Understanding Entropy

Gibbs and Boltzmann Entropy in Classical and Quantum Mechanics

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Recommended with a commentary by Deepak Dhar, Indian Institute of Science Education and Research, Pune.

The concept of entropy in equilibrium systems has been a part of the standard undergraduate physics curriculum for many decades. As such, one would expect that the basic idea is by now well-established, and unlikely to be revised by the latest advances at the frontiers of science. Unfortunately, this is not true for entropy, when we try to extend the idea to non- equilibrium systems.

For equilibrium systems, there are two well-known definitions of entropy, one due to Boltzmann, and the other due to Gibbs. According to the Boltzmann definition, for an isolated system in equilibrium, for a state Γ of the system, with total energy between E_Γ and $E_\Gamma + \Delta E$, with $\delta E \ll E_\Gamma$, we associate an entropy

$$S_B(\Gamma) = k_B \log \Omega(E_\Gamma), \tag{1}$$

where $\Omega(E_\Gamma)$ is the volume of phase space corresponding to energy lying in the interval $(E_\Gamma, E_\Gamma + \delta E)$, with $\delta E \ll E_\Gamma$. The Gibbs definition is defined in terms of the probability density of the representative point Γ in the phase space. If the system is in thermal equilibrium, say in the canonical ensemble, there is an associated probability density $\rho(\Gamma)$ that the phase point Γ characterizing the system occurs within a small volume $d\Gamma$ of this point. For an ensemble defined by this density, the Gibbs entropy is defined as

$$S_G = -k_B \int d\Gamma \rho(\Gamma) \log \rho(\Gamma), \tag{2}$$

where the integral is over $2N$-dimensional phase space, where N is the number of degrees of freedom of the system. For systems in equilibrium, these definitions can be proved to be equivalent (to leading order in the volume of the system).

In the case of quantum statistical mechanics, for systems in equilibrium, in the microcanonical ensemble, the Boltzmann definition becomes

$$S_{B,qm}^{eq} = k_B \log \Omega_{qm}(E_\Gamma), \tag{3}$$

where $\Omega_{qm}(E_\Gamma)$ is the number of eigenstates of the Hamiltonian in the energy interval $(E_\Gamma, E_\Gamma + \delta E)$. The quantity corresponding to the Gibbs definition is the von Neumann entropy,

$$S_{vN} = -k_B Tr \hat{\rho} \log \hat{\rho}, \tag{4}$$

where $\hat{\rho}$ is the density matrix of the system.

There is another function, that looks similar, and is sometimes discussed in the context of the Second Law. It is the Boltzmann H-function, defined in terms of the 1-particle density function $\rho_1(\vec{r}, \vec{p})$, which gives the number density of particles having positions in a small volume near $\vec{r}$, with momentum in a small range near $\vec{p}$. Then one defines, with $(\vec{r}, \vec{p}) \equiv \Gamma^{(1)}$,

$$F = k_B \int d\Gamma^{(1)} \rho_1(\Gamma^{(1)}) \log \rho_1(\Gamma^{(1)}) \tag{5}$$

Boltzmann showed that, under the hypothesis of *stosszahlansatz*, this function decreases monotonically with time. However, this function *cannot* be identified with the negative of thermodynamic entropy, as it takes same value for different classical non-ideal gases in equilibrium, having same temperature, density, and mass per molecule, independent of the interaction potentials.

Can one extend the notion of entropy to non-equilibrium systems? While some physicists think that we do not need to do this at all, let me note that in the usual formulations of the Second Law in classical
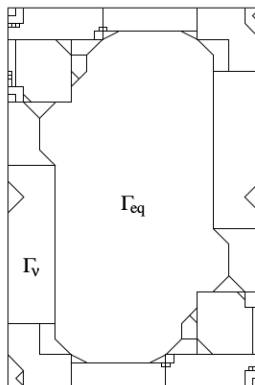
Figure 1: A schematic partition of the constant-energy shell of phase space into macro sets Γ_V , with the thermal equilibrium set taking up most of the volume (not drawn to scale).[from Goldstein et al., Annalen der Physik (2017) 529: 1600301]

thermodynamics (say, "the entropy of an isolated system never decreases"), there is no qualification that one is only dealing with systems with initial and final states in equilibrium. It would restrict the regime of validity of the Second Law enormously, if it only applies when one equilibrium state goes to another equilibrium state. It is desirable to try to extend the notion of entropy to non-equilibrium systems, in a way such that the Second Law continues to be valid.

In this paper, the authors discuss the Boltzmann and Gibbs definitions of entropy, and show that if we want to define the notion of non-equilibrium entropy, an extension of the Boltzmann definition is a good candidate, but a similar extension of the Gibbs definition does not work, and S_G and S_{vN} cannot be taken as the definition of thermodynamic entropy of non-equilibrium systems. Of course, this is not the first time this issue is being discussed. The authors discuss critically earlier approaches. They show that the Boltzmann definition, suitably refined/reinterpreted works, and "von Neumann, Khinchin and Jaynes were all mistaken" (this is a direct quote from the article). If this claim *is* correct, the way we teach entropy at the undergraduate level has to undergo some revision. I have found the arguments of the authors convincing, and hence bring this paper to the attention of our readers.

The first problem with the S_G, or S_{vN}, is that for an isolated system, undergoing evolution under a time independent Hamiltonian, these do not change in time. However, one can easily imagine systems, like a container with two compartment, with a gas from one compartment expanding into the second, initially empty, compartment. For this system, a reasonable definition of entropy should find that as the gas expands, the non-equilibrium entropy increases with time. This clearly does not happen wih S_G, or S_{vN}. This difficulty can be overcome by working with a coarse-grained density function $\tilde{\rho}(\Gamma)$, instead of $\rho(\Gamma)$. But note that this *does* involve changing Eqs. (2) and (4).

The authors note that there is a more philosophic, and perhaps more basic, problem with defining entropy using the approach of Gibbs or von Neumann. By this definition, the entropy is defined for an an ensemble, but not for a single realization. But in classical thermodynamics, entropy is a physical quantity, and 'state function', and should be well-defined for each realization of the system, not only for an ensemble of similarly prepared systems. In the words of Goldstein et al, "while every classical system has a definite phase point X (even if we observers do not know it), a system does not 'have a ρ'; that is, it is not clear which distribution ρ to use."

The Goldstein et al solution for this is to assign to each individual phase point Γ a number equal $\log \Omega(\Gamma)$, where $\Omega(\Gamma)$ is the volume of points in phase space that "macroscopically look the same".

$$S_B(\Gamma) = \log \Omega(\Gamma) \tag{6}$$

The detailed definition of what is macroscopically same makes this somewhat subjective. For example, for a turbulent gas in a box, different microstates described by the same continuum hydrodynamical description,

i.e. same coarse-grained density, velocity and temperature fields, may be treated as looking the same. Then, the constant energy surface is divided into many disjoint sets [Fig.1]. These disjoint sets correspond to macroscopically distinguishable states, and would have very different volumes, corresponding to possibly different entropy densities. In a typical evolution, the representative point moves from a lower volume set to a higher volume set, which is consistent with the Second Law of Thermodyamics. Rare, short-lived fluctuations may take one from a larger set to a smaller set, which are well understood deviations, allowed within the Second Law, and do not signal its breakdown.

For the quantum -mechanical case, they construct the quantum-Boltzmann entropy operator $\hat{S}_{qB}$, whose expectation in any state gives the entropy of that state. The Hilbert space of all states is written as a direct sum of subspaces, where all basis vectors in the subspace are macroscopically similar, and the entropy operator in each subspace is a diagonal operator, equal to Identity matrix times the logarithm of the dimension of the subspace. Then, the quantum entropy operator $\hat{S}_{qB}$ is defined as

$$\hat{S}_{qB} = k_B \sum_{\alpha} \hat{P}_{\alpha} \log \Omega_{\alpha}, \tag{7}$$

where $\hat{P}$ is the projection operator to subspace α, and Ω_{α} is the dimension of the subspace α, and the sum is over all different subspaces α. Note that there is no trace in the equation. For the microcanonical ensemble, the expectation value of this would agree with the Boltzmann definition.

Another problem with the ensemble interpretation that the authors point out is this: Consider a preparation protocol, in which with probability $1/2$, one turns on a heater to heat a sample, and with probability $1/2$, the heater is not turned on. Then, it makes sense to say that with probability $1/2$, the system will be in a high entropy state, say entropy S_1, and else in a lower entropy state with entropy S_2. The formalism for the calculation of entropy should be able to reflect this. But, in the ensemble description, the state is characterized by a phase space density (or density matrix), that is the arithmatic average of the density functions corresponding to the two states. The calculated entropy will only give a single value S_3, which is only a bit more than the average entropy $(S_1 + S_2)/2$. But S_3 is only the average entropy, it is never the observed value of the entropy of the system: it is either S_1, or S_2. It is not clear how one can describe such situations within the Gibbs prescription.

A part of the discussion in the paper is about entropy in the Bohmian version of quantum mechanics, a version that the authors feel partial to. Even for readers not so fond of Bohmian quantum mechanics, the article gives adequate food for thought.