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# Chapter 3

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# Equilibrium Ensembles

In the previous chapters, we have already advanced the notion of *ensembles*. The concept was introduced by Gibbs in 1902, to make the connection between macroscopic thermodynamics and the theory of statistical mechanics he was developing. Classical Thermodynamics deals with a reduced number of variables at a macroscopic scale, where the physical system is subjected to very coarse probes. Those macroscopic observations are insensitive to 'fine details' related to microscopic properties of matter [1]. Time scales are also very different. While macroscopic measurements can typically vary from milliseconds to seconds, characteristic atomic motion may be of the order of $10^{-15}$ seconds. Gibbs realized that, since we are unable to control microscopic details, a large number of microscopic systems are consistent with the 'coarse' properties which we measure at the macroscopic level. The ensemble is then envisioned as an ideal collection of virtual copies of the system, each of which represents a real state in which the system may be, compatible with macroscopic constraints. After Gibbs' prescription, thermodynamic properties are obtained as averages over the representative ensemble. The ensemble may contain a large number of copies of the system, and ideally, an infinite number in the thermodynamic limit. Quantum mechanically, the ensemble is associated to the density operator, an object which fully incorporates microscopic and classical uncertainties. In the previous chapters, we have reviewed its general properties and discussed its time evolution to the equilibrium state. Average values of physical observables are obtained as traces with the density operator.

In this chapter, we consider stationary ensembles, that is ensembles characteristic of thermal equilibrium, where $\partial\boldsymbol{\rho}/\partial t = 0$. For an isolated system, the equilibrium is attained when all the occupation probabilities of microstates are equal. However, this situation is not general, since a thermodynamical system is not always isolated. Different couplings with the environment will change the accessibility of microstates, thus leading to different equilibrium states. We will study here some schemes, which represent typical cases we often encounter in real systems, but generalizations to other conditions are possible (some are left as exercises to the reader). We use a set of 'extensive' thermodynamics variables that are commonplace in macroscopic physics, say $(N, V, E)$, for the number of particles, volume and energy of the system, respectively. The name 'extensive' means that they are proportional to the amount of matter, that is they are additive for independent subsystems. From the quantum mechanical point of view, only the number of particles and the energy are related to dynamical observables, and this fact makes a difference when defining equilibrium ensembles, as we will discuss later on. The most fundamental stationary ensemble represents an ideally isolated system, where the variables $(N, V, E)$ are all constants. Due to obscure historical reasons, it is called *Microcanonical Ensemble.*

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## 3.1 Microcanonical Ensemble ($NVE$)

This is the representative stationary ensemble for a closed system, which does not exchange energy or particles with the environment, and whose volume is constant. A more appropriate name is $NVE$-ensemble, meaning that the three quantities are constant. Since the energy of a physical system may be quantized, the counting of states as a function of $E$ can be highly discontinuous. Then, in order to smooth the counting, we allow microstates in a 'small' interval of the energy $[E, E + \delta E]$, where $\delta E$ is much smaller than the average energy, but bigger than the spacing of energy levels [3]. It can be shown that, in the thermodynamic limit, the contribution of $\delta E$ can be neglected. This uncertainty in the energy is introduced for convenience, and has nothing to do with the microscopic quantum uncertainty related to the time of observation that we discussed in Section 2.4. Let $\Gamma(E)$ be the total number of microstates contained in $[E, E + \delta E]$. In the stationary case, the density operator commutes with the Hamiltonian, and both operators can be diagonalized by a common base of eigenstates. We use the notation $\{|n>\}$ for this base, with the understanding

$$\mathbf{H}\,|n\rangle = E_n\,|n\rangle \ ,$$

$$\boldsymbol{\rho}\,|n\rangle = P_n\,|n\rangle \ .$$

In equilibrium, all allowed states have the same occupancy probability, and the density operator can be written in the form:

$$\boldsymbol{\rho} = \frac{1}{\Gamma(E)} \sum_{E<E_n<E+\delta E} |n\rangle\,\langle n| \ , \tag{3.1}$$

where the number $\Gamma(E)$ yields the proper normalization. Equivalently, we write:

$$P_n = \begin{cases} \frac{1}{\Gamma(E)} \ , \ \text{for } E < E_n < E + \delta E \ , \\ 0 \ , \ \text{otherwise.} \end{cases} \tag{3.2}$$

The density operator (3.1) is of a mixed form, very similar to (2.11), except that here we only allow microstates whose energy $E_n$ satisfies $E < E_n < E + \delta E$. Their number is $\Gamma(E)$ and they are all equiprobable. We know this type of distribution maximizes the entropy, with the auxiliary condition that $\boldsymbol{\rho}$ is normalized. This is an equivalent way to look at the Microcanonical Ensemble: it is the ensemble for which the entropy $\sigma$ is a maximum, with the proviso that all the allowed states have energy in the interval $[E, E+\delta E]$. Since this is a fundamental fact, we give the demonstration below, in spite that the mathematics is the same than the one we have employed in section 2.3. Write the density operator in the form:

$$\boldsymbol{\rho} = \sum_{E<E_n<E+\delta E} P_n\,|n\rangle\,\langle n| \ ,$$

with the condition

$$Tr\ \boldsymbol{\rho} = \sum_{E<E_n<E+\delta E} P_n = 1\ . \tag{3.3}$$

Then, the von Neumann entropy is given by:

$$\sigma = - \sum_{E<E_n<E+\delta E} P_n\ \ln P_n\ ,$$

and we calculate the variation of $\sigma$ subjected to the condition (3.3). The latter introduces a Lagrange multiplier $\lambda$. We maximize the functional:

$$\delta\left(\sigma + \lambda \sum_{E<E_n<E+\delta E} P_n\right) = - \sum_{E<E_n<E+\delta E} \delta P_n(\ln P_n + 1 - \lambda) = 0\ ,$$

where variations $\delta P_n$ are considered as independent. We obtain:

$$\ln P_n = \lambda - 1 = \mathit{constant}\ \ = \ln P$$

The constant is calculated with the normalization:

$$Tr\ \boldsymbol{\rho} = 1 = \sum_{E<E_n<E+\delta E} P_n = P \sum_{E<E_n<E+\delta E} = P\ \Gamma(E)\ ,$$

leading to $P = 1/\Gamma(E)$, which is exactly our definition of the density operator for the Microcanonical Ensemble. We now calculate the equilibrium entropy for this ensemble:

$$\sigma = -\frac{1}{\Gamma(E)} \sum_{E<E_n<E+\delta E} \ln\left(\frac{1}{\Gamma(E)}\right) = \ln \Gamma(E)\ ,$$

which is the celebrated Boltzmann's relation for the entropy [1]. The quantity $\sigma$ is a number, and association with the thermodynamical entropy requires a physical constant

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[1] Except for the Boltzmann constant, this equation is carved on Boltzmann's gravestone, in the Central Cemetery of Vienna.

with the dimension of entropy. This is the famous Boltzmann's constant $k_B$, whose origin will be discussed later in this chapter. For a macroscopic system, the energy spectrum can usually be considered quasi-continuous, with a smooth density of states $D(E)$. In addition of $\Gamma(E)$, we introduce an auxiliary quantity $\Sigma(E)$, defined as the number of microstates with energy $E_n < E$. We directly verify the relation $\Gamma(E) = \Sigma(E + \delta E) - \Sigma(E)$. Since $\delta E << |E|$, we obtain:

$$\Gamma(E) = \frac{\Sigma(E+\delta E) - \Sigma(E)}{\delta E}\delta E \approx \frac{\partial \Sigma(E)}{\partial E}\delta E = D(E)\delta E \ ,$$

with $D(E) = \partial\Sigma/\partial E$ being the density of states. For most systems in the thermodynamic limit, the rate at which the number of microstates increases with energy is so impressive, that for all practical purposes, the entropy can equivalently be expressed in terms of any of the quantities $\Gamma(E)$, $\Sigma(E)$ or $D(E)$. Differences are of the order of $\ln N$ or smaller, and can be neglected in relation to $N$, when $N \to \infty$ (thermodynamic limit). In terms of the density of states, we have the relations:

$$\begin{aligned} &\Sigma(E) = \textstyle\int_{\varepsilon<E} d\varepsilon \ D(\varepsilon) \ , \\ &\Gamma(E) = \textstyle\int_{\varepsilon<E+\delta E} d\varepsilon \ D(\varepsilon) - \int_{\varepsilon<E} d\varepsilon \ D(\varepsilon) \approx D(E)\delta E \ , \end{aligned}$$

which point at the density of states as being the fundamental quantity. The density of states $D(E)$ is often called the *partition function* of the Microcanonical Ensemble.

B

### 3.1.1 Connection with Thermodynamics

At equilibrium, we identify the thermodynamic entropy $S$ with the von Neumann entropy through

$$S = k_B \sigma = -k_B Tr \left( \boldsymbol{\rho} \ln \boldsymbol{\rho} \right) \ , \tag{3.4}$$

where the link is done with the Boltzmann constant. For the Microcanonical Ensemble, we readily obtain the Boltzmann relation

$$S = k_B \ln \Gamma(E) \ . \tag{3.5}$$

Note that $S$ is a function of $N, V$ and $E$, that is

$$S = S(N, V, E) \ ,$$

which is implicitly contained in relation (3.5). This relation also shows the role of the Boltzmann constant, which is to establish a connection between a macroscopic quantity on left side, with a quantity of microscopic origin on the right. The thermodynamics is developed using the *entropic representation*, where the entropy is used as the thermodynamic potential [1]. Fundamental properties of the entropy are fulfilled in this theoretical scheme. By construction, we know that the Second Law of Thermodynamics is satisfied, since the ensemble is obtained by maximizing the entropy. Also, properties of the density operator $\boldsymbol{\rho}$ warrant the extensive character of $S$, *i.e.* the entropy is additive for two systems which do not interact, as shown in subsection 2.3.1. From the statistical mechanics point of view, the thermodynamics is reduced to counting microstates to get the quantity $\Gamma(E)$. This procedure is extremely simple in principle, but calculation of $\Gamma(E)$ may be very involved in many cases, as we shall see in some examples. Now, we have to interpret rules to calculate changes produced in thermodynamic processes. The Microcanonical Ensemble represents an isolated system, with fixed number of particles, volume and energy. But to generate a thermodynamical process we need to operate over the system removing some of the constraints. For instance, we remove a wall to change the volume, or an adiabatic wall is transformed in diathermal, to allow transfer of heat. In equilibrium thermodynamics, transformations are performed very slowly, we say in a *quasi-static* way, following a sequence of equilibrium states (small non-equilibrium transients between different equilibrium states are not considered, not even represented in the space of thermodynamical parameters) [1]. We assume that the system is microcanonically distributed at all moments, and variations of thermodynamical quantities can be computed using the microcanonical ensemble. For an infinitesimal quasi-static transformation, we have:

$$dS\left(N,V,E\right) = \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial N}dN \ . \tag{3.6}$$

A fundamental postulate of thermodynamics considers the entropy as a 'function of state' or as a thermodynamical potential, meaning that $dS$ in (3.6) is a 'perfect differential', *i.e.* variation of $S$ in the parameter space, does not depend on the trajectory.

A sufficient and necessary condition is given by:

$$\frac{\partial^2 S}{\partial V \partial E} = \frac{\partial^2 S}{\partial E \partial V} \, , \frac{\partial^2 S}{\partial N \partial E} = \frac{\partial^2 S}{\partial E \partial N} \, , \frac{\partial^2 S}{\partial N \partial V} = \frac{\partial^2 S}{\partial V \partial N} \, , \tag{3.7}$$

which are called Maxwell relations. We will elaborate more on this later on. Note that the partial derivatives $\left(\frac{\partial S}{\partial E}, \frac{\partial S}{\partial V}, \frac{\partial S}{\partial N}\right)$ are 'intensive parameters', meaning that they are not additive. They represent the counterpart of the extensive parameters defined earlier. Important definitions are in order:

**Definition 16** *Temperature $T$,*

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_{V,N} \, , \tag{3.8}$$

*where we are employing the usual thermodynamic notation for the partial derivatives.*

When we increase de energy, we increase the availability of states, and the entropy also increases. That means that $T > 0$. However, there are anomalous systems, usually containing frozen degrees of freedom, whose entropy is not a monotonically increasing function of the energy. This case will be discussed in a topic on *Negative Temperature.*

**Definition 17** *Pressure $P$,*

$$P \equiv T \left(\frac{\partial S}{\partial V}\right)_{E,N} \, . \tag{3.9}$$

This parameter is in general positive, since an increase of the volume of the system also implies an increase of availability of states.

**Definition 18** *Chemical potential* $\mu$,

$$\mu \equiv -T \left( \frac{\partial S}{\partial N} \right)_{E,V} . \tag{3.10}$$

We will give a physical interpretation of the chemical potential afterwards. In terms of the parameters so defined, we may write the variation of the entropy as:

$$dS\left(N,V,E\right) = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \ , \tag{3.11}$$

which can be solved for the variation of the energy in the form:

$$dE = TdS - PdV + \mu dN \ . \tag{3.12}$$

If the number of particles is constant, we get:

$$dE = TdS - PdV \ , \tag{3.13}$$

which was called the First Law by the founder fathers of Thermodynamics. It recognizes 'heat' as a form of energy, with the heat absorbed by the system given by $đQ = TdS$, where the symbol $đQ$ means that $Q$ is not a function of state. The other term, $đW = -PdV$ , represents the 'work done on the system', and is not a perfect differential either. However, the total energy $E$ is a function of state, with

$$dE = đQ + đW \ ,$$

and is identified with the thermodynamics internal energy $U$. The relation

$$S = S(N,V,E)$$

is solved for $U$ in the form

$$U = E(S, V, N) \ ,$$

with

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \ , \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \ , \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \ . \tag{3.14}$$

We interpret $\mu dN$ as the change in internal energy when we vary the number of particles, at constant $S$ and $V$. The thermodynamic representation with the internal energy $U$ is equivalent to the entropic one, and the First Law simply states that the total energy is conserved ($U$ is a function of state, or equivalently, is a potential). Relations (3.14) can be considered as alternative definitions of the intensive parameters. In the next subsection, we summarize the above results in a form of a prescription.

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### 3.1.2 Recipe (Microcanonical Ensemble)

Let our physical system be in equilibrium with volume $V$, number of particles $N$ and energy $E$, with $\delta E$ being the uncertainty in the energy. The Hamiltonian $\mathbf{H}$ of the system is known, and in principle, we assume that we can get the full spectrum. To get the thermodynamical properties, we follow the recipe below [4]:

a) from the spectrum, we get the density of states $D(\varepsilon)$, and the associated quantities $\Gamma(\varepsilon)$ and $\Sigma(\varepsilon)$, for $E \leq \varepsilon \leq E + \delta E$. Any of the above quantities can be used to get the entropy in the thermodynamic limit, and we choose the one which is more convenient;

b) we obtain the thermodynamic entropy through one of the expressions:

$$S = \begin{cases} k_B \ln \Sigma(\varepsilon) \ , \\ k_B \ln \Gamma(\varepsilon) \ , \\ k_B \ln D(\varepsilon) \ , \end{cases}$$

where $k_B$ is the Boltzmann constant. The origin of $k_B$ will be settled when discussing the absolute temperature scale and the equation of states of an ideal gas;

c) the internal energy $U = E(S, V, N)$ is obtained solving for $E$ in the equation $S = S(N, V, E)$. The equations of states (3.14) are obtained by deriving the potential $U$;

d) other thermodynamical potentials are obtained straightforwardly from the internal energy $U$. ■

EXP **Example 1**

**Ideal Gas model**

The ideal gas is a theoretical model which asymptotically accounts for the properties of real gases at the diluted limit, where particle-particle interactions are neglected. The model is then composed of free particles that collide elastically, but with a very large mean free path. Those properties are believed to be universal at sufficiently high temperatures and low densities. To study the model, we consider free particles enclosed in a cubic box of volume $V = L^3$. We first analyze the single particle case. We assume periodic boundary conditions for the wave function, which is written as a plane wave with well defined momentum $\overrightarrow{\mathbf{p}}$:

$$\psi_{\mathbf{p}}(\mathbf{x}) = \frac{1}{\sqrt{V}} \exp\left(\frac{i}{\hbar}\overrightarrow{\mathbf{p}} \cdot \overrightarrow{\mathbf{x}}\right) \ . \tag{3.15}$$

In (3.15), $\psi$ is normalized to the volume of the sample. Since the system is of finite size, the momentum is quantized, and periodic boundary conditions yield

$$p_j = \hbar \left(\frac{2\pi}{L}\right) \nu_j \quad ,$$

where $\nu_j$ is a number, $\nu_j = 0, \pm 1, \pm 2, ..., \pm\infty$. Boundary conditions are not essential when we study bulk properties in the thermodynamic limit, and periodic boundary conditions are very convenient for counting states, as we will see in a minute. The characteristic volume of a single state in $\overrightarrow{\mathbf{p}}$-space (apart from extra degeneracies) is then given by :

$$\omega = \hbar^3 \left(\frac{2\pi}{L}\right)^3 = \frac{h^3}{V} \ .$$

We calculate the partition function $\Sigma(E)$ for a single particle, which we call $\Sigma_1(E)$:

$$\Sigma_1(E) = \sum_{\vec{\mathbf{p}}} {}' g \ ,$$

where the sign $\sum_{\vec{\mathbf{p}}} {}'$ means that we count all the states with energy $\varepsilon = \vec{\mathbf{p}}^2/2m < E$, and the $g$ factor takes into account degeneracies coming from other degrees of freedom (spin, for example). Now, note that for a large system, as it is the case in the thermodynamic limit, the spectrum is a quasi-continuum. In this case, the counting of states is approximated by an integration over the proper domain in $\vec{\mathbf{p}}$-space, *i.e.* the number of states is proportional to the corresponding $\vec{\mathbf{p}}$-volume. The constant of proportionality is $\omega^{-1} = V\ /h^3$, which is the inverse of the volume of a single state:

$$\sum_{\vec{\mathbf{p}}} {}' \to \left(\frac{L}{h}\right)^3 \int_{\varepsilon<E} d^3p \ .$$

Incidentally, since $L^3 = V = \int_V d^3x$ , the partition function can be written in a very suggestive form:

$$\sum_{\vec{\mathbf{p}}} {}' \to \left(\frac{1}{h}\right)^3 \int_{\varepsilon<E} d^3p \int_V d^3x \ , \tag{3.16}$$

which is the classical prescription given by Gibbs to calculate the partition function as an integral over the phase space [5]. Gibbs also realized that one should divide by a constant to make the integration adimensional (a constant with dimension of an action). With the advent of Quantum Mechanics, we know that the constant is $h$, the Planck constant, which is the minimum volume available for a state in the $xp$-phase space (Uncertainty Principle). Note that the counting given by (3.16) is three dimensional. The above formula can be straightforwardly generalized to arbitrary dimension $n$:

$$\sum{}' \to \int \dots \int \frac{d^n p \; d^n x}{h^n} \; .$$

Let us now calculate explicitly the partition function for a single particle. Given the dispersion relation of a free particle, the relation

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = E \; ,$$

where $m$ is the mass of the particle, represents the surface of a 3-dim sphere in $\overrightarrow{\mathbf{p}}$-space. Integrating for all energies $\varepsilon < E$, means to get the volume of a sphere of radius $\sqrt{2mE}$:

$$\int_{\varepsilon < E} d^3 p = \frac{4\pi}{3}\,(2mE)^{3/2} \, ,$$

yielding

$$\Sigma_1(E) = \frac{4\pi V}{3h^3} g \, (2mE)^{3/2} \; , \tag{3.17}$$

meaning that the number of available states increases with the energy in proportion to $E^{3/2}$. It is interesting to get the density of states for a single particle from (3.17):

$$D_1(E) = \frac{\partial \Sigma(E)}{\partial E} = g\frac{2\pi V}{h^3}\left(2m\right)^{3/2} E^{1/2} \ . \tag{3.18}$$

We now do the counting for the $N-$particle system. The Hamiltonian is

$$\mathbf{H} = \sum_{i=1}^{N} \frac{\overrightarrow{\mathbf{p}}_i^2}{2m} \ ,$$

with all particles having the same mass (identical particles). We renumber the momenta components (in $3-\text{dim}$) :

$$\left(p_1^x, p_1^y, p_1^z, ..., p_N^x, p_N^y, p_N^z\right) = \left(P_1, P_2, ..., P_\nu, ..., P_{3N}\right) \ ,$$

meaning that we are working in a $3N-\text{dim}$ space, with the energy of free particles given by:

$$\varepsilon = \sum_{\nu=1}^{3N} \frac{P_\nu^2}{2m} \ .$$

Calculation of the partition function is readily done:

$$\begin{aligned} \Sigma_N(E) &= \left(\frac{L}{h}\right)^{3N} g^N \int_{\varepsilon<E} d^{3N}P = \left(\frac{1}{h}\right)^{3N} g^N \int d^{3N}x \int_{\varepsilon<E} d^{3N}P = \\ &= \left(\frac{1}{h}\right)^{3N} g^N \ L^{3N}\Omega_{3N} \ , \end{aligned}$$

where $\Omega_{3N}$ is the volume of a sphere of radius $\left(2mE\right)^{1/2}$ in the $3N-$ dim momentum space. One finds

$$\Omega_{3N} = \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)}\left(2mE\right)^{3N/2} \ ,$$

where $\Gamma(x)$ is the Euler Gamma function, and finally we get:

$$\Sigma_N(E) = \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)}\left[gL^3\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right]^N \ . \tag{3.19}$$

With the partition function, we calculate the entropy using the Boltzmann relation

$$S = k_B \ln \Sigma_N(E) \ .$$

When taking the thermodynamic limit, which we represent as $N \to \infty$, we use the Stirling approximation for the factorial:

$$\begin{aligned}\ln\Gamma\left(\frac{3N}{2}+1\right) &\approx \ln\Gamma\left(\frac{3N}{2}\right) \approx \frac{3N}{2}\ln\left(\frac{3N}{2}\right) - \frac{3N}{2} = \\ &= N\ln\left(\frac{3N}{2}\right)^{3/2} - \frac{3N}{2} \ .\end{aligned}$$

Collecting all the terms, we get:

$$S = \frac{3N}{2}k_B + Nk_B \ln\left[gV\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right] . \tag{3.20}$$

The above formula can be solved for the energy:

$$U(S,V,N) = E = \left(\frac{3h^2}{4\pi m}\right)\frac{N}{(gV)^{2/3}}\exp\left(\frac{2S}{3Nk_B}-1\right) ,$$

from where we calculate the intensive parameters. We first get the temperature:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{2U}{3Nk_B} \ ,$$

with the equation of state

$$U = \frac{3}{2} N k_B T \ .$$

For the pressure:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{2}{3V} U = \frac{N k_B T}{V} \ ,$$

yielding the well known equation of state for the ideal gas

$$PV = N k_B T \ .$$

As an illustrative example, let us calculate the entropy using the quantity $\Gamma_N(E) = \delta E \ \left[\frac{\partial \Sigma_N(E)}{\partial E}\right]$. We obtain

$$\Gamma_N(E) = \frac{3N \ \delta E}{2E} \Sigma_N(E) \ ,$$

and the 'new entropy' $\tilde{S} = \ln \Gamma_N(E)$, in the thermodynamic limit, is given by:

$$\tilde{S} = \frac{3N}{2} k_B + N k_B \ln \left[ gV \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + k_B \ln \left( \frac{3N \ \delta E}{2E} \right) ,$$

and clearly the last term can be neglected when $N \to \infty$, resulting $\tilde{S} = S$. Thus we arrive to the conclusion that the width of the allowed range of the energy does not make much difference, whether it is a small $\delta E$ or the whole range $[0, E]$. We realize that this fact is due to the fast rate of increasing of the allowed number of states with the energy [see Eq. (3.19)]. ■

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### 3.1.3 Absolute temperature

The ideal gas model is also important for historical reasons. The concept of the absolute temperature scale and the origin of the Boltzmann constant derive from it. We give below a brief historical account that goes back to the XVII century. Phenomenologically, it was found that all gases comply with Boyle law (1662) at low pressures. It states that

$$\frac{PV}{N} = const.$$

at constant temperature. The value of the constant depends on the temperature scale chosen. Charles (1780) showed that the above ratio is nearly a straight line as a function of temperature, for a wide range of variation. If we use the Celsius or centigrade scale $\Theta$, this straight line can be fitted to the relation

$$PV = NA\left(\Theta + \Theta_0\right) \ , \tag{3.21}$$

where $A$ and $\Theta_0$ are constants. The pressure and the internal energy of the ideal gas go asymptotically to zero for $\Theta \to -\Theta_0$, and this fact led lord Kelvin (1848) to identify this value with the absolute zero temperature, when the motion of molecules has ceased completely. In the Celsius scale, we obtained $\Theta_0 = 273.16$. Kelvin then defined the absolute scale, or Kelvin scale $T$ by

$$T \equiv \Theta + \Theta_0 \ ,$$

and we use letter $K$ for the unit of the scale. In relation (3.21), $N$ stands for the number of molecules, and then $A$ is identical with the Boltzmann constant $k_B$ (Planck, 1900), with value

$$k_B = 8.617332 \times 10^{-5}\ eV \cdot K^{-1}\ .$$

Then, the Boltzmann constant relates absolute temperature with energy. Since $N = \upsilon N_A$, where $\upsilon$ is the number of moles and $N_A$ is the Avogadro number, another way to write the equation of states of an ideal gas is

$$\frac{PV}{\upsilon} = N_A k_B\ T = RT\ ,$$

and the quantity $R \equiv N_A k_B$ is known as the *ideal gas constant.* For more details, we refer the reader to the excellent text by Philip Morse [6]. ■

The above calculation for the free particle already shows that employing the Microcanonical Ensemble may be cumbersome due to the counting of states. Except for a number of few cases, there is little hope that the recipe can be straightforwardly applied to more complex systems. Gibbs already acknowledged the problem, which he circumvented with the introduction of the Canonical Ensemble. But before proceeding in that direction, let us solve another example following the recipe of the Microcanonical Ensemble, just to display the general trends in this type of computation.

EXP **Example 2**

**System of $N$ harmonic oscillators in** $1-\mathrm{dim}$

As in the previous example, we do not consider interactions. The oscillators are trapped in a parabolic potential of infinite height, and the statistical mechanics makes no reference to the volume of the sample (that makes a difference with the free particle case). The Hamiltonian of the system is

$$\mathbf{H} = \sum_{i=1}^{N} \left( \frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 x_i^2 \right),$$

and all the oscillators have the same mass and natural frequency (they are 'identical', more on this later). The spectrum is well known from Quantum Mechanics textbooks, and reads

$$E_N(\nu_{1,}\nu_2, ..., \nu_N) = \frac{N}{2}\hbar\omega + \hbar\omega\left(\nu_1 + \nu_2 + ... + \nu_N\right) \ , \tag{3.22}$$

where $\nu_i = 0, 1, 2, ..., \infty$ is the quantum number of the $i-$th oscillator. However, from (3.22) one notes that the energy of a particular state does not depend on the individual quantum numbers $\nu_i$, but only on the sum of them

$$m = \nu_1 + \nu_2 + ... + \nu_N \ , \qquad (m = 0, 1, 2, ..., \infty) \tag{3.23}$$

in the form

$$E_N(\nu_{1,}\nu_2, ..., \nu_N) = E_N(m) = \frac{N}{2}\hbar\omega + m\hbar\omega \ , \tag{3.24}$$

so we are left with only one quantum number and a big degeneracy $W_N(m)$. To calculate the latter, we have to exercise combinatorial analysis in counting the number of ways an integer $m$ can be decomposed as a sum of $N$ nonnegative integers, as shown in relation (3.23). They are called restricted ordered decompositions or restricted ordered partitions of the integer $m$, because the order of the integers is relevant and all the sequences are counted. This fact means that we distinguish individual oscillators. From the theory of numbers [7], we get the result

$$W_N(m) = \frac{(N+m-1)!}{m!\,(N-1)!} \ , \tag{3.25}$$

and those numbers come from the expansion of the *generating function*

$$\frac{1}{(1-x)^N} = \sum_{m=0}^{\infty} W_N(m)\ x^m \ .$$

An elementary proof of this result will be given afterwards, with the introduction of the Canonical Ensemble, and when establishing inter-relations between ensembles. The numbers given in (3.25) are usually calculated through rather artificial procedures, which are typical of combinatorial analysis [8]. The spectrum given by (3.24) is discrete, and the density of states can readily be obtained as a series of *delta* functions:

$$D_N(E) = \sum_{m=0}^{\infty} W_N(m)\ \delta\left(E - E_N(m)\right)\ , \tag{3.26}$$

where each peak is weighted by its degeneracy. Assume that the energy of the system is around of one of the levels, say $E \approx E_N(M)$, for a given $M$. We calculate the entropy associated with its degeneracy $W_N(M)$. Firstly, note that

$$M = \frac{E}{\hbar\omega} - \frac{N}{2}\ .$$

In the thermodynamic limit, we assume that $N, M \gg 1$, and we use the Stirling approximation for the factorial

$$\begin{aligned} \ln W_N(M) \ &\approx\ (N+M)\ln(N+M) - (N+M) - M\ln M + M - \\ &\quad -N\ln N + N\ . \end{aligned}$$

Now, we introduce a natural adimensional variable

$$\varepsilon \equiv \frac{2E}{N\hbar\omega}\ ,$$

which is the total energy measured in relation to the energy of the ground state, with $1 \leq \varepsilon < +\infty$. One gets:

$$
\begin{aligned}
S &= k_B \ln W_N(M) = \\
&= \frac{N}{2} k_B \varepsilon \ln\left(\frac{\varepsilon+1}{\varepsilon-1}\right) + \frac{N}{2} k_B \ln\left[(\varepsilon+1)(\varepsilon-1)\right] - N k_B \ln 2 \; .
\end{aligned}
\tag{3.27}
$$

We use the entropic representation to get the temperature:

$$
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{k_B}{\hbar\omega} \ln\left(\frac{\varepsilon+1}{\varepsilon-1}\right) . \tag{3.28}
$$

We define for convenience

$$
\beta \equiv \frac{1}{k_B T} \; ,
$$

with dimension inverse of energy. Relation (3.28) is written now as

$$
\beta\hbar\omega = \ln\left(\frac{\varepsilon+1}{\varepsilon-1}\right) \; ,
$$

and this equation can be inverted for the energy in the form

$$
\varepsilon = \coth\left(\frac{\beta\hbar\omega}{2}\right) \; .
$$

Going back to the extensive variable $E$, we can write a more suggestive relation

$$
E = N\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\beta\hbar\omega - 1}\right) \; . \tag{3.29}
$$

When $T \to 0$, $\beta \to +\infty$, and the energy goes to its ground state value, $E \to N\frac{\hbar\omega}{2}$. The classical limit is obtained for $\beta\hbar\omega \approx 0$, which means that the thermal energy is much bigger than the spacing of the quantum levels. From (3.29), one readily obtains

$$E \to E_{class} = N k_B T \ ,$$

which is recognized as the classical result. Now, we show that the inclusion of additional levels in the counting does not modify the above results in the thermodynamic limit ($N \to \infty$). In fact, we have the relation

$$\frac{W_N(M-1)}{W_N(M)} = \frac{M}{N+M-1} \ ,$$

and for $M$ finite, the above ratio vanishes when $N \to \infty$. If we integrate over a finite range of the energy

$$\Gamma(E) = \int_E^{E+\delta E} d\varepsilon \ D_N(\varepsilon) = \sum_{M_0}^{M} W_N(m) \ ,$$

the sum is dominated by the last term with the biggest $m$, in the thermodynamic limit. ■

There is a disturbing detail, when we compare the expressions (3.20) and (3.27) for the entropy. We discover that the entropy of the ideal gas is not extensive, in contrast to the result for the system of harmonic oscillators. We find that the problem comes from a term of the form $N k_B \ln V$ in the model of free particles (remember that the volume is absent for the system of oscillators). Gibbs attributed the result to a wrong counting that did not take into account the identity of particles, *i.e.*, there is an overcounting corresponding to configurations that we cannot distinguish. Gibbs suggested to correct the counting dividing by a factor $N!$, the number of permutations of $N$ identical particles. This correction is known in the literature as the 'Gibbs factor'. If we use the Stirling approximation $\ln N! \approx N \ln N - N$, for large $N$, and combining with the term containing the volume, one obtains:

$$N k_B \ln\left(\frac{V}{N}\right) \ ,$$

which is an extensive quantity. The entropy of the ideal gas now become

$$S = \frac{5N}{2} k_B + N k_B \ln\left[\frac{gV}{N}\left(\frac{4\pi m E}{3h^2 N}\right)^{3/2}\right] \ , \tag{3.30}$$

which is extensive. And why the counting is already correct for the system of oscillators? The Gibbs factor is assumed to correct translational degrees of freedom, and oscillators are localized objects (this is why the volume of the sample is absent in the solution). Translational degrees of freedom will appear when dealing with a 'gas of oscillators', as it is the case of a photon gas. In any case, we will show that the Gibbs factor is an approximation valid near the classical regime. The definite answer to this problem is obtained with the introduction of quantum statistics, when the proper symmetrization of many body quantum states is included in the theory. More on this later. With the above examples, we close this section.