In his treatise *Statistical Thermodynamics*, Erwin Schrödinger declares “There is, essentially, only one problem in statistical thermodynamics: the distribution of a given amount of energy E over N identical systems.” In the following we shall take “systems” to mean molecules and the “distribution” to mean the allocation of energy over N molecules of an isolated ideal gas at equilibrium.

Equilibrium is a fundamental concept of thermodynamics and denotes a stationary state toward which an isolated system evolves. The concept has its origins in classical thermodynamics and was adapted to statistical thermodynamics by Ludwig Boltzmann, who defined equilibrium as the most probable “state distribution” (macrostate), where each macrostate is defined as a set of “permutations” (microstates). Boltzmann [1877] states

> The initial [macro]state in most cases is bound to be highly improbable and from it the system will always rapidly approach a more probable state until it finally reaches *the most probable state, i.e., that of the heat equilibrium.* [italics added]

This definition of equilibrium has gained universal acceptance in the field of statistical mechanics. However, it is contradicted by a paper by Brian Zhang entitled “Coconuts and Islanders” [2019], which shows that macrostates are not necessary for the derivation of the energy distribution.

The most probable macrostate of the energy distribution

Boltzmann [1877] was the first to propose a model which postulates the allocation of discrete energy elements to each molecule, foreshadowing quantum theory. He illustrates this with the numerical example of $M = N = 7$, where M (his λ) is the number of kinetic energy units of energy ϵ. The energy units are distributed among the N molecules such that the total energy E (his L) equals $M\epsilon$. His calculations are displayed in a table listing the microstate count for each of the macrostates whose energy equals the total energy. In his example the most probable macrostate is the one with 420 microstates. Since the total number of microstates is 1716, the probability of the most probable macrostate is $P_{MP} = 420/1716 = .2448$.

To determine how P_{MP} progresses with increasing N, the following results were calculated using the same methodology.

For $M = N = 6$, $P_{MP} = .2597$.

For $M = N = 8$, $P_{MP} = .1740$.

For $M = N = 9$, $P_{MP} = .1555$.

For $M = N = 10$, $P_{MP} = .1364$.

Since P_{MP} monotonically decreases with $M = N$, we can assume that it approaches zero for large values of these variables.

The decreasing probability P_{MP} as N increases implies that the entropy of the most probable macrostate is inadequate for determining the correct entropy, which instead must include all accessible microstates. For the discrete energy distribution, Boltzmann gives the total number of microstates as

$$W_{Tot} = \frac{(M+N-1)!}{M!\,(N-1)!}.$$

For $M = N = 7$, this results in $W_{Tot} = 1716$.

The notion that the most probable macrostate is an attracter toward which the system evolves is contradicted by the vanishingly small probability of the most probable macrostate as N increases, since if the system were by chance in the most probable macrostate, the probability of the system being found in some other macrostate at a later (or former) time approaches unity for large N.

Macrostates are epistemic products of the imagination, mathematical constructs with no physical instantiation. On the other hand, microstates represent particular physical configurations and are ontic representations of the spatial or energy distributions of the molecules. Since in Boltzmann's formulation the current microstate is independent of prior microstates, there is no possibility of a transport equation which describes the evolution of the system over time. (Boltzmann's *H* theorem is a mathematical artifact that was designed to give him the answer he wanted, and bears no relation to the physical interactions of molecules in an ideal gas.)

Coconuts and islanders

Zhang [2019] takes a similar approach to Boltzmann [1877], although with important differences. Zhang's paper describes a model of the energy distribution involving the allocation of coconuts (energy elements) to islanders (molecules). Zhang makes no use of statistical macrostates and calculates the total number of microstates as

$$\Omega_{Tot} = \frac{(M + N - 1)!}{M!\,(N - 1)!},$$

the same as for Boltzmann. However, Zhang models the allocation of coconuts as a Markov process which provides a transport equation. Along the way he proves that the microstates must be equiprobable at equilibrium, which obviates the need for the "fundamental postulate" of a priori equiprobability to be taken on faith, as claimed by virtually all textbooks (see, for example, C. Garrod, *Statistical Mechanics and Thermodynamics* [1995], p. 39). As illustrated by his simulation, his model evolves toward *statistical stationarity*, which is distinct from Boltzmann's equilibrium in that it involves all accessible microstates, not just those of the most probable macrostate.

The evolution of the system towards equilibrium specifies the direction of time, illustrating the second law of thermodynamics. The coconut distribution exhibits positive skewness since if one or both of the islanders has no coconuts, no exchange takes place. The Markov process can therefore be described as a random walk against a barrier.

Zhang differs from Boltzmann in that the latter focuses on the most probable macrostate while the former makes no use of macrostates and bases his analysis on the microstates only. The two approaches yield the same result for the energy distribution, since the most probable macrostate is representative of the overall microstate distribution. However, the entropies of the two approaches differ significantly and will diverge as N increases.

Conclusion

The Boltzmann model fails at each of its goals: to define equilibrium and equilibrium entropy properly, to provide a transport equation and to supply a plausible basis for the second law. Zhang's energy model accomplishes all three by relying only on *physical* microstates and ignoring *epistemic* macrostates.

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