Equilibrium is the fundamental concept of thermodynamics, denoting 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 equated equilibrium to the most probable *macrostate*, where a macrostate is defined as a particular set of *microstates*. The equilibrium macrostate was described by Boltzmann [1877] as an attractor, since “The system of particles always changes from an improbable to a probable [macro]state.”

However, this assertion is contradicted by his model, for which the probability of the current macrostate is *not* conditioned on the prior macrostate(s) and the macrostate probability is not a function of time. This means that, according to his model, the probability of being in a particular macrostate at any given time is the same as its probability at any other time.

While Boltzmann applied this rationale to the velocity/energy distributions of an ideal gas, subsequent authors of textbooks on statistical mechanics extrapolated his reasoning to the spatial distribution of molecules. A common example postulates an isolated box of an ideal gas composed of N identical distinguishable molecules, where the probability of finding n molecules in the right (or left) half of the box is given by the binomial distribution. In this case, the most probable macrostate is the uniform distribution of molecules, where $N/2$ molecules are in each half of the box.

The above is based on the implicit assumption that *N* is even. If *N* is odd, there are *two* most probable macrostates instead of one. So for a single most probable macrostate to exist, *N* must be even.

Boltzmann designated *Z* as the number of microstates in a particular macrostate, which he called the “relative probability”. Z was later changed to *W* by Planck, which has been the common usage ever since. Since the microstates are presumed to be equally probable, the relative probability of the most probable macrostate (for even values of *N*) is

$$W_{MP} = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}$$

Since the total number of microstates for the binomial distribution is $W_{Tot} = 2^N$, the true probability of the most probable macrostate is $P_{MP} = W_{MP} / W_{Tot}$ or

$$P_{MP} = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!\,2^N}$$

Boltzmann claimed that P_{MP} approaches one for large values of *N*, a contention that has been faithfully replicated in all subsequent textbooks.

To test this claim, we can calculate the number of microstates included in the *next* most probable macrostate, which is given as

$$W_{NMP} = \frac{N!}{\left(\frac{N}{2}+1\right)!\left(\frac{N}{2}-1\right)!}$$

This represents the displacement of a single molecule from one half of the box to the other half. The ratio of the most probable macrostate to the next most probable macrostate is therefore

$$R = \frac{\left(\frac{N}{2}+1\right)!\left(\frac{N}{2}-1\right)!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} = \frac{N+2}{N}$$

Since R approaches one as N increases, it is clear that P_{MP} *cannot simultaneously do the same. This ratio is not mentioned in any of the textbooks or papers that I have reviewed over the last 20+ years.*

To verify this conclusion, we can investigate the progression of probabilities for small values of *N*.

For $N = 2$, $P_{MP} = 1/2$.

For $N = 4$, $P_{MP} = 3/8$.

For $N = 6$, $P_{MP} = 5/16$, etc.

It can be seen that P_{MP} decreases monotonically with N, so that instead of approaching one, as Boltzmann claims, it approaches zero.

This was first noticed by John Arbuthnott in 1710 while investigating the sex ratio of births. It's first mention in the context of statistical mechanics was in a paper by Ernst Zermelo from 1896.   Boltzmann's reply encapsulates their disagreement.

> Whereas Zermelo says that the number of [micro]states that finally lead to the Maxwellian state is small compared to all possible [micro]states, I assert on the contrary that by far the largest number of [micro]states are "Maxwellian" and that the number that deviate from the Maxwellian state is vanishingly small.

Neither Zermelo nor Boltzmann provided mathematical justification for their claims, but the formula for the probability of the most probable macrostate can easily be approximated by applying Stirling's formula to the above equation, yielding

$$P_{MP} \approx \sqrt{\frac{2}{\pi N}}$$

for large N. So for N = 100, $P_{MP} \approx .0798$, confirming both Arbuthnott's observation and Zermelo's assertion.

For the general case of the multinomial distribution, where M is the number of individual states or cells, the total number of microstates is $W_{Tot} = M^N$ and the probability of the most probable macrostate is given by

$$P_{MP} \approx \sqrt{\frac{M^M}{(2\pi N)^{M-1}}}$$

For instance, if we divide our box of gas into 4 cells of equal size, $M = 4$. For $N = 100$, $P_{MP} \approx .0010$, so P_{MP} converges to zero much faster than for $M = 2$.

While the above only applies to the spatial distribution of molecules, examination of the energy distribution yields similar results. There are a variety of ways that the decreasing value of P_{MP} with increasing N an be deduced. However, a review of a number of statistical thermodynamics textbooks finds that none of these alternatives have been explored. The orthodox interpretation is that $W_{MP} / W_{Tot} \longrightarrow 1$ for large N, whereas in fact $W_{MP} / W_{Tot} \longrightarrow 0$. Boltzmann's misconception has been faithfully passed down through generations of physicists over the past century and a half, a classic example of what Daniel Kahneman calls "theory blindness", whereby a widely accepted theory dissuades subsequent researchers from considering alternatives.

In summary, Boltzmann's definition of equilibrium is untenable since it simultaneously implies that being in his definition of equilibrium is virtually impossible. This implies that the entropy should incorporate all possible microstates, not just those encompassed by the most probable macrostate. The irrelevance of macrostates renders meaningless the concept of progression through a sequence of macrostates of increasing probability. In addition, any such illusion of progression would be due entirely to regression toward the mean, a statistical artifact of no relevance to the direction of time.

Addendum

It has been suggested that the equilibrium state, while centered on the most probable macrostate, also includes "nearby" macrostates, so that for large N, the probability of being in equilibrium approaches unity. However, this is inconsistent with Boltzmann's definition of the entropy at equilibrium, given by $S_{eq} = k \ln W_{mp}$, where W_{mp} is the number of microstates included in the *single* most probable macrostate. Boltzmann is unequivocal on this point and nowhere in his writings does he suggest that nearby macrostates be included.

Conversely, if the probability of being in equilibrium were to *increase* with N, as Boltzmann believed, the number of microstates included in the most probable macrostate would necessarily approach the total number of microstates in the system. The entropy would then approach $S_{eq} = k \ln 2^N$ and the most probable macrostate would therefore be irrelevant to the concept of equilibrium.

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