Roles for local crowding and pressure in counteracting density fluctuations at equilibrium

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Universite de Rennes1-IRSET. Campus de Beaulieu Bat. 13.
35042 Rennes cedex. denis.michel@live.fr

Abstract What is the probability that all the gas in a box accumulates in the same half of this box? Thought amusing, this question underlies the fundamental problem of density fluctuations in equilibrium, which has profound implementations in many physical fields. The currently accepted solutions are derived from the studies of Brownian motion by Smoluchowski, but they are not appropriate for the directly colliding particles of gases. Two alternative theories are proposed here using self-regulatory Bernouilli distributions. A quantum of space is first introduced to develop a mechanism of matter congestion holding for high densities. In a second mechanism valid in Maxwell-Boltzmann conditions, the influence of local pressure on the location of every particle is examined using classical laws of ideal gases. This approach reveals that a negative feedback results from the reciprocal influences between individual particles and the population of particles, which strongly reduces the probability of atypical microstates. Finally, a thermodynamic quantum of time is defined ($h/4k_BT$) to compare the recurrence times of improbable macrostates predicted through these different approaches.

Keywords: Recurrence time; rare macrostates; density fluctuations; quantum of time.

1 Introduction

If you stand in one side of a closed room and that all the air suddenly accumulates on the other side, you would fatally suffer from depressurization. Yet nobody seems afraid by this horrible scenario. People without notions of statistical mechanics just feel that this is impossible. Statistical physicists consider that this situation is improbable, but so improbable that it is completely negligible. In fact, this probability has never been exactly calculated. This question touches the long standing paradox of macroscopic transitions considered at first glance as irreversible but underlain by microscopic reversibility. New and rigorous calculations will be presented in this article to quantify the recurrences times of Poincaré.

2 Macro-irreversibility resulting from micro-reversible processes

According to the second law of thermodynamics, macrosystem evolutions can be classified into reversible and irreversible ones. From a statistical perspective, irreversible transitions transform macrostates covering a lower number of microstates (less probable) into macrostates covering a higher number of microstates (more probable). A simple example is the expansion in a box of a gas previously confined in a small subvolume after removal of a partition membrane. This rational principle of irreversibility however raised concerns, particularly vehement from Zermelo [1]. For historical reviews on these debates, see [2, 3]. The Loschmidt reversibility paradox [4] stressed that since all microscopic changes are reversible, there is no reason for an ensemble of microscopic changes to be not reversible. This view is supported by the recurrence theorem of Poincaré, which states that any very improbable state, such as a well organized initial state, will necessarily reappear, given sufficient time [5]. Considering the example of gas expansion described above, such an event would be the reclustering of gas particles in a small region of the box. Moreover, as this state will reappear once, it will reappear infinitly often, giving rise to a quasi-periodic phenomenon. The right question is not whether this event can occur or not, but how often it reproduces. As pointed by Zermelo, this paradox ruins the idea of irreversibility. The answer of Boltzmann to Zermelo was: "*Young man, you know mathematics but you don't know physics. Think how long it takes for that to happen? It would take far longer than the age of the universe even for a very small system*". For his calculus, Bolzmann used the example of 1 cm^3 of gas with the assumptions, somewhat puzzling, that the system passes through all its microstates before recurrence and that 10^{27} different microstates take place in one second. To test the answer of Boltzmann, a very small system and the universe age unit will be used at the end of this study. Indeed, the disconnection between realistic observation time windows and the recurrence waiting times would be an excellent argument, but in fact the parameter of time is absent from the microstate enumerations of Boltzmann and this point has never been really quantified. Moreover, the theory generally believed to address this point, that of Smoluchowski, is inappropriate to quantify recurrence periods for self-colliding systems such as gases.

3 Traditional modeling

A traditional tool of statistical mechanics is a box of volume V containing N randomly distributed particles. In this box, the number of particles x present in a subvolume v is subject to fluctuations around a mean value Nv/V. The probability that $x = n$ is currently given by a simple Bernouilli distribution:

$$P(x = n) = \binom{N}{n} \left(\frac{v}{V}\right)^n \left(1 - \frac{v}{V}\right)^{N-n} \tag{1}$$

which says that the probability of location of a single particle is dictated by the fraction of available volumes only [6]. This admitted result can however be questioned because it neglects both particle exclusion and pressure and is valid only for very low densities. The available space is more and more reduced as density increases. As a consequence, Eq.(1)

overestimates the probability of atypical microstates such as those in which near all the particles are in the same side of the box. The absence of consideration for concentrations is well illustrated when $v = V/2$ since in this case, Eq.(1) reduces to $P(x = n) = \binom{N}{n}/2^N$, that is manifestly independent of densities. Two mechanisms are proposed below to restore a role for the relative particle density in the compartments: (**i**) the bulk or congestion hypothesis, only appreciable for highly concentrated systems, and (**ii**) the pressure hypothesis, important for gases in ordinary conditions and dramatically missing in the current approaches to density fluctuations. But let us first point out the assumptions of Smoluchowski which are inappropriate for gases.

4 Brownian motion vs mutual collision

The celebrated study of Smoluchowski on density fluctuations in a medium of constant average density [8], is far from general. Smoluchowski's calculations were celebrated because they remarkably fitted the experiment of Svedberg on particles moving through Brownian motion [9]. But Brownian motion does not result from mutual collisions. The difference is enormous since the main starting assumption of Smoluchowski is that the motions of the different particles are not mutually influenced, so that all possible individual positions have equal *a priori* probabilities. With respect to the problem of density fluctuations, this assumption implies that the probability of entrance of particles in any subvolume, does not depend on the number of particles already contained in it. Accordingly, the basic ingredient used by Smoluchowski was a Poisson distribution $P(x = n) = \nu^n \mathrm{e}^{-\nu}/n!$ corresponding to the limit of the binomial formula of Eq.(1) for very large N and V and a mean value $\nu = Nv/V$. The movements of colloids are the resultant of huge numbers of collisions with solvent molecules but not of direct collisions between the suspended substances. Moreover, the motion of these substances is buffered by surrounding solvent molecules, so that they are not transferred to the other suspended particles, thereby ensuring the mutual independence of these particles and their insensitivity to crowding and pressure. This independence no longer applies to systems made of mutually colliding particles. In sharp constrast, the motion of gas particles is determined by collisions with other gas particles. A very interesting consequence of this situation is that every individual particle is both (**i**) an actor of the collective effect known as pressure, and (**ii**) a receptor of this pressure which influences its own location. These reciprocal influences between the individual and the population is the essence of statistical mechanics and should appear in the formulation of density fluctuations, contrary to Eq.(1) and to the assumptions of Smoluchowski.

5 The congestion mechanism for dense systems

The description of this mechanism necessitates discretizing space. The discretization of space allows to reconcile the classical approaches to statistical dynamics with the principle of spatial exclusion. Indeed, the pioneer versions of the ideal gas theories ignored the size of the particles, which were conceived as superposable points whose number is defined in $\mathbb{N}$, scattered in continuous volumes defined in $\mathbb{R}^3$. Hence, considering $V^N/N!$ as a number

of microstates, as often found in the literature, is formally erroneous. This problem can be solved by discretizing space.

5.1 Quantum of space

The concepts of volume per particle and of mutual exclusion have been introduced in more elaborated versions of kinetic theories, for instance to describe transportation properties such as viscosity, diffusion and thermal conductibility. Moreover, a thermal Planck volume has then been defined as the volume necessary to include a single particle at given temperature, shape and mass, with a mean momentum p. For elementary particles, λ is the thermal wavelength of de Broglie $\lambda = h/p = h/\sqrt{2\pi m k_B T}$ where h is the Planck constant, k_B the Boltzmann constant and T the temperature. This elementary volume allows to define discrete volumes corresponding to the integers closer to V/λ^3. In addition to solve the Gibbs paradox (Michel, submitted), this space discretization can also be useful for calculating fluctuation densities of concentrated systems for which the volume occupied by the particles cannot be neglected.

5.2 Fluctuation probabilities of dense systems

This theory applies to any dense system, including suspensions. If the volumes v and V contain n and $(N-n)$ particles respectively, the probability for a $(N+1)$th particle to be in v is not v/V as assumed in Eq.(1), but $(v-n\lambda^3)/(V-N\lambda^3)$. This difference is of course negligible when V is very large compared to $N\lambda^3$, but not for dense systems. When the intrinsic volume of particles is no longer negligible, the general probability that n particles are present in v can be obtained after defining unitless volumes $\acute{V} = V/\lambda^3$ and $\acute{v} = v/\lambda^3$. This discretization does not forbid using Eq.(1), rewritten for the circumstance

$$P(x=n) = \binom{N}{n} \frac{\acute{v}^n (\acute{V}-\acute{v})^{N-n}}{\acute{V}^N} \tag{2}$$

In this equation, the exponents mean that the entry of a particle in one compartment does not depend on the number of particles already in this compartment. But if minimal space per particle is not negligible, when one a particle in present, $\acute{v}-1$ places remain free; when 2 particles are present, $\acute{v}-2$ places are available etc. Hence, Eq.(2) becomes

$$P(x=n) = \binom{N}{n} \frac{[\acute{v}(\acute{v}-1)...(\acute{v}-n+1)][(\acute{V}-\acute{v})(\acute{V}-\acute{v}-1)...(\acute{V}-\acute{v}-N+n+1)]}{\acute{V}(\acute{V}-1)...(\acute{V}-N+1)} \tag{3}$$

that can be rewritten

$$P(x=n) = \binom{\acute{v}}{n}\binom{\acute{V}-\acute{v}}{N-n} \Big/ \binom{\acute{V}}{N} \tag{4}$$

Note that instead of starting from Eq.(1), the result can be conceived directly from Eq.(4) which describes the number of ways to distribute n and $(N-n)$ particles in $\acute{v}$ and $(\acute{V}-\acute{v})$ cells respectively, among a total number of possible distributions of N particles over $\acute{V}$ cells. Eq.(4) is intrinsically normalized, as should be a probability density function, since

$$\sum_{i=0}^{k} \binom{a}{i}\binom{b}{k-i} = \binom{a+b}{k} \tag{5}$$

One can verify that Eq.(1) is recovered when the particles are very scarce in a very large volume. Indeed, Eq.(3) can be rearranged as

$$P(x=n) = \binom{N}{n} \frac{\acute{v}^n (\acute{V}-\acute{v})^{N-n}}{\acute{V}^N} R \tag{6}$$

with

$$R = \frac{\left[\left(1-\frac{1}{\acute{v}}\right)\left(1-\frac{2}{\acute{v}}\right)...\left(1-\frac{\acute{v}-n+1}{\acute{v}}\right)\right]\left[\left(1-\frac{1}{\acute{V}-\acute{v}}\right)\left(1-\frac{2}{\acute{V}-\acute{v}}\right)...\left(1-\frac{N-n+1}{\acute{V}-\acute{v}}\right)\right]}{\left[\left(1-\frac{1}{\acute{V}}\right)\left(1-\frac{2}{\acute{V}}\right)...\left(1-\frac{N+1}{\acute{V}}\right)\right]} \tag{7}$$

If $\acute{V} >> N$, it is likely that $\acute{v} >> n$ and then that $(\acute{V}-\acute{v}) >> (N-n)$, so that $R \sim 1$. Then, Eq.(6) reduces to Eq.(2) and to Eq.(1) since the λ^3 factor disappears.

A satisfactory behaviour of Eq.(4) is that the probabilities of typical configurations is higher than for Eq.(1), while those of highly asymmetric configurations are much lower (Fig.1). However, this difference is only marginal for moderately dense systems. It can be strikingly increased by introducing a role for local pressures in particle distribution.

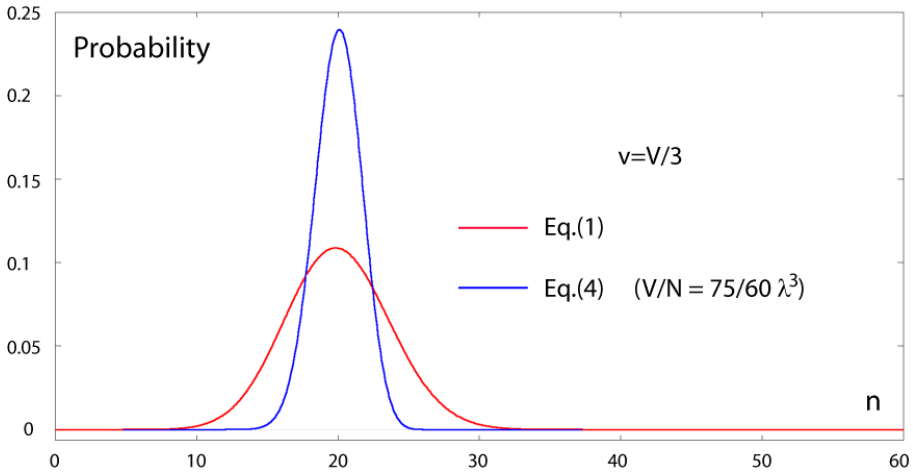


Figure 1. Comparative results of Eqs(1) and (4). For a small but dense system made of 60 particles running and colliding in a box of $V/\lambda^3 = 75$ cells, the curves represent the probabilities of finding n particles in a subvolume of 25 cells, calculated using either Eq.(1) (red) or Eq.(4) (blue, darker). Eq.(1) underestimates the symmetric microstates around the mean density $n = 20$ ($n = Nv/V$) and conversely overestimates the probability of the asymmetric microstates, because it does not take into account the intrinsic volumes of the particles.

6 The pressure feedback

Suppose that a box contains N particles, out of which n are present in a subvolume v and $(N-n)$ are in the remaining volume $(V-v)$. As previously, these compartments are defined

conceptually and are not enclosed by any physical boundary. Now imagine the fate of a single particle present at the interface between v and $(V-v)$. To determine the probability that this particle enters either v or $(V-v)$, it is reasonably not acceptable to neglect the influence of the relative densities in these subvolumes, because of the associated probability of expulsive collisions. This parameter is related to pressure. A crude modeling attempt is proposed to illustrate the consequence of incorporating this parameter, as follows. Pressure represents the density of collisions, itself proportional to the density of the particles $(\frac{N}{V})$ at given temperature (because $P = \frac{N}{V}k_BT$). The probability (written below $P[\in ...]$) for any particle to enter one compartment rather than the other one, is a function of the competitive propensities of these compartments to recruit this particle. These propensities are named F_v and F_{V-v} for the compartments v and $(V-v)$ respectively. Given that they should be normalized to 1 over the whole box, these probabilities take the forms

$$P[\in v] = \frac{F_v}{F_v + F_{V-v}} \tag{8a}$$

and

$$P[\in (V-v)] = \frac{F_{V-v}}{F_v + F_{V-v}} \tag{8b}$$

The propensity to incorporate a particle should now be defined. It seems rational to postulate that F is the product of two parameters which concur equally to take up a particle, which are:

- The fractional volume available in the absorbing compartment (the only parameter considered in Eq.(1)), whose values are $\frac{v}{V}$ for the compartment v and $\left(1-\frac{v}{V}\right)$ for the compartment $(V-v)$.
- The fractional pressure in the rejecting compartment, equivalent to the outside fractional particule density, whose values are here $\frac{(N-n)/(V-v)}{N/V} = \left(1-\frac{n}{N}\right) / \left(1-\frac{v}{V}\right)$ for the compartment v and $\frac{n/v}{N/V} = \left(\frac{n}{N}\right) / \left(\frac{v}{V}\right)$ for the compartment $(V-v)$.

Introducing these values into Eq.(8) gives

$$P[\in v] = \frac{\left(1-\frac{n}{N}\right)\left(\frac{v}{V}\right)^2}{\left(1-\frac{n}{N}\right)\left(\frac{v}{V}\right)^2 + \left(\frac{n}{N}\right)\left(1-\frac{v}{V}\right)^2} \tag{9a}$$

and

$$P[\in (V-v)] = \frac{\left(\frac{n}{N}\right)\left(1-\frac{v}{V}\right)^2}{\left(1-\frac{n}{N}\right)\left(\frac{v}{V}\right)^2 + \left(\frac{n}{N}\right)\left(1-\frac{v}{V}\right)^2} \tag{9b}$$

These equations satisfactorily simplify in singular situations. If the density in v is the same as in $(V-v)$, that is to say when $n = Nv/V$, one obtains

$$P[\in v] = \frac{v}{V} \tag{10a}$$

and

$$P[\in (V-v)] = 1 - \frac{v}{V} \tag{10b}$$

which are simply the probabilities used in Eq.(1). Reciprocally, if the compartments have the same volume ($v = V/2$), then the probabilities become only dependent on the number of particles in these compartments, as expected

$$P[\in v] = 1 - \frac{n}{N} \tag{11a}$$

and

$$P[\in (V - v)] = \frac{n}{N} \tag{11b}$$

This result, symmetric to the previous one found when the number of particles does not matter, is valid for moderate fluctuation ranges around $n = N/2$ and relevant for ordinary macroscopic systems. The next step of the reasoning is to understand that every individual particle can be considered as the Nth component of a population already containing all others, so that all the particles are equally submitted to Eq.(9), which are functions of n ranging from 0 to N and v ranging from 0 to V. A factor 2 is introduced for normalization of the probability that n particles are present in v, yielding the completely developped equation

$$P(x = n) = 2\binom{N}{n}\left(\frac{(N-n)v^2}{(N-n)v^2 + n(V-v)^2}\right)^n\left(\frac{n(V-v)^2}{(N-n)v^2 + n(V-v)^2}\right)^{N-n} \tag{12}$$

This equation holds when $V >> N$, otherwise it requires introducing the bulk approach described previously. Eq.(12) is a self-regulatory Bernoulli distribution embodying the circular influence between individuals and the population, which is a negative feedback. This negative feedback severely readjusts any deviation from equipartition back to equipartition, with a strength even stronger when the gap is large. Numerical application reveals that Eq.(12) tolerates very much less than Eq.(1) atypical microstates such as the strongly asymmetric ones containing few particles in v or $(V - v)$. To concretely conceive this point, if all the particles are already present in the left half of the box (a purely theoretical hypothesis), then the probabilities for an additional particle to enter either the left or right halves are not 1/2 and 1/2 as in Smoluchowski's theory, since there is near 100% chance that it bounces back in the empty side.

7 Recurrence times

Strongly asymmetric distributions are supposed to be so improbable that they never occur. Physically speaking, the recurrence time of Poincaré of extreme microstates is expected to exceed all possible observation windows. However, to formally establish this point, it is first necessary to define the time step separating two different configurations in a box of gaz. Indeed, if particle trajectories are conceived as continuous, then any time window δt, as short as desired, is expected to contain an infinite number of configurations. As noticed by Zermelo, probabilities do not contain temporal terms. This problem forebids the calculation of recurrence times and contradicts the finite number of configurations ($V/N!\lambda^3$) assumed in the Sackur-Tetrode equation. Once again, discretization (in this case of time) can save us.

7.1 Thermal quantum of time

The goal is now to define the time step τ separating two consecutive configurations. There is no reason to define this step as a function of the collisions since it is expected to not depend on the density of a gas at given temperature. Instead, it is proposed here that this quantum of time is the time necessary to cross the length unit below which successive configurations cannot be distinguished, because of the uncertainty principle. This is precisely what is the thermal wavelength of de Broglie λ. Hence, for a mean particle velocity $\langle v \rangle = \sqrt{8k_BT/\pi m}$ obtained by averaging the velocities distribution [11], one obtains

$$\tau = \frac{\lambda}{\langle v \rangle} = \frac{h}{4k_BT} = 4 \times 10^{-14} \text{ s at } T = 300 \text{ K} \tag{13}$$

Recurrence times can now be calculated.

7.2 Calculation of recurrence times

7.2.1 For a microstate

A microstate of probability $P = 1/\Omega$, is expected to reappear after a mean waiting time $\langle T \rangle = \Omega\tau$, regardless of the initial observation time.

7.2.2 For a macrostate

A macrostate covers a certain number of microstates giving the same macroscopic outcome X; for example those in which all the particles are in the same half of a box. The probability of a macrostate X is the fraction of these microstates $P_X = \Omega_X/\Omega$. The mean recurrence time of a macrostate is of course lower than those of its constituent microstates, such that

$$\langle T \rangle_X = \frac{\Omega}{\Omega_X}\tau = \frac{\tau}{P_X} \tag{14}$$

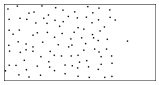
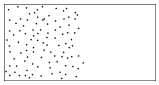
Strictly speaking, $\langle T \rangle_X$ is not a period because rare events are not regularly spaced in time contrary to the numerical estimate of Boltzmann. Given the memoryless nature of transitions resulting from numerous chaotic collisions [12], the probability that a given state occurs before t is

$$P(X \leq t) = 1 - \mathrm{e}^{t/\langle T \rangle_X} \tag{15}$$

To get a concrete idea of the potency of Eq.(12) compared to Eq.(1), the recurrence times expected from the classical and the pressure approaches, are compared in the case of the distribution of only 100 gas particles (Table 1). Results are obtained by integrating the probability density functions Eqs(1) and (12).

The system considered in Table 1 is very small since it corresponds to only 0.37 billionth of a picoliter of gas under one atmosphere, but it is however sufficient to reveal the astonishing gap between the predictions of Eq.(1) and Eq.(12). Even when using the time step arbitrarily used by Boltzmann (10^{-25} s) which is many times shorter than τ used here, the former calculation gives amazingly smaller recurrence times. This difference results from the introduction of a role, so far neglected, for pressure. When taking this role into account,

Table 1: Recurrence times of atypical macrostates in which more than 90 out of 100 particles are confined in 3/4 or 1/2 box. The results shown are obtained with the classical approach (Eq.(1)) and with the pressure feedback model examined here (Eq.(12))(Note that the unit of age of the universe is used in reference to the response of Boltzmann to Zermelo quoted previously, but it is purely illustrative and not very rigorous since τ is likely to have been much shorter in the primordial universe).

Macrostate	Model	Recurrence time
	Eq.(1)	0.5 nanosecond
$\geq 90\%$ particles in 3/4 of the box	Eq.(12)	2 hours 45 minutes
	Eq.(1)	1 hour 47 minutes
$\geq 90\%$ particles in a half-box	Eq.(12)	10^{47} universe ages

recurrence times of Poincaré, even for very small systems, become purely mathematical but no longer physical, in agreement with the response of Boltzmann to Zermelo, thus restoring the idea of macroscopic irreversibility.

8 Discussion

The tool of discretization is used twice in this study: for space in the bulk approach, and for time for measuring recurrence times. The discretization of physical parameters previously conceived as continuous, is illustrated by the Planck's constant and long proved successful by allowing to get rid of dimensions in mathematical treatments and, incidentally, opened the way to quantum mechanics. As established for matter since Boltzmann, and for energy since Planck and Einstein, the continuous appearance of space and time could be also, after all, only illusions resulting from scale separation. Anyway, their discretization allows to generalize the use of powerful discrete probabilities. Following the advice of Mark Kac, for finding a lot of solutions in mathematical physics, "Be wise, discretize!". The thermodynamic quantum of time $h/4k_BT$ defined and used in this article is satisfactory enough in that it is universal, only dependent on temperature but not on parameters such as specific densities and masses. This time step could be very useful to make the connection between probabilities and time. It is important to precise that this time step is microscopic and reversible, valid as well in equilibrium and nonequilibrium situations. In this respect, it should not be confused with the thermodynamic arrow of time, which is macroscopic by nature and defined by the tendency of equilibration [13]. For example, the arrow of time, but not time steps, disappears for resting water in a bucket, in spite of its incessant microscopic movements.
It is shown here that the propensity of dynamic systems to homogenize is much stronger than previously anticipated. The new formulations provided are original and highlight the

reciprocal influences between individuals and the population which are a fundament of statistical mechanics. This study formally quantifies and further supports the probabilistic view of Boltzmann without denying the existence of fluctuations. The fluctuation theorem saying that microscopic fluctuations cause local decreases in entropy even in isolated systems, misleadingly connects microscopic phenomena to entropy, whereas Boltzmann clearly indicated that this notion is purely macroscopic and meaningless at the microscopic scale. The present study also provides tools for explicitly quantifying the nonphysical status of the Poincaré recurrence theorem. According to this theorem, after sufficiently long time, any finite system can turn into a state which is very close to its initial state, which means that the second law of thermodynamics will be broken in even macroscopic scale. But only brains of mathematicians can be not impressed by the value of the "sufficiently long time" given by Eq.(12) in Table 1. Mathematical modeling of physical phenomena, though incomplete, is certainly one of the noblest successes of humankind, but care should be taken, particularly in the field of probabilities, to always distinguish between mathematics and physics, following the recommendation of Boltzmann. For instance, certain asymptotes which are never reached from a mathematical viewpoint, are reached in the real world. Conversely, infinitesimal probabilities which exist mathematically, must be translated as "never" in the real world.

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