables. One has

$$-S=\left(\frac{\partial G}{\partial T}\right)_P, \qquad V=\left(\frac{\partial G}{\partial P}\right)_T \tag{132}$$

and the Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T=\left(\frac{\partial V}{\partial T}\right)_P. \tag{133}$$

Thermodynamic potentials are useful because they generate Maxwell relations that can be used to calculate thermodynamic coefficients that is difficult to measure, such as $(\partial S/\partial P)_T$ in Eq. (133). Also one of thermodynamic potentials can be calculated in statistical physics and then all other thermodynamic properties follow from it. For instance, once F has been calculated, one can obtain the entropy from Eq. (128). After that one obtains the internal energy as

$$U=F+TS=F-T\left(\frac{\partial F}{\partial T}\right)_V \tag{134}$$

and the heat capacity as

$$C_V=T\left(\frac{\partial S}{\partial T}\right)_V=-T\left(\frac{\partial^2 F}{\partial T^2}\right)_V. \tag{135}$$

On the other hand, the second of Eqs. (128) yields the equation of state.

For the perfect gas, combining Eqs. (58), (126), and (114) yields

$$F=C_VT+U_0-C_VT\ln\left(TV^{\gamma-1}\right)-TS_0. \tag{136}$$

One can check that Eqs. (134) and (135) yield the familiar results for the perfect gas. On the other hand, from Eq. (128) with the use of Eq. (50) follows the equation of state

$$P=-\left(\frac{\partial F}{\partial V}\right)_T=\frac{C_VT\left(\gamma-1\right)}{V}=\frac{\nu RT}{V}. \tag{137}$$

XV. OPEN SYSTEMS AND CHEMICAL POTENTIAL

In the above considerations, the mass of the system was considered as constant and dropped from the arguments of thermodynamic functions. If the system can exchange mass with the environment or there are chemical reactions in the system, the mass or masses of components change and can cause change of other quantities. For instance, if mass is added to the system with a constant volume, the pressure typically increases. In the sequel, we will consider the number of particles N instead of the mass or the number of kilomoles ν. The connection between N and ν has been discussed above, see Eqs. (6) and below. Using N is preferable in statistical physics, while ν is more convenient in chemistry.

With account of mass changes, the internal energy becomes a function of three variables, $U=U(S,V,N)$, and the main thermodynamic identity, Eq. (84), should be modified as follows:

$$dU=TdS-PdV+\mu dN. \tag{138}$$

Here

$$\mu=\left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{139}$$

is the chemical potential per particle. One can also use chemical potential per kilomole by writing $\mu d\nu$ in Eq. (138). For a multicomponent system such as a mixture of different gases described by numbers of particles N_i, one has to replace $\mu dN\Rightarrow\sum_i\mu_i dN_i$.

Eq. (139) looks nontrivial since special care should be taken to keep entropy constant while adding particles to the system. However, one can find a simpler representation for the chemical potential using the scaling argument. Since all arguments in $U(S,V,N)$ are extensive quantities, multiplying them all by a parameter λ means simply increasing the whole system by λ that leads to the increase of U by λ. Mathematically, for any function f this property can be expressed in the form

$$\lambda f\left(x,y,z\right)=f\left(\lambda x,\lambda y,\lambda z\right). \tag{140}$$

Differentiating this equation with respect to λ and then setting $\lambda \Rightarrow 1$ results in the Euler's theorem

$$f=x\frac{\partial f}{\partial x}+y\frac{\partial f}{\partial y}+z\frac{\partial f}{\partial z}. \tag{141}$$

For $U(S,V,N)$ the partial derivatives here are coefficients in Eq. (138), so that one obtains

$$U=TS-PV+\mu N. \tag{142}$$

Using the definition of the Gibbs free energy, Eq. (130), one can rewrite this relation in the form

$$G=\mu N. \tag{143}$$

That is, the chemical potential is the Gibbs free energy per particle.

For open systems, the differentials of thermodynamic potentials, Eqs. (123), (127), and (131), are modified as follows:

$$\begin{aligned} dH &= TdS+VdP+\mu dN && (144)\\ dF &= -SdT-PdV+\mu dN && (145)\\ dG &= -SdT+VdP+\mu dN. && (146) \end{aligned}$$

From Eq. (143) follows

$$dG=\mu dN+Nd\mu \tag{147}$$

that, combined with Eq. (146), yields

$$SdT-VdP+Nd\mu=0, \tag{148}$$

the Gibbs-Duhem equation.

A. *The Ω-potential

Another thermodynamic potential for open systems is the Ω-potential that is sometimes convenient in statistical physics. Ω-potential is defined by

$$\Omega=-PV=F-G \tag{149}$$

expressed in terms of T, V, and μ as native variables. To obtain its differential, one can combine Eqs. (145) and (147) that yields

$$d\Omega=-SdT-PdV-Nd\mu. \tag{150}$$

This formula implies

$$S=-\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu},\qquad P=-\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}=-\frac{\Omega}{V},\qquad N=-\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \tag{151}$$

If Ω is found, other thermodynamic potentials can be obtained from it. From Eq. (143) follows

$$G=-\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \tag{152}$$

Then from Eq. (149) one obtains

$$F=\Omega-\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \tag{153}$$

For the internal energy from $U=F+TS$ one obtains

$$U=\Omega-\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}-T\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}. \tag{154}$$

Finally, from $H=U+PV=U-\Omega$ follows

$$H=-\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}-T\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}. \tag{155}$$

XVI. ENTROPY MAXIMUM, THERMODYNAMIC EQUILIBRIUM, PHASE TRANSITIONS

A. Heat exchange

When two bodies with temperatures T_1 and T_2 are brought in thermal contact, the heat flows from the hot body to the cold body, so that the temperatures equilibrate. This is the second law of thermodynamics that follows from experiments. It was shown above, see Eq. (83), that the total entropy $S=S_1+S_2$ in the process of equilibration (i.e., relaxation) increases. When the equilibrium is reached, S should attain its maximal value. Investigating the behavior of the total entropy near its maximum is the subject of this chapter.

Consider first the simplest case in which the two bodies do not exchange mass and keep their volumes unchanged. Then the transferred heat is the only source of the energy change, $dU_1=\delta Q_1$ and $dU_2=\delta Q_2$. Since the system of two bodies is isolated from the rest of the world, $\delta Q_1+\delta Q_2=0$ anf thus $dU_1+dU_2=0$. The corresponding changes of the entropies up to the second order in the transferred energy are given by

$$dS_1=\left(\frac{\partial S_1}{\partial U_1}\right)_V dU_1+\frac{1}{2}\left(\frac{\partial^2 S_1}{\partial U_1^2}\right)_V (dU_1)^2 \tag{156}$$

and similarly for dS_2. For the defivatives one has

$$\begin{aligned}\left(\frac{\partial S}{\partial U}\right)_V &= \frac{1}{T}\\ \left(\frac{\partial^2 S}{\partial U^2}\right)_V &= -\frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_V=-\frac{1}{T^2C_V}.\end{aligned} \tag{157}$$

Eliminating $dU_2=-dU_1$ one obtains

$$dS=dS_1+dS_2=\left(\frac{1}{T_1}-\frac{1}{T_2}\right)dU_1-\frac{1}{2}\left(\frac{1}{T_1^2C_{V1}}+\frac{1}{T_2^2C_{V2}}\right)(dU_1)^2. \tag{158}$$

One can see that the extremum of S corresponds to $T_1=T_2$, the thermal equilibrium. The quadratic term in this formula shows that this extremum is a maximum, provided the heat capacicies are positive,

$$C_V>0. \tag{159}$$

The latter is the condition of thermodynamic stability. The state with $C_V<0$ would be unstable as the heat flow from the hot to cold body would lead to the increase of the differences of their temperatures instead of equilibration. The initial state with $T_1=T_2$ would be unstable with respect to the transfer of a small amount of energy between them as a result of a fluctuation that would lead to an avalanch-like further transfer of energy in the same direction since the temperature on the receiving side would decrease. As $C_P>C_V$, one concludes that C_P is also positive. Eq. (159) complements the condition of mechanical stability, Eq. (9).

At equilibrium, $T_1=T_2=T$, Eq. (158) becomes

$$dS=-\frac{1}{2T^2}\left(\frac{1}{C_{V1}}+\frac{1}{C_{V2}}\right)(dU_1)^2. \tag{160}$$

If the second body is much larger than the first one, it can be considered as a bath. In this case $C_{V2} \gg C_{V1}$ and the second fraction in the above formula can be neglected. Using $dU_1 = C_{V1} dT_1$ and dropping the index 1 for the bathed system, one obtains

$$dS = -\frac{C_V}{2T^2} (dT)^2 . \tag{161}$$

This formula gives the entropy decrease caused by the deviation of the system's temperature by a small amount dT from the bath temperature T.

B. General case of thermodynamic equilibrium

Let us consider now two systems in contact that can exchange energy, volume, and mass. Exchanging volume means that there is a movable membrane between the two bodies so that the bodies can do work on each other. Exchanging mass means that this membrane is penetrable by particles. Resolving Eq. (138) for dS one obtains, to the first order,

$$dS_1 = \frac{1}{T_1} dU_1 + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \tag{162}$$

and a similar expression for dS_2. Here one could include second-order terms like those in Eq. (156) to find extended conditions of stability. Using the constraints

$$dU_1 + dU_2 = 0, \qquad dV_1 + dV_2 = 0, \qquad dN_1 + dN_2 = 0, \tag{163}$$

one obtains for the total entropy change

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 . \tag{164}$$

Carnot's theorem proves that from the experimental fact (or postulate) of the heat flow from the hot to cold body follows that the entropy of an isolated system can only increase. This statement turns out to be more general than the initial observation. Indeed, the entropy increases also in the case of free expansion of a gas, see Eq. (115). Here the numbers of gas molecules in different regions of space equilibrate rather than temperature. The law of the entropy increase mandates now that the free expansion process goes in the direction of expansion and not in the the direction of compression. A noteworthy thing is that we do not have to adopt the irreversibility of the free expansion as an additional postulate because it already follows from the existing postulate of the temperature equilibration. Thus we require that $dS \geq 0$ in Eq. (164). This has three consequences:
(i) The energy flows from the hotter body to the colder body;
(ii) The body with a higher pressure expands at the expence of the body with lower pressure;
(iii) The particles diffuse from the body with a higher chemical potential μ to that with the lower μ.
The thermodynamic equilibrium is characterized by

$$T_1 = T_2, \qquad \text{(thermal equilibrium)} \tag{165}$$
$$P_1 = P_2, \qquad \text{(mechanical equilibrium)} \tag{166}$$
$$\mu_1 = \mu_2, \qquad \text{(diffusive equilibrium).} \tag{167}$$

Next, the total entropy should have a maximum with respect to all three variables at the equilibrium. Investigating this requires adding second-order terms to Eq. (164) as was done in the case of the pure heat exchange in the previous section. The analysis is somewhat cumbersome but the results can be figured out. First, the condition of thermal stability, Eq. (159), should be satisfied. Second, the condition of mechanical stability, Eq. (9), should be satisfied. Third, the diffusive stability condition should exist to the effect that adding particles to the system at constant volume and internal energy should increase its chemical potential. This condition has yet to be worked out but one can expect that it follows from the other two conditions, that is, it is not the third independent condition.

C. Phase transitions

The results for the diffusive equilibrium in the preceding section can be applied to phase transitions. If different phases of the same substance, such as solid, liquid, and gas, are in contact, particles can migrate from one phase to the other across the phase boundary. In this case the phase with a higher chemical potential recedes and the phase with a lower chemical potential grows. The phase boundary moves across the sample until the receding phase disappears completely. In basic thermodynamic systems the chemical potentials of the phases μ_i depend on P and T, so that for a given set P, T the phase with lowest chemical potential will be realized. Transitions between the phases occur at $\mu_i(P,T) = \mu_j(P,T)$ that describes lines in the P, T diagram. Phase transitions of this kind are called *first-order* phase transitions. In the first-order phase transitions, phases are labeled by discrete variables i, such as 1 for solid, 2 for liquid, and 3 for a gas.

Another kind of phase transitions are *second-order* phase transitions. In the second-order phase transitions, phases are described by the so-called order parameter (say, η) that is zero in one of the phases and nonzero in the other phase. Most of the second-order transitions are controlled by the temperature, and $\eta = 0$ in the high-temperature (symmetric) phase. As the temperature is lowered across the phase transition point T_c, the order parameter continuously grows from zero, usually as $\eta \propto (T_c - T)^\beta$ with a *critical index* $\beta > 0$ close to T_c. The temperature dependence of the order parameter and other thermodynamic quantities is *singular* at T_c, unlike the situation in first-order transitions. An example of a second-order transition is ferromagnetic ordering below the Curie point T_C in iron and other ferromagnetic materials.

Phase transformation in second-order phase transitions can be formally considered in the same way as above. If one obtains the chemical potential in the form $\mu(\eta)$, one can consider boundaries between regions with different values of η and thus of μ. Then the particles will migrate from the phase with the higher μ to that with the lower μ, so that the spatial boundary between the phases will move until the equilibrium state with the lowest μ is established. Moreover, since η can change continuously, η can adjust in the uniform way without any phase boundaries in the whole system, decreasing its chemical potential everywhere. In isolated systems the number of particles is conserved, so that the minimum of μ implies a minimum of the Gibbs potential G, see Eq. (143). If pressure and volume are irrelevant in the problem, such as in the case of magnetism, G is the same as the free energy F, so this is F that has to be minimized with respect ot the order parameter η.

One can suggest a more direct, although somewhat formal, view on aproaching equilibrium, including second-order phase transitions and leading to the same results. As approaching equilibrium is an irreversible process, one has $TdS \geq \delta Q$, the inequality being due to the relaxation of additional variables other than P, V, such as the order parameter η. In this case instead of Eq. (84) one has $dU \leq TdS - PdV$ and thus instead of Eqs. (127) and (131) one has

$$\begin{aligned} dF &\leq -SdT - PdV \\ dG &\leq -SdT + VdP. \end{aligned} \tag{168}$$

We assume that there is no dissipative work that could make these inequalities to equalities, as discussed in Sec. XII. If T and V are kept constant, relaxation in the system leads to decrease of the free energy F that reaches its minimum at equilibruim. If T and P are kept constant, the same is valid for the Gibbs free energy G. Practically, if one finds F (or G) as a function of the order parameter η, one can determine the equilibrium value of η from

$$\partial F(\eta)/\partial\eta = 0. \tag{169}$$

An example of this scheme is a mean-field theory of ferromagnetism considered below in the statistical mechanics.