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About the Correlation and Physical Foundation of Thermodynamic and Information Entropy: Γ-Phase Space and the Impact to the Outer World

Pedagogic Research Article

F.B. Rosmej[1,2,3,4]*, V.A. Astapenko[4], V.S. Lisitsa[3,4,5] and V.A. Kurnaev[3]

[1] *Sorbonne Université, Faculty of Science and Engineering, UMR 7605, case 128, 4 Place Jussieu, F-75252 Paris Cedex 05, France*
[2] *LULI, Ecole Polytechnique, CNRS-CEA, Physique Atomique dans les Plasmas Denses - PAPD, Route de Saclay, F-91128 Palaiseau Cedex, France*
[3] *National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Institute of Laser and Plasma Technologies, Plasma Physics Department, Kashirskoe sh. 31, Moscow 115409, Russia*
[4] *Moscow Institute of Physics and Technology - MIPT, Institutskii per. 9, Dolgoprudnyi 141700, Russia*
[5] *National Research Center "Kurchatov Institute", Kurchatov sq.1, Moscow 123182, Russia*
Corresponding author: frank.rosmej@sorbonne-universite.fr

Abstract. Although the term "Entropy S" has been introduced to thermodynamics by Clausius already in the 19th century and Boltzmann's genius relation $S = k_B \ln W$ that relates thermodynamics and statistics dates now back to more than a century, it is still controversially discussed up to present days while it became of increasing interest for the study of atoms and ions in dense and complex environments. The introduction of many different terms like, e.g. thermodynamic entropy, statistical entropy, information entropy, Boltzmann entropy, and many other definitions make it very difficult for students (and also for the non-specialized researcher) to understand, what are the common and different properties. It is the purpose of the present paper, to present an entirely physical approach to entropy and to show, that essentially all different terms and definitions have in fact common basic physical foundations. Based on an approach of statistical mechanics and elementary quantum mechanics we explore the phase space properties of N-particle systems and show, that Boltzmann's logarithmic entropy relation can be derived from physical constraints. Based on these considerations we discover that information is not a separate supplementary quantity but impacts on the outer world in the sense of entropy.

Keywords. Thermodynamics; Statistics; Entropy; Information entropy; Γ-phase space

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I. Introduction

The word “Entropy” is an old Greek artificial word creation (entropia) and means “the possibility to convert something”. The entropy S in units of (Joule/Kelvin) has been introduced by Rudolf Clausius in 1865 [1] in connection with the thermodynamic cycle processes. These cycle processes had been studied before by Sadi Carnot in 1824 [2], son of the French mathematician Lazard Carnot who proposed in 1803 the dissipation of useful energy [3] when he investigated the efficiency of heat engines.

In the framework of traditional thermodynamics that is operating with state functions, entropy can be just considered as a convenient state function that permits to handle more easily certain case studies [4]. According to the first law of thermodynamics, firstly formulated by Robert Mayer in 1842 [5], the energy U of the system is increased by the quantity of heat δQ, absorbed by it and decreased by the external work, δW, performed, i.e. $dU = \delta Q - \delta W$. In an isolated system, the total energy is conserved. The internal energy is a state function, because it does not depend on the path. Mathematically, the internal energy is therefore a total differential and any closed path gives $\oint dU = 0$. On the other hand, the quantities δQ and δW cannot be written as a total differential because in general $\oint dQ \neq 0$ and $\oint dW \neq 0$. We therefore use the differential δQ instead dQ and δW instead dW to indicate that these quantities are not total differentials.

In thermodynamics, entropy (sometimes also called “thermodynamic entropy”) is given by $dS = \delta Q_{\mathrm{rev}}/T$, where δQ_{rev} is the heat exchange for reversible processes [4]. The factor $1/T$ can just be considered as an integrating factor that makes entropy a total differential. The independence from the path can be assured, substituting $\delta W = p \cdot dV$ and the first law of thermodynamics into the expression for the entropy:

$$dS = \frac{dU + pdV}{T}. \tag{I.1}$$

An important step forward in thermodynamics has been achieved by L. Boltzmann with his genius entropy relation [6]:

$$S = k_B \cdot \ln W. \tag{I.2}$$

Here, k_B is the Boltzmann constant and W is the number of microstates for given macroscopic parameters like energy, volume and number of particles. Boltzmann himself never formulated eq. (I.2) for the entropy in this manner, eq. (I.2) was in fact proposed by M. Planck [7]. However, eq. (I.2) was implicitly contained in Boltzmann’s more complex studies. The important point of eq. (I.2) is that it links thermodynamics with statistical physics and since then, entropy became an active field of research up to present days [8–12].

The introduction of many different terms for entropy, like thermodynamic entropy, statistical entropy, Boltzmann entropy, von Neumann entropy, Tsallis entropy, information entropy and others combined with many different definitions and approaches makes it more and more difficult to understand what entropy really is. At the same time, the variational principle applied to entropy and to the free energy in thermodynamic equilibrium has received particular attention in the high-energy high-density community in order to study the impact of a dense complex environments on atoms and ions [13–16]. Some of its related issues, like e.g. the equation of state or fundamental studies of the ionization potential depression of atoms and ions in dense plasmas are controversy discussed up to present days [16–28].

Entropy has received also a "public acceptance" as a measure for disorder while at present many rather inconvenient descriptions of entropy have also appeared in textbooks and it has already been explicitly pronounced [29, 30] that entropy needs clarifications.

It is the purpose of the present paper, to provide a physical approach to the basic principles of entropy and a statistical foundation to some related thermodynamical quantities. Using basic elements of quantum mechanics we show, that Boltzmann's entropy relation can be derived from physical constraints. Moreover, this approach discovers, that information needs to impact on the outer world in order to derive a consistent theory of entropy. It appears that this consistent consideration has resemblance to quantum mechanics and to the impact of quantum mechanical measurements on the system itself.

II. The Statistical Description of a System with External Forces and the Γ-Phase Space Properties

II.1 Hamilton's Equation of Motion and the Phase Space Volume

Let us consider a system, where all N particles are assumed to be identical and each possessing f degrees of freedom. The total degree of freedom of the system is then given by

$$F = f \cdot N. \tag{II.1.1}$$

The system evolution is described by the Hamilton's canonical equations [31–33]:

$$\dot{p}_k = -\frac{\partial H}{\partial q_k}, \tag{II.1.2}$$

$$\dot{q}_k = \frac{\partial H}{\partial p_k}, \tag{II.1.3}$$

where H is the Hamilton function. The q_k's and p_k's denote the generalized space and momentum coordinates of each particle in the system. The index "k" is a running index for the particles and also for the degrees of freedom, i.e. $k = 1 \ldots F$ (e.g. $q_1 = x_1$, $q_2 = y_1$, $q_3 = z_1$, $p_4 = x_2, \ldots$). The system evolution is therefore described by the trajectory of one point in the F-dimensional space, the so-called Γ-phase space. If we assume that the Hamilton function represents the total energy of the system and that external forces are described by the parameter ζ, i.e.

$$E = H(p_k, q_k, \zeta, t) \tag{II.1.4}$$

the system evolution takes place in the Γ-phase space volume that is given by

$$\Omega_\Gamma = \Omega_\Gamma(E,\zeta) = \int \dots \int_{H(p,q,\zeta)\le E} \dots \int dp_1 \dots dp_F dq_1 \dots dq_F . \tag{II.1.5}$$

The system evolution is therefore described by the trajectory of one point that moves exclusively inside the volume Ω_Γ given by eq. (II.1.5).

In order to illuminate the meaning of the multiple phase space integrals, let us obtain an explicit expression for the phase space volume for an ideal monoatomic gas. As the particles are not interacting, the Hamilton function is simply given by

$$H(p,q) = \sum_{k=1}^{N} \frac{1}{2m}\left(p_{k,x}^2 + p_{k,y}^2 + p_{k,z}^2\right) . \tag{II.1.6}$$

The integrals over the generalized coordinates q can easily be performed because the Hamilton function depends only on the generalized momenta:

$$\Omega_\Gamma(E,V,N) = V^N \int_{H(p,q)\le E} dp_1 \dots dp_F . \tag{II.1.7}$$

V is the volume that confines the N particles. The remaining integrals over the generalized impulses can be transformed to an integral over a sphere with radius $R = \sqrt{2mE}$ because

$$\sum_{k=1}^{N}\left(p_{k,x}^2 + p_{k,y}^2 + p_{k,z}^2\right) \le \left(\sqrt{2mE}\right)^2 . \tag{II.1.8}$$

With $dp_1 \dots dp_F = d^3p_1 \dots d^3p_N = d^{3N}p$ we obtain from eq. (II.1.7)

$$\Omega_\Gamma(E,V,N) = V^N \int_{H(p,q)\le E} d^{3N}p . \tag{II.1.9}$$

The remaining integral of eq. (II.1.9) is therefore an integral over a sphere with 3N-dimensions in momentum space. The volume V of a sphere with radius R in γ dimensions is given by

$$V_\gamma(R) = \frac{\pi^{\gamma/2}}{(\gamma/2)!} R^\gamma \tag{II.1.10}$$

from which the differential volume element (the volume of the shell between R and $R+dR$) follows simply by differentiation:

$$dV_\gamma(R) = \frac{\gamma\,\pi^{\gamma/2}}{(\gamma/2)!} R^{\gamma-1} dR . \tag{II.1.11}$$

Substituting eqs. (II.1.8) and (II.1.11) in (II.1.9) we obtain

$$d^{3N}p = \frac{3N\pi^{3N/2}}{(3N/2)!} p^{3N-1} dp = \frac{3N\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2mE}\right)^{3N-1}\left(\frac{m}{\sqrt{2mE}}\right) dE \tag{II.1.12}$$

and therefore

$$dp_1 \dots dp_F = \frac{\pi^{3N/2}}{(3N/2-1)!}(2m)^{3N/2} E^{3N/2-1} dE . \tag{II.1.13}$$

Injecting eq. (II.1.12) and (II.1.13) into eq. (II.1.9) we obtain

$$\begin{aligned}\Omega_\Gamma(E,V,N) &= \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2-1)!}\int_0^E E^{3N/2-1} dE \\ &= \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} E^{3N/2}\end{aligned} \tag{II.1.14}$$

Let us now consider changes of the system evolution due to the external forces (e.g., forces that move a prop inside a cylinder to compress a gas). If the external parameter changes from ζ to $\zeta + d\zeta$ the temporal change of the Hamilton function (and therefore the temporal change of the energy) is given by

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \vec{v}_\Gamma \cdot \mathrm{grad}(H). \tag{II.1.15}$$

Because the generalized velocity in Γ-Phase space is given by

$$\vec{v}_\Gamma = (\dot{q}_1, \ldots \dot{q}_F, \dot{p}_1, \ldots \dot{p}_F) \tag{II.1.16}$$

and

$$\mathrm{grad}(H) = \left\{ \frac{\partial H}{\partial q_1}, \ldots, \frac{\partial H}{\partial q_F}, \frac{\partial H}{\partial p_1}, \ldots, \frac{\partial H}{\partial p_F} \right\} \tag{II.1.17}$$

we obtain with the help of the eqs. (II.1.2)-(II.1.3)

$$\vec{v}_\Gamma \cdot \mathrm{grad}(H) = 0\,. \tag{II.1.18}$$

Substituting eq. (II.1.18) into eq. (II.1.15) we see, that the total temporal change of the Hamilton function due to an external force is only given by the local temporal changes and not by flows over gradients in Γ-phase space:

$$\frac{dH}{dt} = \frac{\partial H}{\partial \zeta}\frac{d\zeta}{dt}. \tag{II.1.19}$$

II.2 Quasi-Stationary Perturbations

If ζ changes during the time τ by the amount $d\zeta$, the change of energy is given by

$$\Delta E = \int_t^{t+\tau} \frac{\partial H}{\partial \zeta}\, \dot{\zeta}\, dt'. \tag{II.2.1}$$

Let us assume that changes in ζ within the time interval τ are small (means $\dot{\zeta}$ is small in eq. (II.2.1)), the derivative can then be approximated by

$$\dot{\zeta} \approx \frac{\Delta\zeta}{\tau} \tag{II.2.2}$$

and Eq. (II.2.1) can then be rewritten as

$$\frac{\Delta E}{\Delta \zeta} \approx \frac{1}{\tau}\int_t^{t+\tau} \frac{\partial H}{\partial \zeta}\, dt'. \tag{II.2.3}$$

The right hand side of eq. (II.2.3) is identical to the time average of $\partial H/\partial\zeta$ over τ:

$$\left\{\frac{\partial H}{\partial \zeta}\right\}_\tau := \frac{1}{\tau}\int_t^{t+\tau} \frac{\partial H}{\partial \zeta}\, dt'. \tag{II.2.4}$$

Combining eqs. (II.2.3) and (II.2.4), we have

$$\Delta E \approx \left\{\frac{\partial H}{\partial \zeta}\right\}_\tau \Delta\zeta\,. \tag{II.2.5}$$

We can now explore more precisely the condition that changes of the Hamiltonian due to ζ-variations are very slowly, i.e., the case of small derivatives $\dot{\zeta}$ in eq. (II.2.1). Let τ_{system} be the time needed for the system to turn to equilibrium after a perturbation. Let us consider

$$\tau_{\text{system}} \ll \tau_{\text{perturb}}\,, \tag{II.2.6}$$

where τ_{perturb} is the time scale of the perturbation. Under condition (II.2.6) the system has always enough time to return to equilibrium after each small change induced by the external forces. Condition (II.2.6) is called the *quasi-stationary* condition. In this case the time average over τ in eq. (II.2.5) is very close to the time average for infinite times (indicated with parenthesis $\{\ldots\}$ sans index) because the system had enough time to turn to equilibrium. Therefore,

$$\left\{\frac{\partial H}{\partial \zeta}\right\}_\tau \approx \lim_{\tau\to\infty}\left\{\frac{1}{\tau}\int_t^{t+\tau}\frac{\partial H}{\partial \zeta}\,dt'\right\} := \left\{\frac{\partial H}{\partial \zeta}\right\}. \tag{II.2.7}$$

The time average on the right hand side of eq. (II.2.7) can then be replaced by the ensemble average(indicated by a bar over the variable $\bar{X}$) according to the ergodic theorem:

$$\left\{\frac{\partial H}{\partial \zeta}\right\} = \overline{\frac{\partial H}{\partial \zeta}}, \tag{II.2.8}$$

where the ensemble average is given by ($\beta = 1/kT$)

$$\overline{\frac{\partial H}{\partial \zeta}} = \frac{\int (\partial H/\partial\zeta)\cdot\exp\left(-\beta\cdot H(p,q)\right)\cdot d\Omega_\Gamma}{\int \exp\left(-\beta\cdot H(p,q)\right)\cdot d\Omega_\Gamma}. \tag{II.2.9}$$

We note, that except a normalization factor, the exponential weight factor in eq. (II.2.9) is equal to the Gibb's canonical distribution function. The ensemble average can likewise be expressed as

$$\overline{\frac{\partial H}{\partial \zeta}} = \frac{\int_E^{E+dE}\frac{\partial H}{\partial \zeta}d\Omega_\Gamma}{\int_E^{E+dE}d\Omega_\Gamma} \tag{II.2.10}$$

because it can be shown (see Appendix I), that almost all volume of the Γ-phase space volume Ω_Γ is contained in a thin shell between E and $E+dE$ and that the most probable distribution function over the radius of this shell is a constant one (Appendix II). Eq. (II.2.10) is called the microcanonical ensemble average. Combining eqs. (II.2.5) and (II.2.7), (II.2.8), we obtain for quasi-static perturbations

$$dE = \overline{\frac{\partial H}{\partial \zeta}}\,d\zeta. \tag{II.2.11}$$

II.3 Deformations of Phase Space Volume due to Quasi-Stationary Perturbations

The total change of the phase space volume is given by

$$d\Omega_\Gamma(E,\zeta) = \frac{\partial\Omega_\Gamma(E,\zeta)}{\partial E}dE + \frac{\partial\Omega_\Gamma(E,\zeta)}{\partial\zeta}d\zeta. \tag{II.3.1}$$

The change of Ω_Γ due to changes in the parameter ζ can be written as

$$\frac{\partial\Omega_\Gamma}{\partial\zeta}d\zeta = \Omega_\Gamma(E,\zeta+d\zeta) - \Omega_\Gamma(E,\zeta), \tag{II.3.2}$$

whereas the change of Ω_Γ due to changes in the energy is given by

$$\frac{\partial\Omega_\Gamma}{\partial E}dE = \Omega_\Gamma(E+dE,\zeta) - \Omega_\Gamma(E,\zeta). \tag{II.3.3}$$

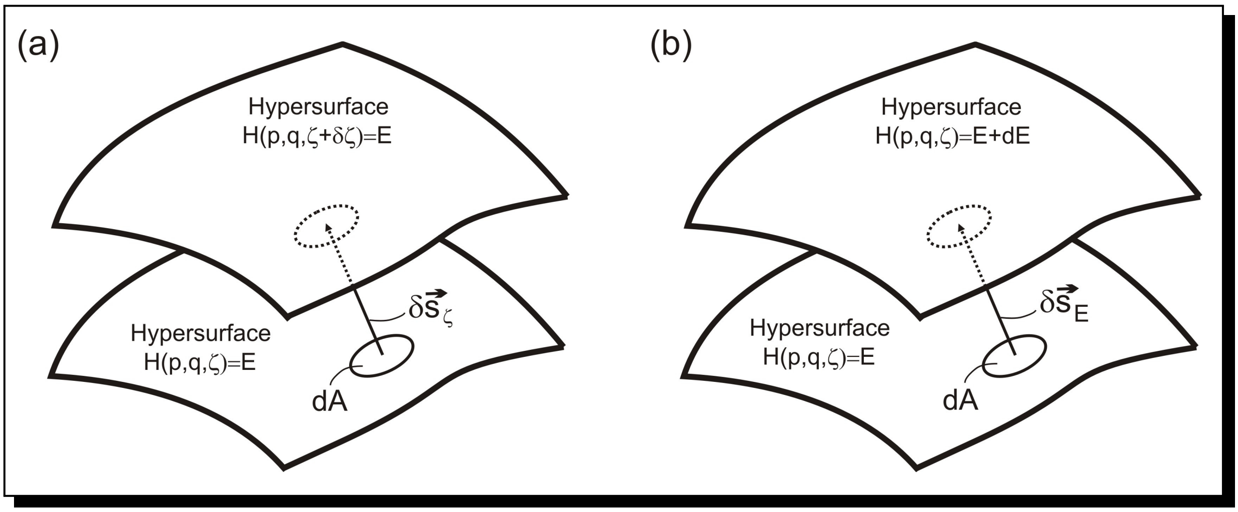

Figure 1. Visualization of the change of the phase space volume due to changes in the parameter ζ (a) and due to changes in energy (b).

The change in the phase space due to the parameter changes in ζ corresponds to the volume that is enclosed by the two hypersurfaces $H(p,q,\zeta)=E$ and $H(p,q,\zeta+\delta\zeta)=E$:

$$\frac{\partial\Omega_\Gamma}{\partial\zeta}\delta\zeta = \int_{H(p,q,\zeta)}^{H(p,q,\zeta+\delta\zeta)} dp_1\ldots dp_F dq_1\ldots dq_F\,. \tag{II.3.4}$$

If dA designates a surface element on the hyper-sphere and $\delta s_\zeta := \left|\delta\vec{s}_\zeta\right|$ the perpendicular distance between these hypersurfaces (see Figure 1a) we have

$$\frac{\partial\Omega_\Gamma}{\partial\zeta}\delta\zeta = \int \delta s_\zeta dA\,. \tag{II.3.5}$$

As grad(H) is a vector parallel to the vector $\delta\vec{s}_\zeta$ (see Figure 1a), we can replace grad$(H)\cdot\delta\vec{s}_\zeta$ by $=|\text{grad}(H)|\cdot\delta s_\zeta$. δs_ζ and grad(H) are therefore related via the total change of the Hamilton function (note that ζ is a parameter in the Γ-phase space and *not* an additional generalized coordinate):

$$dH = \left\{\sum_k \frac{\partial H}{\partial p_k}dp_k + \frac{\partial H}{\partial q_k}dq_k\right\} + \frac{\partial H}{\partial\zeta}\delta\zeta = |\text{grad}(H)|\cdot\delta s_\zeta + \frac{\partial H}{\partial\zeta}\delta\zeta\,. \tag{II.3.6}$$

The changes of dH due to changes in ζ are performed for constant energy (i.e. $dH=0$):

$$\delta s_\zeta = -\frac{\frac{\partial H}{\partial\zeta}\delta\zeta}{|\text{grad}(H)|}\,. \tag{II.3.7}$$

Substituting eq. (II.3.7) into (II.3.5) gives

$$\frac{\partial\Omega_\Gamma}{\partial\zeta}\delta\zeta = -\delta\zeta\int \frac{\partial H}{\partial\zeta}\frac{dA}{|\text{grad}(H)|}\,. \tag{II.3.8}$$

We now consider the change of the phase space volume due to changes in energy:

$$\frac{\partial\Omega_\Gamma}{\partial E}dE = \int_{H(p,q,\zeta)=E}^{H(p,q,\zeta)=E+dE} dp_1\ldots dp_F dq_1\ldots dq_F\,. \tag{II.3.9}$$

As grad(H) is a vector parallel to the vector $\delta\vec{s}_E$(see Figure 1b), we can replace grad$(H)\cdot\delta\vec{s}_E$ by $=|\text{grad}(H)|\cdot\delta s_E$ where $\delta s_E := |\delta\vec{s}_E|$. δs_E and grad(H) are therefore related via the total change of the Hamilton function according:

$$dH = \left\{ \sum_k \frac{\partial H}{\partial p_k} dp_k + \frac{\partial H}{\partial q_k} dq_k \right\} + \frac{\partial H}{\partial \zeta} \delta\zeta = |\text{grad}(H)| \cdot \delta s_E + \frac{\partial H}{\partial \zeta} \delta\zeta. \tag{II.3.10}$$

The changes of dH due to changes in energy are performed for constant ζ (i.e. $\delta\zeta = 0$), therefore

$$\delta s_E = \frac{dE}{|\text{grad}(H)|}. \tag{II.3.11}$$

If dA designates a surface element on the hypersphere and δs_E the perpendicular distance between these hypersurfaces (see Figure 1b) we have

$$\frac{\partial \Omega_\Gamma}{\partial E} dE = \int \delta s_E dA. \tag{II.3.12}$$

Substituting eq. (II.3.11) into eq. (II.3.12) provides

$$\frac{\partial \Omega_\Gamma}{\partial E} dE = dE \cdot \int \frac{dA}{|\text{grad}(H)|} \tag{II.3.13}$$

With eqs. (II.3.8) and (II.3.13) the total change of the phase space volume (eq. (II.3.1)) is given by:

$$d\Omega_\Gamma(E,\zeta) = \left\{ \int \frac{dA}{|\text{grad}(H)|} \right\} \cdot dE - \left\{ \int \frac{\partial H}{\partial \zeta} \frac{dA}{|\text{grad}(H)|} \right\} \cdot \delta\zeta. \tag{II.3.14}$$

Combining eqs. (II.2.5), (II.2.11) and (II.3.14), we find

$$d\Omega_\Gamma(E,\zeta) = 0. \tag{II.3.15}$$

Therefore, the phase space volume remains constant for quasi-stationary changes although the geometrical form of the phase space volume changes in time due to the changes of the external parameter ζ. This is the so-called adiabatic invariance of the Γ-phase space volume.

III. The Physical Meaning of the Γ-Phase Space Volume

III.1 Relation between Γ-Phase Space, Heat δQ and work δW

The above-described properties of the phase space volume Ω_Γ now permit to explore its deep physical meaning. Combining eqs. (II.3.1) and (II.3.8) and solving for the energy, we obtain

$$dE = \frac{d\Omega_\Gamma(E,\zeta)}{\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E}} + \delta\zeta \cdot \frac{\int \frac{\partial H}{\partial \zeta} \frac{dA}{|\text{grad}(H)|}}{\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E}}. \tag{III.1.1}$$

With the help of Figure 1b and eqs. (II.2.10) and(II.3.11) the last term can be transformed to an expression for the ensemble average because the most probable distribution over the spherical shell is constant (Appendix II):

$$\overline{\frac{\partial H}{\partial \zeta}} = \frac{\int_E^{E+dE} \frac{\partial H}{\partial \zeta} d\Omega_\Gamma}{\int_E^{E+dE} d\Omega_\Gamma} = \frac{\int_{\text{surface}} \frac{\partial H}{\partial \zeta} \cdot \delta s_E \cdot dA}{\int_{\text{surface}} \delta s_E \cdot dA} = \frac{\int_{\text{surface}} \frac{\partial H}{\partial \zeta} \cdot \frac{dE \cdot dA}{|\text{grad}(H)|}}{\int_{\text{surface}} \frac{dE \cdot dA}{|\text{grad}(H)|}} = \frac{\int \frac{\partial H}{\partial \zeta} \cdot \frac{dA}{|\text{grad}(H)|}}{\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E}}. \tag{III.1.2}$$

Substituting eq. (III.1.2) into eq. (III.1.1) provides

$$dE = \frac{d\Omega_\Gamma(E,\zeta)}{\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E}} + \delta\zeta \cdot \overline{\frac{\partial H}{\partial \zeta}}. \tag{III.1.3}$$

The last term on the right side of eq. (III.1.3) is the energy change of the system due to the variation of the external parameter, i.e., the work δW done at the system due to the parameter change:

$$\delta W = \overline{\frac{\partial H}{\partial \zeta}} \cdot d\zeta. \tag{III.1.4}$$

In order that eqs. (III.1.3) and (II.1.4) correspond to the 1st law of thermodynamics ($dU = \delta Q + \delta W$), the first term on the right hand side of eq. (III.1.3) must be the heat δQ transferred to the system, i.e.

$$\delta Q = \frac{1}{\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E}} d\Omega_\Gamma(E,\zeta)\,. \tag{III.1.5}$$

III.2 Relation between Γ-Phase Space Volume, the 1st Law of Thermodynamics and Entropy

The physical meaning of the phase space volume itself can now be obtained as follows. Let us combine eq. (III.1.3), (III.1.4):

$$[dE - \delta W]\frac{\partial \Omega_\Gamma(E,\zeta)}{\partial E} = d\Omega_\Gamma(E,\zeta). \tag{III.2.1}$$

Comparing eq. (III.2.1) with the 1st law of thermodynamics, namely

$$[dE - \delta W]\cdot \frac{1}{T} = dS \tag{III.2.2}$$

we might attribute on a basis of a naive identification of terms that the phase space volume $\Omega_\Gamma(E,\zeta)$ corresponds to entropy S because the partial derivative of entropy with respect to energy is equal to the temperature, i.e. $(\partial S/\partial U)_V = 1/T$. It can, however, be seen that this identification of entropy with the phase space volume cannot be correct. In fact, if the number of particles is doubled, the entropy should double too (and in fact also all other thermodynamic potentials). For a large number of particles N we can obtain from eq. (II.1.14) with the help of Stirling's formula $n! \approx \sqrt{2\pi n}\, n^n e^{-n}$ a closed expression for the Γ-phase space volume:

$$\Omega_\Gamma(E,V,N) = V^N \cdot \left(\frac{4\pi\cdot e\cdot m}{3}\cdot\frac{E}{N}\right)^{\frac{3N}{2}} \cdot \frac{1}{\sqrt{2\pi}\cdot\sqrt{3N/2}}. \tag{III.2.3}$$

It can immediately been seen from eq. (III.2.3) that if the number of particles are doubled, the phase space volume grows exponentially with volume V and energy per particle (E/N). Therefore, the phase space volume cannot be identified with the entropy.

In fact, from a mathematical point of view we can multiply eq. (III.2.1) with any function or perform any other operational manipulation (e.g., integrals, derivatives,…). As the phase space volume depends on energy and external parameters ζ any function depending on other variables would not allow to maintain the so-called extensitivity of the entropy (i.e., $\alpha\cdot S(U,V,N) = S(\alpha\cdot U, \alpha\cdot V, \alpha\cdot N)$ for an arbitrary positive constant α). We are therefore left with functions that depend on $\Omega_\Gamma(E,\zeta)$ itself. As the phase space volume (III.2.3) depends exponentially on the number of particles N with respect to volume V and the energy per particle

E/N the only way to assure extensitivity is via a logarithmic functional dependence of the phase space volume and some constants because in the thermodynamic limit E/N is a constant (note, that multiplication with $1/\sqrt{N}$ — last factor in eq. (III.2.3) has a vanishing contribution, as will be shown below). We therefore need to multiply eq. (III.2.1) with $\frac{1}{\Omega_\Gamma}$ to obtain the requested logarithmic derivative of $\Omega_\Gamma(E,\zeta)$. In order to be most general let us multiply eq. (III.2.1) also with some constants, namely a constant k and $\frac{1}{\Omega_0}\cdot\frac{1}{(1/\Omega_0)}$. Ω_0 is a constant phase space volume that ensures a dimensionless quantity in the logarithm:

$$[dE-\delta W]\frac{\partial\Omega_\Gamma(E,\zeta)/\Omega_0}{\partial E}\frac{k}{\Omega_\Gamma(E,\zeta)/\Omega_0}=\frac{k}{\Omega_\Gamma(E,\zeta)/\Omega_0}d\Omega_\Gamma(E,\zeta)/\Omega_0, \tag{III.2.4}$$

$$[dE-\delta W]\frac{\partial(k\ln[\Omega_\Gamma(E,\zeta)/\Omega_0])}{\partial E}=d\,(k\ln[\Omega_\Gamma(E,\zeta)/\Omega_0]). \tag{III.2.5}$$

Eq. (III.2.1) can now be identified with the first law of thermodynamics from eq. (III.2.2). We then need to identify the phase space volume with entropy according (S_0 is an integration constant)

$$S-S_0=k\ln[\Omega_\Gamma(E,\zeta)/\Omega_0] \tag{III.2.6}$$

and the term

$$\frac{\partial(k\ln[\Omega_\Gamma(E,\zeta)/\Omega_0])}{\partial E}=\frac{1}{T} \tag{III.2.7}$$

to temperature. Eq. (III.2.7) indicates that k cannot be arbitrary as it defines the scale for the temperature. In fact, eq. (III.2.7) must corresponds to the thermodynamic relation

$$\left(\frac{\partial S}{\partial E}\right)_V=\frac{1}{T} \tag{III.2.8}$$

and therefore k has to be identified with the Boltzmann constant $k_B=1.38\cdot10^{-23}J/K$.

III.3 Elementary Phase Space Volume Ω_E

At present, the volume Ω_0 has been an arbitrary volume in phase space for eq. (III.2.5). In the framework of classical mechanics, particle location can be performed with infinite precision in geometrical space and simultaneously with infinite precision in velocity space. Therefore, there exist no lower bound for Ω_0 implying that Ω_0 can be even of differential small size in a mathematical sense. In quantum mechanics, however, the Heisenberg uncertainty relation sets a lower limit to the precision for the simultaneous knowledge of the geometrical and momentum coordinates.

The lower limit of the phase space volume can be directly obtained from the Bohr-Sommerfeld quantization condition [34]

$$\frac{1}{2\pi}\oint p\,dq=\left(n+\frac{1}{2}\right)\hbar. \tag{III.3.1}$$

Figure 2 illustrates the relevant phase space volume for one coordinate x and momentum p_x. This implies that we have to attribute to each system point (the “quantum state”, i.e. the "particle" or the "configuration") in the phase space a volume

$$\Omega_E = (2\pi\hbar)^f\ , \tag{III.3.2}$$

where $2f$ is the dimension of the phase space for one particle (i.e. the degrees of freedom). The phase space volume $\Omega_E = (2\pi\hbar)^f$ is therefore the size of the elementary phase space volume for one particle. This result is independent from the coordinate system. From Hamilton's equations of motion $\dot{q}_k = \partial H/\partial p_k$ we derive immediately the dimension of the product of the generalized coordinates: $[q_k p_k] = Js$ because $[H] = J$. Therefore, even in the coordinate free formulation of eq. (III.3.1) we see that the phase space volume has a lower limit that is given by eq. (III.3.2).

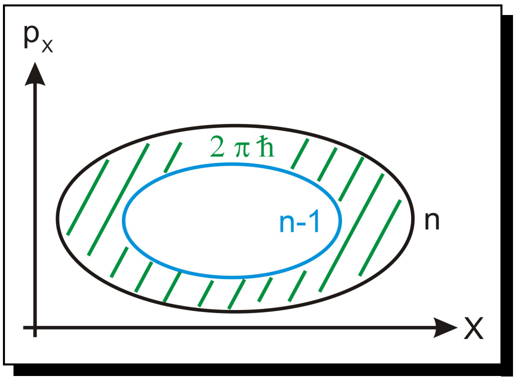

Figure 2. Illustration of the elementary phase space volume $\Omega = 2\pi\hbar$ by means of the Bohr-Sommerfeld quantization condition. The outer phase space volume (black curve) is given by $\oint p_x dx = 2\pi(n+1/2)\hbar$, the inner curve (blue curve) by $\oint p_x dx = 2\pi((n-1)+1/2)\hbar$ and the difference (green color) by $\oint p_x dx - \oint p_x dx = 2\pi\hbar$.

The finiteness of the phase space volume Ω_E permits to reformulate the phase space volume Ω_Γ in eqs. (III.2.6)-(II.2.7) in terms of a number of elementary phase space volumes. Note, that in an entirely classical description, this is impossible, because there exist no elementary phase space volume.

We can likewise introduce to eq. (III.2.5) a normalization volume $\Omega_0 = \Omega_E \cdot N! = (2\pi\hbar)^f \cdot N!$ instead of $\Omega_0 = \Omega_E = (2\pi\hbar)^f$. In this case the entropy according (III.2.6) is expressed in terms of the number of physically different configurations, i.e.

$$S - S_0 = k_B \ln\left[\frac{\Omega_\Gamma(E,\zeta)}{\Omega_E \cdot N!}\right]. \tag{III.3.3}$$

The factor $1/N!$ is known as the Gibbs's correction factor [35] that accounts for the indiscernibility of particles. So far, the identification of the normalization volume as $\Omega_0 = \Omega_E \cdot N!$ is a possible option for eq. (III.2.6). When considering, however, the mixing entropy of gases $\Delta S_{\text{mix}} = (N_A + N_B)\cdot R \cdot \left\{\ln\left(\frac{V_A+V_B}{V_A}\right) + \ln\left(\frac{V_A+V_B}{V_B}\right)\right\}$ (where N_A and N_B are the number of particles A and B, V_A and V_B are their respective volumes), the identification $\Omega_0 = \Omega_E$ leads to a mixing entropy $\Delta S_{\text{mix}} > 0$ even if the two gases are identical, i.e. $A = B$. This makes no sense and is due to the fact, that in classical physics, the particles can be distinguished from each other: therefore, an exchange of particles provides a different configuration. Really, an exchange of particles does not provide a physically different configuration (indistinguishable particles in quantum physics) and therefore the number of different configurations is reduced by a factor of $N!$ which is just the number of possible exchanges between N particles.

The entropy according eq. (III.3.3) permits finally to determine the integration constant for the entropy. At zero temperature, the system takes the lowest energy state. If the degeneracy or the number of quantum states is $g_0 = \Omega_\Gamma(E)/(\Omega_E \cdot N!)$, the entropy is given by

$$S = k_B \ln[g_0] + S_0. \tag{III.3.4}$$

For a pure substance, the presence of quantum states with the same energy is a rather exceptional case. Small field interactions, which are usually neglected, will remove the degeneracy and we have $g_0 = 1$:

$$S = k_B \ln[1] + S_0 \tag{III.3.5}$$

i.e.

$$S = S_0. \tag{III.3.6}$$

As the integration constant $S = S_0$ is independent of energy, volume, pressure, temperature and external parameters (see eqs. (III.2.5) and (II.2.6)) it is the same for all systems and can be set to zero in agreement with the 3$^{\text{rd}}$ law of thermodynamics (Nernst theorem [35]):

$$S_0 = 0. \tag{III.3.7}$$

Therefore, we arrive at the final expression that links Γ-phase space and entropy:

$$S(E,V,N,\zeta) = k_B \ln\left[\frac{\Omega_\Gamma(E,\zeta)}{\Omega_E \cdot N!}\right] = k_B \ln W(E,V,N,\zeta), \tag{III.3.8}$$

where W is the number of possible different configurations for given energy, temperature, number of particles and volume. The entropy according eq. (III.3.8) is the so-called statistical entropy.

The entropy of eq. (III.3.8) is now accessible to a clear microscopic interpretation: For given macroscopic parameters (E,V,N,ζ) we encounter many different microscopic configurations $W(E,V,N,\zeta)$, or, in other words, there are many microscopic configurations (q_k, p_k)that are compatible with $E = H(p_k, q_k, \zeta, t)$ (see eq. (II.1.4)).

Let us verify now explicitly for an ideal gas that entropy is an extensive quantity. Substituting eqs. (III.2.3) and (III.3.2)) into eq. (III.3.8), we obtain

$$S = Nk_B\left\{\frac{5}{2} + \ln\left[\frac{1}{(2\pi\hbar)^f}\cdot\frac{V}{N}\cdot\left(\frac{4\pi\cdot m}{3}\cdot\frac{E}{N}\right)^{\frac{3}{2}}\right] - \frac{1}{N}\ln\left(\sqrt{6}\cdot\pi N\right)\right\}. \tag{III.3.9}$$

For a large number of particles (thermodynamic limit) the third term in parenthesis vanishes and the ratios (E/N) and (V/N) are constant. Therefore, the entropy

$$S = Nk_B\left\{\frac{5}{2} + \ln\left[\frac{1}{(2\pi\hbar)^f}\cdot\frac{V}{N}\cdot\left(\frac{4\pi\cdot m}{3}\cdot\frac{E}{N}\right)^{\frac{3}{2}}\right]\right\} \tag{III.3.10}$$

is extensive as it is proportional to the number of particles in the thermodynamic limit. We note, that eq. (III.3.10) does not give rise to any variant of Gibbs' paradox: $\Delta S_{\text{mix}} = 0$ if $A = B$. Therefore, when dividing eq. (III.2.1) with different factors (like, e.g. done in eq. (III.2.4)) that leave the differential form of eq. (III.2.1) unchanged, the additional physical conditions for the thermodynamic temperature scale, the 3rd law of thermodynamics, the extensitivity of entropy, the existence of an elementary phase space volume (due to the Heisenberg uncertainty relation) and Gibbs' paradox finally request multiplication with the factor $\frac{k_B}{\Omega_0 \cdot N!} \cdot \frac{1}{1/(\Omega_0 \cdot N!)}$. Therefore, all constants that are "arbitrary" from a mathematical point of view need definite identification from a physical point of view. Likewise, for an ideal gas, Boltzmann's genius entropy formula appears to be a logical consequence rather than a pure definition. For a non-ideal gas, the situation is different: due to the particle correlation, extensitivity and the simple combinatory counting of the number of independent states via N! do not hold strictly any more. In this respect, Boltzmann's entropy formula can be considered as a definition.

IV. How Information Impacts on the Outer World

IV.1 Missing Information and the Logarithmic Dependence for Intelligent Questions

Let us consider an example where we have to find out the box where the money is, Figure 3. Figure 3a depicts an example where only one box is available to put the money, i.e. $W(a) = 1$. Figure 3b is an example, where two boxes are available, i.e. $W(b) = 2$, in Figure 3c $W(c) = 4$, in Figure 3d $W(d) = 8$, in Figure 3e $W(e) = 16$. The missing information, namely where the money is not (indicated with non-colored volumes), is different for each figure.

It is evident, that for the case of Figure 3a, no question is necessary to know where the money is because only one box is available, $W(a) = 1$: the money must therefore be located in exactly this box. Therefore, no information is missing. For Figure 3e the situation is quite different. There are 16 boxes available ($W(e) = 16$) and in this situation we are missing considerable information about the location of the money.

How to quantify which information is higher and which is lower ? This could be characterized by the number of pertinent questions to find out in which box the money is. If the number of such "intelligent" questions is high, the missing information was high. If the number of questions is low, the missing information was low.

The number of intelligent questions to find out where the money is can be determined as follows:

- for case (a), there is only one possibility to locate the money and the number of intelligent questions is zero to find out where the money is, is given by: $N_{\text{question}} = 0$.
- for case (b), there are two possibilities to locate the money, therefore only one intelligent questions is needed to find out where the money is: $N_{\text{question}} = 1$.
- for case (c), there are 4 possibilities to locate the money, therefore two intelligent questions

are needed to find out where the money is (first question: left ?, second question: up ?): $N_{\text{question}} = 2$.

- for case (d), there are 8 possibilities to locate the money, therefore 3 intelligent questions are needed to find out where the money is (first question: left ?, second question: up ?, third: behind?): $N_{\text{question}} = 3$.
- for case (e), there are 16 possibilities to locate the money, therefore 4 intelligent questions are needed to find out where the money is (first question: left half?, second question: outer right ?, third: up?, fourth: behind?): $N_{\text{question}} = 4$.

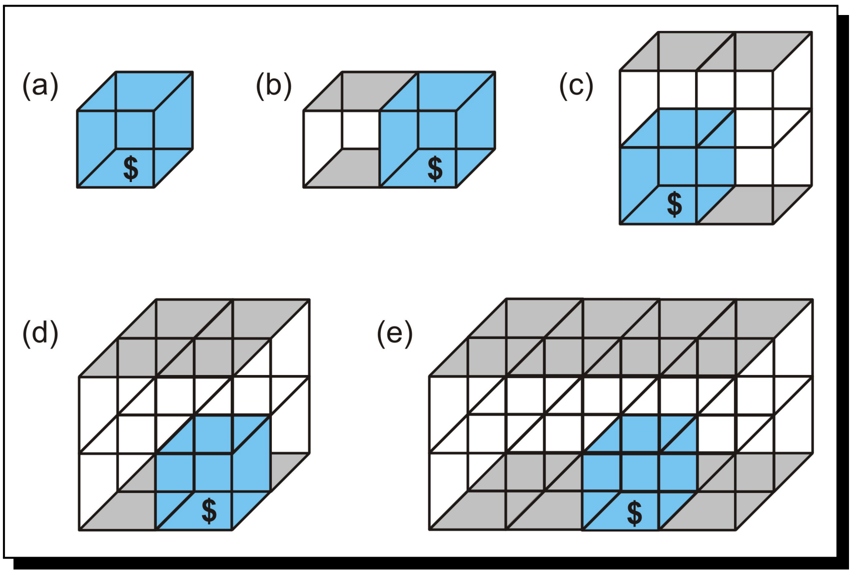

Figure 3. Examples of boxes and location of the money (blue box). (a) there exist only one box, i.e. $W(a) = 1$, (b) $W(b) = 2$, (c) $W(c) = 4$, (d) $W(d) = 8$, (e) $W(e) = 16$.

These illustrations hint to the following relation between the number of boxes W and the number of intelligent questions N_{question} to find out where the money is:

$$W = 2^{N_{\text{question}}}. \tag{IV.1.1}$$

Therefore, the number of questions is not directly related to the number of boxes, but rather to its logarithm:

$$N_{\text{question}} = \log_2 W. \tag{IV.1.2}$$

As the number of questions can be identified as a quantitative measure of missing information, we observe that the missing information depends in a logarithmic manner on the number of boxes:

$$I_{\text{missing}} = C \cdot N_{\text{question}} = C \cdot \log_2 W. \tag{IV.1.3}$$

The constant C defines only the measurement unit. If we say that one question corresponds to one *"Bit"* of information, $C = 1$ and

$$I_{\text{missing}}(1Bit) = 1 = \log_2 2. \tag{IV.1.4}$$

Because $N_{\text{question}} = \frac{1}{\ln 2} \ln W$ we also can say that one *"Nat"* of information corresponds to $I_{\text{missing}}(1Nat) = I_{\text{missing}}(1Bit)/\ln 2$.

IV.2 Information and Entropy

So far, the considerations about information appeared as an isolated topic. However, information has a much deeper physical meaning and impact to the world. This point of view has historical roots to J.C. Maxwell and discussions by L. Szillard [36] (and later application to non-equilibrium systems [37]). Let us assume that we operate a shutter in a system of volume V, particle number N and constant temperature T that separates two volumes V_1 and V_2 (i.e., $V = V_1 + V_2$) in such a manner, that it let only pass particles from left to right. After some time, all particles are confined in the right volume V_2. For simplicity, let us assume that the shutter has negligible mass, so that no mechanical work is needed for its operation and that the two volumes have equal size, e.g. $V_1 = V_2$. From the 1st law of thermodynamics ($dU = 0 = T \cdot dS - p \cdot dV$) and the ideal gas equation ($p \cdot V = N \cdot k_B T$) we see, that the entropy is independent from the temperature and depends only on the relative volumes:

$$dS = N \cdot k_B \cdot \frac{dV}{V}, \tag{IV.2.1}$$

i.e.

$$S - S_2 = N \cdot k_B \cdot \int_{V_2}^{V} \frac{dV}{V} = N \cdot k_B \cdot \ln\left(\frac{V}{V_2}\right) = N \cdot k_B \cdot \ln 2. \tag{IV.2.2}$$

As all particles are now confined in the volume V_2 we can initiate an isothermal expansion (just removing the shutter) to get mechanical work done:

$$W = N \cdot k_B T \cdot \int_{V_2}^{V} \frac{dV}{V} = N \cdot k_B T \cdot \ln\left(\frac{V}{V_2}\right) = N \cdot k_B T \cdot \ln 2. \tag{IV.2.3}$$

From eq. (IV.2.1) it follows, that this work can be expressed in terms of entropy differences:

$$W = T \cdot (S - S_2). \tag{IV.2.4}$$

After isothermal expansion, were starts the selection with the shutter and again, mechanical work can be performed. Due to this activity, entropy is reduced providing the possibility to perform mechanical work (eq. (IV.2.4)). This means, that would nothing else change in the outer world heat would be entirely transformed to mechanical work via the periodic operating shutter machine. However, the 2nd law of thermodynamics forbids the transformation of mechanical work entirely at the expense of heat for a periodic process: the maximum efficiency is given by the Carnot process [4, 35], namely

$$\eta_{\text{Carnot}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}}. \tag{IV.2.5}$$

Eq. (IV.2.5) indicates, that the maximum efficiency is always smaller than one and a periodically machine operation not only absorbs heat Q_{in} but also needs to transfer heat Q_{out} from the system to the outer world.

We are therefore looking more carefully to the circumstance, whether really nothing has changed in the outer world when the shutter is operated. What could this be ? In fact, when we operate a shutter we are part of the outer world, and we obtain the knowledge that particle 1 is in the right half of the volume V (i.e. is confined in volume V_2), that particle 2 is in the right half, . . . that particle N is in the right half. And it is this information in the outer world, that has changed: we can operate the shutter only, when we do have information about the particle. In order to avoid contradiction with the 2nd law of thermodynamics, we need to request, that the information for one particle is at least equivalent to an entropy of magnitude $\Delta S_{\text{information}} = +k_B \cdot \ln 2$ in order to compensate the loss of entropy $\Delta S_{\text{Shutter}} = -k_B \cdot \ln 2$ in the system resulting from the sorting of the particles by means of the shutter operation [36, 38]. In this case, the total change of entropy would be zero and, according eq. (IV.2.4) no work could be performed:

$$\Delta W_{\text{total}} = T \cdot \Delta S_{\text{total}} = T \cdot (\Delta S_{\text{information}} + \Delta S_{\text{Shutter}}) = 0\,. \tag{IV.2.6}$$

Therefore, we could not operate a magic periodically operating machine that only transforms heat into work.

IV.3 Information Entropy and its Impact to the Outer World

So far, the introduction of the information entropy in eq. (IV.2.6) has been entirely motivated by the conservation of the 2nd law of thermodynamics. But what could be the motivation that entropy is directly aligned to information ? Let us consider Figure 4.

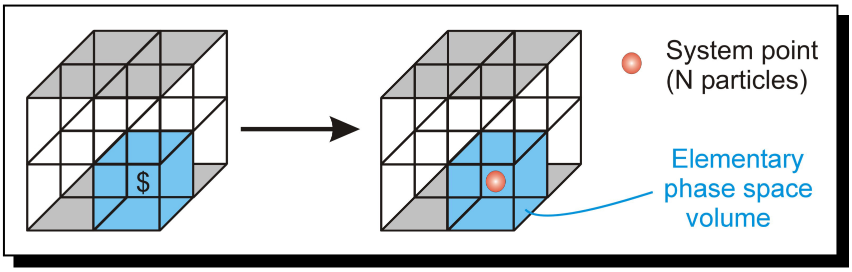

Figure 4. Identification of missing information with entropy.

Figure 4 schematizes that the number of elementary phase space volumes correspond to the number of boxes. Therefore, the number of physically different configurations $W(E, V, N, \zeta)$ from eq. (III.3.8) corresponds (according eq. (IV.1.3)) to missing information $I_{\text{missing}} = C \cdot \log_2 W(E, V, N, \zeta)$. In view of the above discussion of the shutter operation, it is therefore useful, to define the constant C in a manner, that the missing information is measured in units of $C = k_B/\ln 2$. Entropy, as Figure 4 illustrates, corresponds therefore to missing information:

$$S(E,V,N,\zeta) = k_B \ln W(E,V,N,\zeta) = I_{\text{missing}}. \tag{IV.3.1}$$

Evidently, the sum of the missing and available information is constant:

$$I_{\text{missing}} + I_{\text{available}} = \text{const.} \tag{IV.3.2}$$

We therefore arrive to the conclusion, that entropy and information are strongly linked to each other and are by no means two independent and different measures. Inserting (IV.3.1) in (IV.3.2) we obtain:

$$S + I_{\text{available}} = \text{const.} \tag{IV.3.3}$$

The measurement (done by the shutter) reduces the entropy of the particles in the volume V, but increases at least the entropy by the same amount for the detector (or us while operating the shutter). The sum of the entropy of the system (that performs mechanical work) and information (of the outer world)must therefore be constant. The information entropy of the measurement device is therefore an important element for the consistency of thermodynamics.

Similar considerations can be performed in the velocity space. We operate the shutter now in a manner, that it lets pass only the fast particles from the left to the right and the slow particles from right to left. After some time, the right part of the volume is hotter than the left part and mechanical work can be performed via the equilibration of the temperature differences.

IV.4 Entropy and Disorder

Let us finish with some remarks about the relation of entropy and disorder. Consider a system characterized by a number of configurations $W(E,V,N)$. The number of configurations might be a certain combination of all objects in your office. It is evident, that the number of configurations that merit an assignment of the word "order" is much less than the number of combinations of objects, that merit the assignment "disorder". Therefore, the probability that order changes to disorder is larger than those that disorder turns to order. The office would therefore turn in most of the cases from order to disorder unless not external action avoids it. This is in coincidence with the experience. It is also in coincidence with the 2^{nd} law of thermodynamics because the action to create order is correlated to external work, that is in turn related to an increase of entropy (e.g. eq. (IV.2.4)).

V. Conclusion

We have employed the differential form of the 1^{st} law of thermodynamics to link entropy to Γ-phase space. It is demonstrated, that extensitivity of thermodynamic functions, thermodynamic temperature, the indistinguishable of particles, the elementary phase space volume due to the Heisenberg-relation and the 3^{rd} law of thermodynamics implies logarithmic dependence from the Γ-phase space volume and suggests that integration constants are zero while free factors are Boltzmann's constant k_B, elementary phase space volume $\Omega_0 = (2\pi\hbar)^f$ (f is the degree of freedom for one particle) and Gibbs' correction factor$1/N!$. This physical approach points naturally to Boltzmann's genius entropy relation, the statistical foundation of thermodynamics and the correlation of entropy to missing information. It likewise points naturally to a quantification of information, so-called information entropy and the finding that the available information is not an isolated quantity but linked to the "outer world" via the relation $S + I_{available} = const.$ that states that the sum of the entropy and information is constant.

The entirely physical point of view (accompanied by explicit derivations of equations) will be also helpful for physics teachers, professors and students.

Acknowledgements

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Appendix 1. About the Properties of a High-Dimensional Phase Space

It is the purpose of this appendix to show, that a) for a high dimensional case the volume of a spherical outer shell in phase space is almost identical to the total phase space volume, and b) that the necessary mathematical conditions concern physically relevant cases. Let us demonstrate explicitly these properties for an ideal gas and consider the difference of the phase space volumes for the energies $E - \delta E$ and E, i.e.

$$\Delta\Omega_\Gamma = \Omega_\Gamma(E,N,V) - \Omega_\Gamma(E-\delta E,N,V) = \int_{E-\delta E<H(p,q)<E} d\Omega_\Gamma. \tag{A1.1}$$

With the help of the phase space volume for an ideal monoatomic gas (see eq. (II.1.14)), i.e.

$$\Omega_\Gamma(E,N,V) = \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} \cdot E^{3N/2} \tag{A1.2}$$

we can transform the integration variables to energy space and obtain

$$\begin{aligned}\Delta\Omega_\Gamma &= \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} \cdot \left\{E^{3N/2} - (E-\delta E)^{3N/2}\right\} \\ &= \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} \cdot E^{3N/2}\left\{1 - \left(1 - \frac{\delta E}{E}\right)^{3N/2}\right\}\end{aligned} \tag{A1.3}$$

If

$$\delta E/E \ll 1 \tag{A1.4}$$

the term in parenthesis can be well approximated by an exponential function that can be obtained as follows. Setting $x = \delta E/E$ and $m = 3N/2$ we first consider the identity

$$(1-x)^m - e^{-mx} = e^{-xm}\left\{e^{m\ln(1-x)+xm} - 1\right\}. \tag{A1.5}$$

A series development of

$$m \cdot \ln(1-x) + x \cdot m = m \cdot \left\{-x + O(x^2) + x\right\} = m \cdot O(x^2) \tag{A1.6}$$

provides

$$(1-x)^m - e^{-mx} = e^{-xm+NO(x^2)} - e^{-xm} \to 0 \text{ if } x \ll 1. \tag{A1.7}$$

Therefore, eq. (A1.3) can be approximated by

$$\Delta\Omega_\Gamma \approx \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} \cdot E^{3N/2}\left\{1 - \exp\left(-\frac{\delta E}{E} \cdot \frac{3N}{2}\right)\right\}. \tag{A1.8}$$

Let us assume that

$$\frac{\delta E}{E} \cdot \frac{3N}{2} \gg 1. \tag{A1.9}$$

(eq. (A1.9) will be physically motivated below). In this case, the exponential function in eq. (A1.8) vanishes and we obtain

$$\Delta\Omega_\Gamma \approx \frac{V^N \pi^{3N/2}(2m)^{3N/2}}{(3N/2)!} \cdot E^{3N/2}. \tag{A1.10}$$

Comparing eq. (A1.2) with (A1.10) we obtain:

$$\Delta\Omega_\Gamma \approx \Omega_\Gamma. \tag{A1.11}$$

This indicates, that in a high dimensional space the volume in the shell between the radii $E - \delta E$ and E is almost identical to the total volume from 0 until E if conditions (A1.4) and (A1.9) hold true.

Does the combination of parameters according eqs. (A1.4) and (A1.9) describe physical systems of practical interest in order to conclude from eq. (A1.11) that the shell contains almost all volume? For this purpose we study the energy distribution function for N particles and consider the probability $p(E,N)$ to find N-particles within $E - dE$ and E where $E = E_1 + \ldots E_N$. This probability is given by (assuming thermodynamic equilibrium where each particle distribution function is given by a Maxwellian)

$$p_N(E) \cdot dE = \int d^3v_1 \int d^3v_2 \ldots \int_E^{E+dE} \ldots \int d^3v_N \left(\frac{m}{2\pi kT}\right)^{\frac{3N}{2}} exp\left(-\frac{m(v_1^2 + v_2^2 + \ldots + v_N^2)}{2kT}\right). \tag{A1.12}$$

The integrations can easily be carried out with the help of the Gamma-function

$$\int_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}}. \tag{A1.13}$$

We note that for integer and half integer arguments, the gamma function is simply given by $\Gamma(n) = (n-1)!$ and $\Gamma(1/2 + n) = \sqrt{\pi}\frac{(2n)!}{4^n n!}$). This provides a closed expression for $p(E,N) := p_N(E)$:

$$p(E,N) = \frac{1}{\Gamma(3N/2)} \cdot \frac{E^{3N/2-1}}{(kT)^{3N/2}} \cdot e^{-E/kT}. \tag{A1.14}$$

The width δE of eq. (A1.14) an be estimated with the help of the Full Width at Half Maximum (FWHM). For these purposes we transform to the variables

$$x = E/kTq \tag{A1.15}$$

and

$$q = 3N/2 - 1 \tag{A1.16}$$

to obtain

$$p(E,N)dE = p(x,q)dx \tag{A1.17}$$

with

$$p(x,q) = \frac{q^{q+1}e^{-q}}{\Gamma(q+1)} \cdot \left\{x \cdot e^{-x+1}\right\}^q . \tag{A1.18}$$

The energy of the system is proportional to the number of particles, therefore, for a large number of particles, the variable x from eq. (A1.15) is independent from the number of particles. The Half Width at Half Maximum (HWHM) x_{HWHM} of eq. (A1.18) is given by

$$p(x_{HWHM}, q) = \frac{1}{2} \cdot p(x_{\max}, q) \tag{A1.19}$$

where $x_{\max} = 1$ is the argument for which the function $p(x,q)$ has its maximum. From eq. (A1.19) we obtain

$$(x - x_{\max})_{HWHM} = \frac{\sqrt{2\ln 2}}{\sqrt{q}}. \tag{A1.20}$$

Transforming back to energies with the help of eqs. (A1.15) and (A1.16) we obtain

$$\Delta E_{FWHM} = 2\sqrt{2\ln 2} \cdot \sqrt{3N/2 - 1} \cdot kT. \tag{A1.21}$$

For the relative width we obtain

$$\frac{\Delta E_{FWHM}}{E} = \frac{2\sqrt{2\ln 2} \cdot \sqrt{3N/2 - 1} \cdot kT}{3NkT/2}. \tag{A1.22}$$

As the probability to find energy values $E > E_{\max} + \Delta E_{FWHM}$ is very small we can estimate the thickness δE of the shell in energy space via the FWHM:

$$\frac{\delta E}{E} \approx 4\sqrt{\frac{\ln 2}{3}} \cdot \frac{1}{\sqrt{N}} \approx \frac{2}{\sqrt{N}}. \tag{A1.23}$$

As the particle number is of the order of *mol*, the relation (A1.4) is therefore well validated. Substituting eq. (A1.23) into eq. (A1.9) we obtain

$$\frac{\delta E}{E} \cdot \frac{3N}{2} = 4\sqrt{\frac{\ln 2}{3}} \cdot \frac{1}{\sqrt{N}} \cdot \frac{3N}{2} = 2\sqrt{3\ln 2} \cdot \sqrt{N} \gg 1. \tag{A1.24}$$

Therefore, also the relation (A1.9) is well validated. The physical conclusion from the relations (A1.23) and (A1.24) is, that for an overwhelming number of practical cases (when the number of particles is large), almost the total Γ-phase space volume of the thermodynamic system is contained in a very thin shell between $E - \delta E$ and E. This result has an important physical interpretation. If the system contains only a small number of particles, a given temperature does not define the energy of the system because the distribution function is very broad. Therefore Gedanken-Experiments that involve only one particle have to be considered with care.

For a large number of particles, however, the width of the energy distribution function is very small and a given temperature does well characterize the energy of the system because the difference between the mean energy $\bar{E}$ and the maximum energy $E_{\max}$ is negligible. And it is just this circumstance that permits to characterize the energy of a gas via the temperature and the number of particles only: $U = \frac{3}{2}NkT \approx \bar{E} \approx E_{\max}$.

Appendix 2. About the most Probable Distribution Over the Thin Shell δE in Γ-phase Space

For a given macroscopic state, the system can adopt many different microstates. If the system is isolated, the possible microstates are located on the energy surface $H(p,q) = E$. Due to the external forces (parameter ζ) the system is not isolated and we conveniently operate with the phase space density $\rho(p,q) = \rho(q_1,\ldots,q_F,p_1,\ldots,p_F,t)$: it determines the probability to find a certain microscopic configuration (p,q) between (p,q) and $(p+dp,q+dq)$ that is compatible with $H(p,q,\zeta) = E$. The phase space density is normalized according

$$\int \rho(p,q)dpdq = 1 \tag{A2.1}$$

where $(p,q) = (q_1,\ldots,q_F,p_1,\ldots,p_F,t)$ and $dpdq := dq_1\ldots q_F dp_1\ldots p_F$. If $G(p,q)$ is an observable quantity, we will observe for a given macroscopic state a mean value $\overline{G(p,q)}$ that is composed from each microstate multiplied with its proper weight, i.e.

$$\overline{G(p,q)} = \int \rho(p,q)\cdot G(p,q)\cdot dpdq. \tag{A2.2}$$

Let us consider N_Γ identical copies that form an ensemble. Each copy consists of N particles and is characterized by the same macroscopic parameters like, e.g. (E,V,N). At a certain time t each system has adopted the microstate $\rho_k = (p_k,q_k,t)$ where the index k indicates the number of the identical copy, i.e. $k = 1\ldots N_\Gamma$. We divide the hypersurface into N_σ different surface elements $\Delta\sigma_i$ of equal size, see Figure A1. Each surface element contains N_i copies of a N-particle system, i.e.

$$N_\Gamma = \sum_{i=1}^{N_\sigma} N_i = \text{const.} \tag{A2.3}$$

The number of systems N_i located on the surface element $\Delta\sigma_i$ corresponds to the statistical weight of this surface element and we can interpret the ratio

$$g_i = \frac{N_i}{N_\Gamma} \tag{A2.4}$$

as the probability that a microstate is located in the surface element $\Delta\sigma_i$. The probability (A2.4) in the discrete model corresponds therefore to the probability $\rho(p,q)dpdq$ in the continuous representation.

The number of possibilities to select a group of systems N_i out of N_Γ systems is calculated as follows. The number of possibilities to select N_1 systems out of a total number N_Γ is given by $N_\Gamma \cdot (N_\Gamma - 1)\ldots(N_\Gamma - N_1 + 1) = N_\Gamma!/(N_\Gamma - N_1)$. As any permutation among the N_1 systems does not change anything for the surface element $\Delta\sigma_1$ the number of different configuration on this surface element is given by $N_\Gamma!/(N_\Gamma - N_1)! \cdot N_1!$.

In a similar manner, we obtain for the next surface element $\Delta\sigma_2$ the number of different configurations: $(N_\Gamma - N_1)\ldots(N_\Gamma - N_1 - N_2 + 1)/N_2! = (N_\Gamma - N_1)!/(N_\Gamma - N_1 - N_2)! \cdot N_2!$. Because $(N_\Gamma - N_1 - N_2 \ldots - N_\sigma)! = 0! = 1$ we obtain for the total number of configurations (which is just the product of the number of configurations for each surface element):

$$W = N_\Gamma! \prod_{i=1}^{N_\sigma} \frac{g_i^{N_i}}{N_i!} \tag{A2.5}$$

because $g_i$is the probability to find one system inside $\Delta\sigma_i$: $g_i^{N_i}$ is then the probability to find N_i systems in $\Delta\sigma_i$ as the different copies of the system in Γ-phase space are statistically independent from each other.

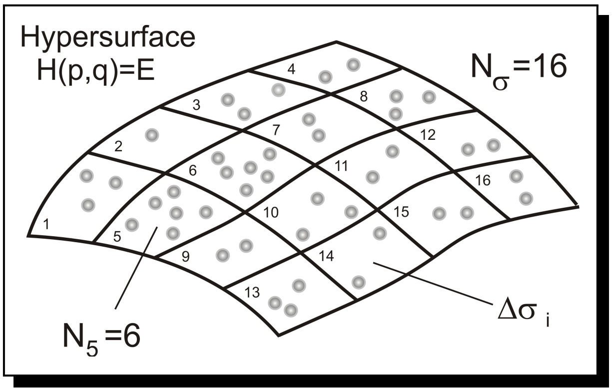

Figure A1. Microcanonical distribution of N_Γ systems on the hypersurface $H(p,q) = E$. $\Delta\sigma_i$ is a surface element on the hypersurface in Γ-phase space that is composed from N_σ surface elements. Each surface element $\Delta\sigma_i$ contains N_i systems. The figure shows an example where the hypersurface is divided into 16 surface elements ($N_\sigma = 16$): e.g. in the surface element $\Delta\sigma_5$ we find $N_5 = 6$ systems where each system contains N particles.

We are now interested to find the most probable distribution of systems over the cells of the hypersurface, i.e. we are looking to determine the extremum of eq. (A2.5). Due to the factorials, the differentiation of eq. (A2.5) is not a simple task. However, the variation of eq. (A2.5) can easily performed if we replace the factorials by Stirling's formula (N_Γ and N_i are large numbers, in the limit $N_\Gamma \to \infty$ and $N_i \to \infty$). Due to the Π-product it is more advantageous to look for the maximum of $\ln(W(N_i))$ instead of $W(N_i)$ itself. Using Stirling's simplest approximation, namely $\ln N! \approx N \ln N - N$ we obtain:

$$\ln(W) = \ln N_\Gamma! + \sum_{i=1}^{N_\sigma} N_i \ln g_i - \ln N_i!$$

$$\approx N_\Gamma \ln N_\Gamma - N_\Gamma + \sum_{i=1}^{N_\sigma} N_i \ln g_i - (N_i \ln N_i - N_i). \tag{A2.6}$$

At maximum, the total differential of eq. (A2.6) must vanish. Because the total number of systems is conserved, i.e.

$$dN_\Gamma = \sum_{i=1}^{N_\sigma} dN_i = 0 \tag{A2.7}$$

we have

$$\begin{aligned} d\{\ln W\} &= \sum_{i=1}^{N_\sigma} dN_i \ln g_i - (dN_i \ln N_i + dN_i - dN_i) \\ &= -\sum_{i=1}^{N_\sigma} dN_i \{\ln N_i - \ln g_i\} = 0. \end{aligned} \tag{A2.8}$$

The variation of all N_i is not simple, because they are not independent from each other due to relation (A2.7). Therefore we cannot conclude that the parenthesis on the right hand side of eq. (A2.8) vanishes. However, eqs. (A2.7)–(A2.8) can be combined with the help of a Lagrange parameter (i.e. we add $0 = \lambda \cdot \sum_{i=1}^{N_\sigma} dN_i = 0$ to eq. (A2.8)):

$$d\{\ln W\} = -\sum_{i=1}^{N_\sigma} dN_i \{\ln N_i - \ln g_i - \lambda\} = 0. \tag{A2.9}$$

Now, we are authorized to perform an independent variation for each dN_i, which indicates that the parenthesis in eq. (A2.9) must vanish:

$$\{\ln N_i - \ln g_i - \lambda\} = 0. \tag{A2.10}$$

From eq. (A2.10) it follows

$$N_i = g_i e^\lambda. \tag{A2.11}$$

Eq. (A2.11) shows that the number of systems in the hypersurface element $\Delta\sigma_i$ is proportional to the probability g_i. A principle hypothesis in statistical physics is that all points in phase space are of equal importance, i.e. the probability g_i to find the system in the hypersurface element $\Delta\sigma_i$ is proportional to the size of this hypersurface element:

$$g_i \propto \Delta\sigma_i. \tag{A2.12}$$

Therefore

$$N_i \propto \Delta\sigma_i. \tag{A2.13}$$

If the surface elements $\Delta\sigma_i$ are chosen to be small and of equal size, the number of systems N_i in each $\Delta\sigma_i$ must be equal too, i.e.

$$N_i = \text{const}. \tag{A2.14}$$

It follows therefore from eq. (A2.14) that the most probable distribution of systems on the hypersurface is a population of each surface element $\Delta\sigma_i$that is a constant (independence from the index “i”). Therefore, a Γ-phase space density that is constant on the hypersurface is the most probable distribution, i.e.

$$g_i = \frac{N_i}{N_\Gamma} = \begin{cases} \text{const.} & \text{if } H(p,q) = E \\ 0 & \text{otherwise} \end{cases} . \tag{A2.15}$$

As has been shown above (eq. (A1.23)) the thickness of the shell in the high-dimensional energy space is very small and vanishes in the thermodynamic limit. Therefore, eq. (A2.15) can be applied to a small energy shell too:

$$\rho(p,q) = \begin{cases} \text{const.} & \text{if } E - \frac{\delta E}{2} < H(p,q) < E + \frac{\delta E}{2} \\ 0 & \text{otherwise} \end{cases} \tag{A2.16}$$

E defines a hypersurface $H(p,q) = E$ in Γ-phase space whereas the shell thickness δE characterizes an energy variation around this energy. The physical reason for the possibility of this energy variation is the finite width (although extremely small, see eq. (A1.23)) of the energy distribution function in systems with a finite number of particles.

We note, that every constant of motion reduces the dimension of the phase space and the dimension of the Γ-phase space is not $2F = 2f \cdot N$ but $2F - 1$. Therefore, the integral over the phase space density that has the form (A2.16) would vanish. One therefore needs to invoke the δ-function to avoid vanishing integrals. The δ-function, however, is not compatible with the ergodic theorem but it can be shown that the function of eq. (A1.18) is an analytical representation of the δ-function, i.e.

$$\rho(p,q) = \begin{cases} \gamma \cdot \lim\limits_{N\to\infty} \sqrt{\dfrac{\frac{3}{2}N-1}{2\pi}} \cdot \left(\dfrac{E}{\bar{E}}\right)^{\frac{3N}{2}-1} \cdot \exp\left[-\left(\dfrac{3}{2}N-1\right)\left(\dfrac{E}{\bar{E}}-1\right)\right] = \gamma \cdot \delta\left(E-\bar{E}\right) \\ \qquad \text{for } \bar{E} - \dfrac{\delta E}{2} < H(p,q) < \bar{E} + \dfrac{\delta E}{2} \\ 0 \qquad \text{otherwise} \end{cases} \tag{A2.17}$$

where the mean energy $\bar{E}$ is given by

$$\bar{E} = \frac{3}{2} NkT . \tag{A2.18}$$

The normalization constant γ can be determined from the normalization condition of the Γ-phase space density:

$$\int \rho(p,q) dpdq = 1 , \tag{A2.19}$$

i.e.

$$\gamma = \frac{1}{\int_{\bar{E}-\frac{\delta E}{2} < H < \bar{E}+\frac{\delta E}{2}} \delta(E-\bar{E}) \cdot dpdq} ,. \tag{A2.20}$$

Due to the δ-function the integral (A2.20) over the hypersurface can be transformed into an integral over the surface of the sphere, i.e.

$$\sigma(E) = \int_{E=H(p,q)} d\sigma . \tag{A2.21}$$

It is important to understand the different physical meaning of the generalized coordinates: a given volume V confines the particles and therefore limits the coordinates q_k while the given system energy is responsible for the fact that the system point moves only on the hypersurface in the Γ-phase space. Because all volume is almost identical to the volume of the outer spherical shell (see eq. (A1.11)), volume and hypersurface are related by

$$\sigma(E) = \frac{\partial \Omega}{\partial E} \tag{A2.22}$$

from which it follows

$$\gamma = \frac{1}{\sigma(E)} \,. \tag{A2.23}$$

$\rho(p,q)$ from eq. (A2.17) is the so-called micro-canonical distribution function and mean values according eq. (A2.2) are the so-called micro-canonical ensemble average.

In almost all practical applications the number of particles is finite (although large) and we therefore encounter a finite width (eq. (A1.23)) for the analytical representation of the δ-function (eq. (A2.17)). The micro-canonical distribution function according eq. (A2.17) is therefore consistent with the quasi-ergodic theorem.

With the help of the micro-canonical ensemble average and relation (III.3.8) it can readily bebe shown (expressing entropy in terms of partition function and internal energy, i.e. $S = k_B \cdot \ln(Z + \beta \cdot U)$), that the ensemble averaged entropy is given by

$$S = \overline{-k_B \ln \rho(p,q)} \,. \tag{A2.24}$$

For the discrete case, eq. (A2.24) takes the form

$$S = -k_B \sum_{i=1}^{N_{\text{mico}}} p_i \cdot \ln(p_i) \,. \tag{A2.25}$$

N_{micro} is the number of micro-configurations and p_i is the probability for each configuration. It is interesting to note, that eq. (A2.25) is formally identical to "Shannon's information entropy" [39] and that exactly this information entropy is needed to have our shutter operation discussed in the main part of the paper respecting the 2$^{\text{nd}}$ law of thermodynamics (see § IV.2).

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

The authors wrote, read and approved the final manuscript.

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