

Supplement

*Appendix: Physical background*¹

The aim of this section is to describe with detail the preliminaries on Statistical Mechanics needed to explain the Boltzmann distribution and its derivation. These studies help to understand the way a physical system at a given time t found “out of equilibrium” approaches “equilibrium state” with time.

• The Statistical Basis of Thermodynamics

In order to provide us some ground for a statistical interpretation of thermodynamics, general considerations regarding the statistical nature of the macroscopic system shall be introduced. We will be considering that the system under study is on state of equilibrium, unless otherwise stated.

i) *Macroscopic and microscopic states*

The macrostate of the given system is defined by parameters N , V and E : under the following frame: the system formed by N identical particles enclosed in volume V . We consider the case where N is of order 10^{23} , which carries us into the thermodynamic limit of the system with both N and V infinite where particle density $n = \frac{N}{V}$ remains fixed at a preassigned value. Within the thermodynamic limit, we may define extensive and intensive properties of the system. The extensive ones are directly proportional to the size of the system, thus proportional to N or to V . On the contrary, the intensive ones remain independent.

We consider the case where the i -particles composing the system are independent as they do not interact with each other, with n_i particles with individual energy ε_i . The total energy E of the system is the sum of the individual particles:

$$E = \sum_i n_i \varepsilon_i \quad \text{given} \quad N = \sum_i n_i \quad (1)$$

In agreement with quantum mechanics, individual energies ε_i are discrete and their values depend on the volume V the particles are confined. Therefore, the possible values of the total energy E are also discrete. Nevertheless, for the case in which container V is large and thus the spacing of the different energy values is so small compared to the total energy of the system, E might be considered a continuous variable.

¹Sources: Kittel (1969), Ortin *et al.* (2006) and Pathria RK (1996).

The macrostate of the given system (N, V, E) can be realized in a large number of different ways, which implies that at a molecular level many possibilities exist. For the particular case of non-interacting particles, by means of expressions in (1), there will be a large number of different ways in which the total energy E of the system can be distributed among the N particles constituting it. Each of these different ways define a microstate of the given system. We assume by means of the “equal a priori probabilities” postulate for all microstates that the system is equally likely to be in any one of these microstates at any time t with a given macrostate.

$\Omega(N, V, E)$ symbolizes the number of all possible microstates, as a function of N , V and E . The dependence on V is due to the reason that possible values ε_i of the individual particle energy ε are a function of V by the nature of the system, such as the relativistic distinction of the system which has an impact on the physical dimensions of the container that appear in the boundary conditions imposed on the wave functions of the system.²

Regarding the evaluation of the number Ω , we shall explicitly assume the particles to be distinguishable, so that if a particle in state “ i ” gets interchanged with a particle in state “ j ” the resulting microstate is counted as distinct.

Complete thermodynamics of the given system can be derived from the number Ω , and from its dependence on the parameters N , V and E . First we are going to discuss how this number Ω relates to thermodynamic quantities by bringing out the true nature of the number Ω so that we can carry out further derivations from it. That way, we can then discuss the ways in which the number $\Omega(N, V, E)$ can be computed.

ii) *Physical significance of the number $\Omega(N, V, E)$: “thermal contact” problem between two physical systems.*

We consider physical systems A_1 and A_2 separately in equilibrium. A_i (for $i = 1, 2$) system with macrostate (N_i, V_i, E_i) and $\Omega_i(N_i, V_i, E_i)$ possible

²The explicit dependence of the number $\Omega(N, V, E)$ on V and thus to the equation of state of all classical systems of non-interacting particles must be remarked. If there is no spatial correlation between the particles, the number of ways in which the N particles can be spatially distributed in the system will equal to the product of the numbers of ways in which the individual particles can be accommodated in the same space independently of one another. Thus the probability of any particle to be found in a particular region of the available space is completely independent of the location of the rest of them. This will only be true when the mutual interactions among particles are negligible, and the quantum effects are negligible. With N and E fixed, each of these numbers will be directly proportional to V , the container’s volume. Therefore, the total number of ways will be directly proportional to the N -th power of V .

microstates. The two systems are brought into thermal contact with each other. The wall that separates them is rigid (constant volumes V_i), impenetrable (fixed particle number N_i) and conducting so systems are able to exchange energy between the two. Energy of interaction between systems is neglected. The composite system ($A^{(0)} \equiv A_1 + A_2$) has energy $E^{(0)}$:

$$E^{(0)} \equiv E_1 + E_2 = \text{constant} \quad (2)$$

Given *Postulate 1*, sub-system A_i is equally likely to be in any one of the $\Omega_i(E_i)$ microstates at any time t . Therefore, the composite system $A^{(0)}$ is equally likely to be in any one of the $\Omega^{(0)}(E_1, E_2)$ microstates. By means of the restriction condition (2), it is easy to see the number $\Omega^{(0)}$ varies with E_1 .

$$\Omega^{(0)}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1) \cdot \Omega_2(E(0) - E_1) = \Omega^{(0)}(E_0, E_1) \quad (3)$$

The aim is to calculate the value of the variable E_1 at which the composite system $A^{(0)}$ will be in equilibrium. That is, to calculate the energy exchange for the sub-systems A_1 and A_2 to be in mutual equilibrium. Mathematically, it is the value that maximizes the number $\Omega^{(0)}(E_0, E_1)$.

When a physical system is left to itself, its natural behavior is to increase the number of microstates progressively until it finally settles down in a microstate that handles the largest possible number of microstates. Within the statistical frame, we seek for a macrostate with a larger number of microstates as the most probable one. In general, the number of microstates belonging to any macrostate that differs even slightly from the most probable macrostate, is “orders of magnitude” smaller than the number of microstates belonging to the latter. Hence, the most probable state of a system is the state in which the system spends the most of its time: the equilibrium state of the system.

Let us define \bar{E}_1 as the equilibrium values for E_i . Regarding (2) and (3), we maximize $\Omega^{(0)}$:

$$\Omega_2(E_2) \cdot \left(\frac{\partial \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\bar{E}_1} + \Omega_1(E_1) \frac{\partial E_2}{\partial E_1} \cdot \left(\frac{\partial \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\bar{E}_2} = 0 \quad (4a)$$

while from (2),

$$\frac{\partial E_2}{\partial E_1} = -1 \quad (4b)$$

We substitute (4b) into (4a),

$$\frac{1}{\Omega_1(E_1)} \cdot \left(\frac{\partial \Omega_1(E_1)}{\partial E_1} \right)_{E_1=\bar{E}_1} = \frac{1}{\Omega_2(E_2)} \cdot \left(\frac{\partial \Omega_2(E_2)}{\partial E_2} \right)_{E_2=\bar{E}_2} \quad (4c)$$

and now rearrange considering the derivative of the logarithm, we finally obtain,

$$\left[\frac{\partial (\ln \Omega_1(E_1))}{\partial E_1} \right]_{E_1=\bar{E}_1} = \left[\frac{\partial (\ln \Omega_2(E_2))}{\partial E_2} \right]_{E_2=\bar{E}_2} \quad (4d)$$

Parameter β is defined as,

$$\beta = \left[\frac{\partial (\ln \Omega(N, V, E))}{\partial E} \right]_{N, V, E=\bar{E}} \quad (5)$$

By relating equations (4d) and (5) we might conclude that the equality of the parameters β_1 and β_2 simplifies as equilibrium condition for sub-systems A_1 and A_2 respectively.

Thus when two physical systems are brought into thermal contact allowing energy exchange between them, the energy exchange happens and goes on until the equilibrium values E_1 and E_2 of the variables E_1 and E_2 are reached. Net exchange of energy between the two sub-systems ends once E_i equilibrium values are reached (so $\beta_1 = \beta_2$) and that is when the system happens to have achieved the state of mutual equilibrium³. We call up thermodynamic entropy S of the system

$$\left(\frac{\partial S}{\partial E} \right) = \frac{1}{T} \quad (6)$$

Equations (5) and (6) can be transformed as

$$\left(\frac{\partial S}{\partial E} \right) = \frac{1}{T} \longrightarrow \Delta S = \frac{1}{T} \text{ and } \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N, V, \bar{E}} = \beta \longrightarrow \Delta \ln \Omega = \beta \quad (7)$$

Quotient between them leads us to

$$\frac{\Delta S}{\Delta \ln \Omega} = \frac{\frac{1}{T}}{\beta} = \frac{1}{\beta T} = \text{constant} \quad (8)$$

From which it is concluded there is a relation between thermodynamic quantity S and statistical quantity Ω such as

$$S = k \ln \Omega \quad (9)$$

³As an analogy to this result we may find the “zero law of thermodynamics”, which stipulates the existence of a common parameter T for two or more physical systems in mutual equilibrium, so we somehow expect that the parameter β is somehow related to the thermodynamic temperature T of a given system.

that determines the absolute value of the entropy of a given physical system as a function of the total number of accessible microstates to it in conformity with a given macrostate. Relation in (9) is of extreme importance for the fact that establishes the link between the microscopic and the macroscopic. The “unique configuration” is the state with entropy zero as there only one microstate accessible ($\Omega = 1$). Also, the entropy of a system may be defined as a measure of the disorder or chaos dominating in the system, thus relation (9) can be interpreted as the microscopical increase of disorder. The larger the disorder, the larger the number of microstates the system can have. The larger the choice of microstates, the lesser the degree of predictability or the level of order in the system. So the unique state ($\Omega = 1, S = 0$) is where complete order prevails.

By (8) and (9), we write

$$\beta = \frac{1}{kT}, \text{ where } k = k_B \quad (10)$$

where the universal k_B is the Boltzmann constant.

We now examine a more complex exchange between sub-systems A_1 and A_2 , with movable, impenetrable and conducting separating wall. Thus, apart from the exchange of energy, volumes V_1 and V_2 also become variable while the total volume remains constant.

By means of analogous procedure, it is easy to demonstrate how the equilibrium conditions between the A_1 and A_2 are indeed the same as before. Now $\Omega^{(0)}(V^{(0)}, E^{(0)}; V_1, E_1)$ is maximum when

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1} \right)_{N_1, V_1; E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2} \right)_{N_2, V_2; E_2 = \bar{E}_2} \quad (11a)$$

$$\left(\frac{\partial \ln \Omega_1}{\partial V_1} \right)_{N_1, V_1; E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial V_2} \right)_{N_2, V_2; E_2 = \bar{E}_2} \quad (11b)$$

We get two parameters for each subsystem, β_i and η_i which relate again with physical meaning by means of thermodynamics formula

$$dE = TdS - PdV + \mu dN \quad (12)$$

where P is the thermodynamic pressure and μ the chemical potential. This takes us to the new equilibrium conditions,

$$T_1 = T_2 \text{ and } P_1 = P_2 \quad (13)$$

In addition, if we take the exchange between the two sub-systems a step forward, and the wall between them allows variation in all three parameters (energy E , volume V and particles N) the thermodynamic equilibrium conditions are indeed

$$T_1 = T_2, P_1 = P_2 \text{ and } \mu_1 = \mu_2 \quad (14)$$

These conclusions are identical with the ones following from statistical considerations.

Results from above demonstrate how Thermodynamics can be derived from statistics: for macrostate (N, V, E) of a system, the number of all possible microstates $\Omega(N, V, E)$ accessible to the system can be determined related to the entropy of the system $S(N, V, E)$ by means of fundamental formula (9).

• **Elements of the Ensemble Theory: The Canonical Ensemble**

Now that we have gone through the establishment of the relation between thermodynamics and statistics, we pick up the discussion from before: principal goal is the determination of the number $\Omega(N, V, E)$ of distinct microstates accessible to the system in order to then derive complete thermodynamics from these numbers. The calculation of these numbers is quite of a challenge for the majority of physical system. The ensemble theory must be developed in order it provide an alternative approach to the calculation of Ω .

Let us consider a large number of systems, as if they were “mental copies” of the given system at a certain time. The original macrostate outlines these “copies” somehow in all kind of possible microstates. An ensemble is defined as the average behavior of any system in this collection, which is assumed to be identical to the averaged behavior of the given system at a certain time. In the ensemble theory, we may find microcanonical, canonical and grandcanonical ensembles. We are going to study our systems within the canonical ensemble, where the macrostate of the systems is defined as a function of parameters N , V and T .⁴

Given energy levels E_r (independent of the temperature of the system), probability P_r is the probability for a system to be found in one of the states characterized by the energy value E_r in the ensemble at any time t . The dependence of P_r on E_r can be determined in two ways. One consists of studying the statistics of the energy exchange between the system regarded

⁴We choose T and not energy E (as in microcanonical) of a system because in principle energy is variable that can take values between zero and infinity.

in equilibrium with a heat reservoir at a common temperature T . The other one consists in regarding the system as a member of the canonical ensemble (N, V, T) and study the statistics of the process in which the \mathcal{N} identical systems of the ensemble share energy. Within the thermodynamic limit, we expect the final result in either case to be the same. Once probability P_r is determined, the rest easily comes out.

i) *Equilibrium between a system and a heat reservoir*

We consider system A immersed in a very large heat reservoir A' at any time with energy values E_r and E'_r respectively. Composite system $A^{(0)}$ ($\equiv A + A'$) has energy $E^{(0)}$. These systems achieve a state of mutual equilibrium when they have the same temperature T . At any time t , their energies can take values from 0 to $E^{(0)}$, thus restrictive condition becomes

$$E_r + E'_r = E^{(0)} = \text{constant} \quad (15)$$

Due to the fact that reservoir A' is much larger than system A , any $E^{(0)}$ is much larger than any E_r value. In consequence,

$$E^{(0)} \gg E_r \longrightarrow \frac{E_r}{E^{(0)}} \ll 1 \quad (16a)$$

$$\frac{E_r}{E^{(0)}} = \frac{E^{(0)}}{E^{(0)}} - \frac{E'_r}{E^{(0)}} = 1 - \frac{E'_r}{E^{(0)}} \ll 1 \quad (16b)$$

$\Omega'(E'_r)$ represents the large number of states of the reservoir A' compatible with energy value E'_r once the state of system A is specified⁵. Probability grows with the number of states available to the reservoir. From *Postulate 1* the various possible states are equally likely to occur; as a consequence, probability is directly proportional to this number:

$$P_r \propto \Omega'(E'_r) = \Omega'(E^{(0)} - E_r) \quad (17)$$

Given (16b) and (15) we expand the logarithm (for convergence) of (17) around the value $E'_r = E^{(0)}$ so $E_r = 0$:

$$\begin{aligned} \ln \Omega'(E'_r) &= \ln \Omega'(E^{(0)} - E_r) = \\ &= \ln \Omega'(E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial E'} \right)_{E'=E^{(0)}} (E'_r - E^{(0)}) + \dots \simeq \\ &\simeq \text{constant} - \beta' E_r \quad (18) \end{aligned}$$

⁵The prime on the symbol Ω emphasizes the fact that its functional form depends on the nature of reservoir A' .

Note that from definition (5)

$$\beta = \left[\frac{\partial(\ln \Omega(N, V, E))}{\partial E} \right]_{N, V, E=\bar{E}} \longrightarrow \left(\frac{\partial \ln \Omega'}{\partial E'} \right)_{N, V} \equiv \beta' \quad (19)$$

and we recall equilibrium condition along with (10) $\beta' = \beta = \frac{1}{kT}$ to finally get:

$$P_r = C \cdot \exp(-\beta E_r) \quad (20)$$

C is the normalization constant determined so the total number of particles that occupy the accessible levels is N .

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad (21)$$

The sum in the denominator in (21) is for all states accessible to the system A . Note that it does not depend on the physical nature of the reservoir A' at all.

ii) A system in the canonical ensemble

Let us analyze the same situation but from the ensemble point (canonical ensemble (N, V, T)) of view which of course at the thermodynamic limit we expect the final result in either case to be the same.

The process under study consists of \mathcal{N} identical systems of the ensemble (which may be labeled as $1, 2, 3, \dots, \mathcal{N}$) that share a total energy \mathcal{E} . Energy eigenvalues of the systems are represented by E_r ($r = 0, 1, 2, \dots$). $U = \frac{\mathcal{E}}{\mathcal{N}}$ is the average energy per system in the ensemble, and n_r the number of systems which, at any time t , have the energy value E_r . Clearly the set of numbers $\{n_r\}$ satisfy the restrictive conditions

$$\sum_r n_r = \mathcal{N} \text{ and } \sum_r n_r E_r = \mathcal{E} = \mathcal{N}U \quad (22)$$

Any set $\{n_r\}$ that satisfies conditions (22) represents a possible way of distribution of the total energy \mathcal{E} among the \mathcal{N} members of the ensemble. So between those members of the ensemble for which the energy values are different, we may rearrange and get a different state from the original one. This can be realized in a $W\{n_r\}$ different number of ways:

$$W\{n_r\} = \frac{\mathcal{N}!}{n_0!n_1!n_2!\dots} \quad (23)$$

Again, all possible states of the ensemble compatible with restrictive conditions (22) are equally likely to occur. Distribution set $\{n_r\}$ may appear with a frequency directly proportional to number $W\{n_r\}$. The “most probable” mode of distribution $\{n_r^*\}$ is in theory the one for which number W is a maximum. By analogous procedures

$$\ln W = \ln(\mathcal{N}!) - \sum_r \ln(n_r!) \quad (24)$$

Stirling formula⁶ is applied to (24) as the final goal is treated under the thermodynamic limit where $\mathcal{N} \rightarrow \infty$ so values of n_r will also tend to infinitive.

$$\ln W = \mathcal{N} \ln(\mathcal{N}) - \sum_r n_r \ln(n_r) \quad (25)$$

Set $\{n_r\}$ is now transferred to a slightly different set $\{n_r + \delta n_r\}$. So expression (25) becomes

$$\delta(\ln W) = - \sum_r (\ln n_r + 1) \delta n_r \quad (26)$$

As set $\{n_r\}$ is maximal, variation $\delta(\ln W)$ should vanish. In addition, restrictive conditions (22), regarding variations on the set convert into and

$$\sum_r \delta n_r = 0 \text{ and } \sum_r E_r n_r = 0 \quad (27)$$

Altogether by the method of Lagrange multipliers⁷ seeking set $\{n_r^*\}$ is determined by the following condition

$$\sum_r \{ -(\ln n_r^* + 1) - \alpha - \beta E_r \} \cdot \delta n_r = 0 \quad (28)$$

where α and β are the Lagrangian undetermined multipliers that obey conditions (27). The variations δn_r in (26) are completely arbitrary, so the only way to satisfy (28) is that all its coefficients must vanish

$$\ln n_r^* = -(\alpha + 1) - \beta E_r \text{ for all } r \quad (29)$$

In other words,

$$n_r^* = C \cdot \exp -(\beta E_r) \quad (30)$$

⁶Stirling formula: $\ln(n!) \approx n \ln n - n$

⁷The method of Lagrange multipliers, is a strategy for local maximum and minimum of a function subject to equality constraints – we have the case of 2 (multiple and not single) constraints.

where C is an undetermined parameter. For C and β to be determined, we subject (30) to conditions (22), with the final result that

$$\frac{n_r^*}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} = P_r \quad (31)$$

with parameter β as a solution of the equation

$$U = \frac{E}{\mathcal{N}} = \frac{\sum_r E_r \cdot \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad (32)$$

that combining statistical considerations with thermodynamic ones, it comes out that parameter $\beta = \frac{1}{kT}$.

iii) Physical significance of statistical quantities in the canonical ensemble

We now recall some thermodynamic relations involving the Helmholtz free energy $A(= U - TS)$ with the aim of getting information about the various macroscopic properties of the system on the basis of the preceding statistical results. For this,

$$dA = dU - TdS - SdT = -SdT - PdV + \mu dN \quad (33)$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N,V}, \quad T = - \left(\frac{\partial A}{\partial V} \right)_{N,T}, \quad \mu = - \left(\frac{\partial A}{\partial N} \right)_{V,T} \quad (34a)$$

$$U = A + TS = A - T - \left(\frac{\partial A}{\partial T} \right)_{N,T} = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{N,T} = \left[\left(\frac{\partial(A/T)}{\partial(1/T)} \right) \right]_{N,T} \quad (34b)$$

From all these, follows the correspondence between statistical and thermodynamics quantities as

$$\beta = \frac{1}{kT} \text{ and } \ln \left\{ \sum_r \exp(-\beta E_r) \right\} = \frac{A}{kT} \quad (35)$$

where k is indeed the Boltzmann constant. Equations (35) build the most fundamental result of the canonical ensemble theory:

$$A(N, V, T) = -kT \ln Q_n(V, T) \quad (36)$$

where

$$Q_N(V, T) = \sum_r \exp \left(-\frac{E_r}{k_B T} \right) \text{ and } P_r = Q^{-1} \exp(-\beta E_r) \quad (37)$$

which is the partition function of the system. Since $Pr = Q^{-1}exp(-\beta E_r)$ it follows

$$S = -k \langle \ln P_r \rangle \quad \text{since } S = -k \sum_r P_r \ln P_r \quad (38)$$

The importance of this relation is that it shows that the entropy of a physical system is exclusively and completely determined by the probability values P_r (of the system being in different dynamic states accessible to it). From (38), we might conclude that if the system's ground state ($T = 0K$) is unique, then the system can only be found in this particular state and in no other as probability Pr is equal to 1 for this state (and 0 for the rest). This implies that entropy $S = 0$. Thus null entropy and full statistical order go together: complete predictability of the system. As the number of accessible states increases, (more and more of the P_r become nonzero) the entropy of the system increases. As the number of states becomes extremely large, most of the P_r values become exceedingly small (and their logarithms assume larger negative values). The result is that the entropy becomes extremely large along with the high degree of statistical disorder (or unpredictability) in the system.

By application of (38) in the microcanonical ensemble where for each member system of the ensemble we have a group of Ω states, all equally likely to occur. The value of P_r is $\frac{1}{\Omega}$ for each of these states and 0 for the rest. As a consequence, we obtain the main result in the microcanonical ensemble theory:

$$S = -k \left\{ \sum_r \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) \right\} = k \ln \Omega \quad (39)$$

REFERENCES

- Kittel C (1969) *Thermal Physics*. Chapters 2,3,4 and 6. John Wiley & Sons Inc
- Ortin J y JM Sancho Herrero (2006) *Curso de Física Estadística*. Capítulos 1,2,3 y 4. Universitat de Barcelona
- Pathria RK (1996) Chapters 1,2 and 3 *Statistical Mechanics* Butterworth-Heinemann