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Entropy of simple gas models: an accessible approach to information-theoretic and thermodynamic concepts

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Abstract

A simple derivation of the entropy of the ideal and the dilute hard-sphere gas up to a normalization constant is presented, using only high school-level mathematics. The connection between information theory and thermodynamics, as well as the role of Heisenberg's uncertainty principle in the transition from the classical to the quantum description of physical systems, is highlighted in a concise manner accessible to non-experts with a general interest in the natural sciences. A brief discussion is also devoted to the ultra-relativistic gas which can be analysed with the same elementary approach used for the non-relativistic case.

Keywords: entropy, thermodynamics, foundations of quantum mechanics, information theory, classical statistical mechanics

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1. Introduction

The derivations of the entropy formulas presented in this paper are not intended to provide fully rigorous mathematical proofs, but rather to illustrate in a transparent and pedagogical way the relationship between the information-theoretic and thermodynamic concepts of entropy, including the role of the Heisenberg uncertainty principle.

The discussion begins with the case of the non-relativistic ideal gas in order to illustrate the core idea of the present work. While the entropy of a given amount of gas is derived only up to an additive constant, this very fact highlights the scientific achievement of the two young scientists Otto Sackur and Hugo Tetrode, whose early deaths curtailed promising careers (for an excellent review see [1]). In the formative years of quantum mechanics, their work demonstrated that Planck's constant plays a fundamental role not only for photons, but also for material particles. The method presented here also allows for a straightforward treatment of the ultra-relativistic case. Finally, a brief remark is made on the thermodynamic difference between an ultra-relativistic gas and a photon gas, i.e., blackbody radiation.

2. Non-relativistic ideal gas

We consider an ideal gas consisting of N point-like (structureless) particles of mass m. In thermodynamics, the state of such a system is characterized by a minimal set of quantities, such as the number of particles N, the total energy E, and the gas volume V. However, in classical reality, the thermodynamic state of an ideal gas is underpinned by a microscopic state that requires a vast amount of information to be described precisely—namely, the positions and velocities of each of the N particles.

In the following, we consider the information-theoretic entropy S_I as established and formalized by Shannon [2] as the effort required to describe the microscopic state of the gas that is hidden behind the mere specification of the three macroscopic quantities N, E, and V. For practical reasons, it is not possible to specify the position or velocity of a particle with arbitrary precision. In quantum mechanics, it is fundamentally impossible to speak of an exact position and momentum simultaneously. Bearing this in mind, we now estimate the memory required to record the current microscopic state of an ideal gas as precisely as possible—effectively a measure of the system's complexity.

To express the value G of a physical quantity $\mathcal{G}$ with relative precision $\Delta G/G$, approximately

$$d \simeq \log \frac{G}{\Delta G} \tag{1}$$

decimal digits are needed, where log denotes the common logarithm. For instance, a relative precision of one part in a million requires about 6 digits, and one part in a billion requires about 9 digits. However, decimal notation is not necessary, so we use the natural logarithm ln to express that the storage requirement scales with $\ln(G/\Delta G)$. Of course, using the binary logarithm $\log_2(x) = \ln(x)/\ln(2)$ for $x > 0$ would yield the memory requirement in bits.

Units such as the trit (base 3), dit (decimal digit: base 10), and nat are seldom used in practice to measure memory capacity. However, the nat $\simeq 1.443$ bits is common in information theory because the use of natural logarithms displays some advantages from a mathematical point of view.

In Cartesian coordinates, the kinetic energy

$$E_{\rm kin} = \frac{1}{2} m\vec{v}^2 = \frac{\vec{p}^{\,2}}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{2}$$

of a non-relativistic gas particle is determined by its velocity $\vec{v} = (v_x, v_y, v_z)$, or its momentum $\vec{p} = m\vec{v} = (p_x, p_y, p_z)$. Since the total energy E of the gas is distributed over its N particles, the average kinetic energy per particle is

$$\bar{E}_{\rm kin} = E/N. \tag{3}$$

Hence, the typical magnitudes of the momentum components are of the order of

$$\left(\frac{2m\bar{E}_{\rm kin}}{3}\right)^{1/2} = \left(\frac{2mE}{3N}\right)^{1/2} \simeq \left(\frac{mE}{N}\right)^{1/2} = p_{\rm typ}\,. \tag{4}$$

Accordingly, to store $3N$ momentum components of the typical size (4) with precision Δp, the

required memory $S_{I,\mathrm{Mom}}$ (given here and below in nats) is

$$S_{I,\mathrm{Mom}} \simeq 3N\ln\frac{p_{\mathrm{typ}}}{\Delta p} = 3N\ln\left(\frac{mE}{\Delta p^2 N}\right)^{1/2} = N\ln\left(\frac{mE}{\Delta p^2 N}\right)^{3/2}. \tag{5}$$

The logarithmic term in relation (5) could be refined with a constant γ

$$\ln\left(\frac{mE}{\Delta p^2 N}\right)^{3/2} \to \ln\left(\gamma\frac{mE}{\Delta p^2 N}\right)^{3/2} = \ln\left(\frac{mE}{\Delta p^2 N}\right)^{3/2} + \ln\gamma \tag{6}$$

which captures the influence of the precise momentum distribution of the particles in the gas, allowing for a sharpening of the estimate of the required information storage—an option we will revisit at the end of this paper.

A similar argument applies to the particle positions. Assuming that the gas occupies a cube of edge length L and volume $V = L^3$, capturing N positions in three dimensions with resolution Δx requires

$$\tilde{S}_{I,\mathrm{Pos}} \simeq 3N\ln\left(\frac{L}{\Delta x}\right) = N\ln\left(\frac{V}{\Delta x^3}\right) \tag{7}$$

nats. Thus, the total storage required is given, up to minor corrections, by

$$S_{I,\mathrm{Mom}} + \tilde{S}_{I,\mathrm{Pos}} \simeq N\ln\left(\frac{mE}{\Delta p^2 N}\right)^{3/2} + N\ln\left(\frac{V}{\Delta x^3}\right) = N\ln\left(\frac{V}{\Delta x^3}\left(\frac{mE}{\Delta p^2 N}\right)^{3/2}\right). \tag{8}$$

However, this expression has a catch if we wish to relate it to thermodynamic entropy: it is not extensive, i.e., it does not scale proportionally with the system's size. The solution to this puzzle lies in the fact that elementary particles of the same kind are indistinguishable, which means that a dataset describing the momenta and positions of N particles is equivalent to a dataset in which the N particle entries are merely permuted. We are thus free to systematically sort the particle positions and describe them with reduced numerical effort.

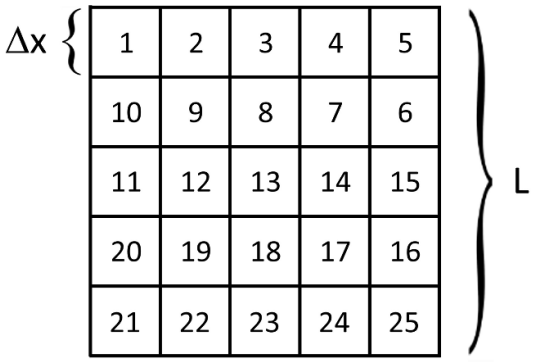

Figure 1. Possible numbering of area cells Δx^2 within a square of area L^2 with $L = 5\Delta x$, allowing simple particle position identification in a two-dimensional gas.

As a first strategy, we divide the cube volume V into $(L/\Delta x)^3 = V/\Delta x^3$ cells, which we then label in three dimensions, for example, analogously to the two-dimensional representation in figure 1.

Without loss of generality, we can assume that $L/\Delta x$ is an integer. If a particle is located in such a cell, then the cell in the range from 1 to $(L/\Delta x)^3$ determines the particle's position with the required precision Δx.

Now, with N particles uniformly distributed, the storage requirement for all positions is only

$$S_{I,\mathrm{Pos}} = N\ln\frac{V}{N\Delta x^3} + o(N), \tag{9}$$

since it is not necessary to store the full cell number on the order of $(L/\Delta x)^3 = V/\Delta x^3$, but only the *difference* of the numbers of consecutive occupied cells, which on average is given by $(V/\Delta x^3)/N$.

Capturing coordinates and momenta of N indistinguishable point particles with precision Δx and Δp then amounts to a memory of

$$\begin{aligned} S_{I,\mathrm{Mom}} + S_{I,\mathrm{Pos}} &\simeq N\ln\left(\frac{mE}{\Delta p^2 N}\right)^{3/2} + N\ln\left(\frac{V}{N\Delta x^3}\right) \\ &= N\ln\left(\frac{V}{N\Delta x^3}\left(\frac{mE}{\Delta p^2 N}\right)^{3/2}\right) \\ &= S_I, \end{aligned} \tag{10}$$

and S_I is indeed an extensive quantity like the thermodynamic entropy, since one has ($\lambda > 0$)

$$S_I(\lambda E, \lambda N, \lambda V) = \lambda S_I(E, V, N)\,. \tag{11}$$

The above argument can be made somewhat more explicit in combinatorial terms: If N indistinguishable particles are distributed among $K = V/\Delta x^3 \gg N \gg 1$ cells, this can be done in

$$Z = \binom{K+N-1}{K} = \frac{(K+N-1)!}{K!\,(N-1)!} \tag{12}$$

different ways. One therefore requires $\log_2 Z$ bits, or equivalently $\ln Z$ nats, to characterize a specific configuration. Using the Stirling approximation $\ln n! \simeq n\ln n - n$ and $\ln(1+x) \simeq x$ for $|x| \ll 1$, one obtains for $K \gg N$

$$\begin{aligned}
\ln Z &\simeq \ln\binom{K+N}{K} = \ln\binom{K+N}{N} \\
&\simeq (K+N)\ln(K+N) - K\ln K - N\ln N \\
&= (K+N)\ln\left(1+\frac{N}{K}\right) + (K+N)\ln K \\
&\quad - K\ln K - N\ln N \\
&\simeq (K+N)\frac{N}{K} + N\ln K - N\ln N \\
&\simeq N + N\ln\frac{K}{N} \simeq N\ln\frac{K}{N} = N\ln\frac{V}{N\Delta x^3}
\end{aligned} \tag{13}$$

in agreement with equation (9).

The final link between the dimensionless information entropy S_I and thermodynamic entropy S is established via a proportionality constant with the physical unit of entropy in physics, i.e. the Boltzmann constant $k_{\mathrm{B}} = 1.380649 \cdot 10^{-23}\,\mathrm{J\cdot K^{-1}}$. Moreover, since the product $\Delta x \cdot \Delta p$ has the dimension of action, with a dimensionless ad hoc normalization constant σ and Planck's constant $h = 6.62607015 \cdot 10^{-34}\,\mathrm{J\cdot s}$, we may introduce quantum physics via Heisenberg's indeterminacy principle and write

$$\Delta x \cdot \Delta p = \sigma^{-1/3} \cdot h\,, \tag{14}$$

yielding the following Ansatz for the thermodynamic entropy formula of an ideal gas

$$S(E, V, N) = k_{\mathrm{B}} N \ln\left(\frac{\sigma}{h^3}\frac{V}{N}\left(\frac{mE}{N}\right)^{3/2}\right). \tag{15}$$

Indeed, it is a fundamental fact of quantum mechanics that the microscopic state of the gas cannot, in principle, be specified more precisely than is expressed by the entropy formula (15) (with a specific value of σ!).

Solving for E gives

$$E(S, V, N) = \frac{h^2}{\sigma^{2/3} m}\frac{N^{5/3}}{V^{2/3}}\exp\left(\frac{2S}{3k_{\mathrm{B}}N}\right). \tag{16}$$

From the fundamental thermodynamic relation (including the chemical potential μ for the sake of completeness)

$$dE = TdS - pdV + \mu dN\,, \tag{17}$$

we find the connection between energy and temperature of the ideal gas

$$T = \left.\frac{\partial E}{\partial S}\right|_{N,V} = \frac{2}{3k_{\mathrm{B}}}\frac{E}{N} \quad \text{or} \quad E = \frac{3}{2}Nk_{\mathrm{B}}T, \tag{18}$$

and the thermodynamic expression for the pressure yields the ideal gas law

$$p = -\left.\frac{\partial E}{\partial V}\right|_{S,N} = \frac{2}{3}\frac{E}{V} \quad \text{or} \quad pV = Nk_{\mathrm{B}}T. \tag{19}$$

Indeed, the entropy $S(E, V, N)$ of a thermodynamic system encodes complete information about its macroscopic properties. One must, however, be cautious not to treat S as a function of intensive variables such as T, V, and N, since during phase transitions, temperature and energy are not uniquely related.

The entropy formula (15) was independently derived in 1912 by Tetrode and Sackur [3–6] through more detailed analysis. With the numerical constant $\sigma = (4\pi/3)\mathrm{e}^{5/2}$, it is known as the *Sackur–Tetrode equation*. Tragically, Sackur (1880–1914) died in an explosion while mixing two liquids in the laboratory of Fritz Haber, Tetrode (1895–1931) who published his first research paper on the Sackur–Tetrode equation at the age of 17 died prematurely of tuberculosis.

The Sackur-Tetrode equation is semiclassical and exhibits the flaw that it may yield negative entropy. Its range of validity is therefore limited to cases where

$$\frac{V}{N} \gg \left(\frac{hc}{k_{\mathrm{B}}T}\right)^3. \tag{20}$$

However, it makes perfectly sense for a dilute gas, and in fact the major achievement of Sackur and Tetrode was the correct determination of σ. They devised a test of their entropy formula by applying it to the monatomic vapour of mercury, and found a satisfactory numerical agreement with the value of Planck's constant [1].

3. Dilute hard-sphere gas (DHSG)

A simple model that at least approximately takes into account the finite spatial extent of gas particles is the DHSG model. In such a gas, the gas particles are modelled as completely elastically scattering, but otherwise non-interacting spheres of radius r. In the case of low particle density, the equation of state of the hard-sphere gas is approximately given by(see e.g. [7])

$$p\,(V-4NV_K) = NkT \quad \text{with} \quad V_K = \frac{4\pi}{3}r^3\,, \quad (21)$$

where V_K denotes the volume of a single sphere, and the entropy follows in strict analogy to that of the van der Waals gas as

$$S\,(E,V,N) = k_{\text{B}} N \ln\left(\frac{\tilde{\sigma}}{h^3}\,\frac{V-4NV_K}{N}\left(\frac{mE}{N}\right)^{3/2}\right). \quad (22)$$

Equation (22) can again be understood from an information-theoretic perspective: The hard spheres move exactly as in the ideal gas with momenta $\sim (mE/N)^{1/2}$, which are determined by the total energy E of the system.

More interesting is the volume contribution $\sim \ln(V-4NV_K)$ in expression (22). In this term, the gas volume reduced by *four times* the total volume of the spheres appears; a result which greatly occupied van der Waals himself [8]. Indeed, a single sphere generates an excluded volume of $8V_K$, within which no further sphere centre can be located, since the minimal distance between two spheres is $2r$, as depicted in figure (2).

Equation (12) must therefore be modified slightly: If a first particle is positioned randomly in one of the $K = V/\Delta x^3$ cells, then this particle blocks $8V_K/\Delta x^3$ cells for the subsequent particle. Once this second particle has been positioned, a volume $2\cdot 8V_K/\Delta x^3$ is excluded for the third particle, and so forth. On average, a volume of

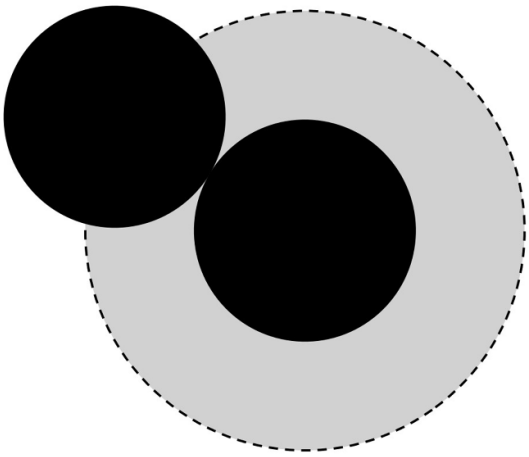

Figure 2. Excluded volume (grey) by one sphere of a pair of hard spheres.

$(N/2)\cdot 8V_K = 4NV_K$ is blocked during the distribution process, and to good approximation this yields a number of possible spatial particle configurations of

$$Z' \simeq \binom{K'+N-1}{K'} \quad \text{where} \quad K' = \frac{V-4NV_K}{\Delta x^3}\,, \quad (23)$$

which ultimately leads to the corresponding volume term in equation (22).

4. Ultra-relativistic ideal gas

When the energy ϵ of a particle is much higher than its rest mass, the relation $\epsilon = pc$ which is exact for massless particles becomes a valid approximation. In an ultra-relativistic gas with total energy E distributed over N particles, the typical momentum components $p_{x,y,z}$ of a particle (up to a factor of order unity) is given by

$$p_{\text{typ}} = \frac{E}{Nc}\,. \quad (24)$$

Following the line of arguments discussed above directly leads to the entropy

$$\begin{aligned} S(E,V,N) &= k_{\text{B}} N\left[\ln\left(\frac{V}{N\Delta x^3}\right) + 3\ln\left(\frac{\sigma' E}{\Delta p N c}\right)\right] \\ &= k_{\text{B}} N \ln\left(\frac{\tilde{\sigma}}{(hc)^3}\,\frac{V}{N}\left(\frac{E}{N}\right)^3\right) \end{aligned} \quad (25)$$

or

$$E(S,V,N) = \frac{hc}{\tilde{\sigma}^{1/3}} \frac{N^{4/3}}{V^{1/3}} \exp\left(\frac{S}{3k_{\mathrm{B}}N}\right), \quad (26)$$

and therefore we have in analogy with equations (18) and (19)

$$3k_{\mathrm{B}}T = E/N, \quad p = \frac{1}{3}\frac{E}{V} \quad \text{and} \quad pV = Nk_{\mathrm{B}}T. \quad (27)$$

The pressure is thus equal to one third of the energy density, as is also the case for blackbody radiation. However, the entropy of blackbody radiation cannot be directly related to that of an ultra-relativistic gas. The reason lies in the fundamental difference that, in the case of the ultra-relativistic gas, the particle number is assumed to be fixed; no thermal particle creation or annihilation is considered. In contrast, massless photons can be created or annihilated at any temperature.

5. Conclusion

The aim of this presentation is to illustrate, in a concise and transparent manner, the relationship between information-theoretic and thermodynamic quantities. It is indeed remarkable that abstract concepts such as information are intimately connected with familiar physical quantities like pressure and temperature.

The close connection between thermodynamic observables and information-theoretic quantities illustrated in this paper may also be seen as being in the spirit of John Archibald Wheeler's celebrated 'It from Bit' idea: the notion that information is not merely a tool for describing physics, but perhaps one of its most fundamental ingredients.

Data availability statement

No new data were created or analysed in this study.

Author contribution

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Conceptualization (lead), Investigation (lead), Methodology (lead), Writing – original draft (lead), Writing – review & editing (lead)

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