The evolution of a 2D ideal gas toward the state of thermodynamic equilibrium
The Boltzmann's H-theorem - The Maxwell-Boltzmann distribution

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Synopsis

In this work we describe the theoretical model of an ideal 2-dimensional gas. The velocity probability density function is defined and its evolution with time is derived. This has been accomplished by means of a "master" equation[1,2] which expresses the variation of the velocity probability density function caused by the mutual interactions of the particles. From the master equation we derive the condition satisfied by the probability density in the equilibrium state, and we formulate its analytic expression: the Maxwell-Boltzmann (M-B) distribution. Then, we formulate the Boltzmann's H-theorem. We prove that the velocity probability density function converges with time to the M-B distribution, independently on the initial velocity distribution of the gas.

In the virtual environment of the simulation the user can test experimentally the Boltzmann H-theorem in the case of a 2-dimensional ideal gas. He can check in real time if the particles' velocity probability distribution converges with time to the Maxwell-Boltzmann distribution, irrespectively of the analytic form of the initial distribution.

Open the simulation here: **The evolution of a 2-dimensional ideal gas toward the equilibrium state. The Boltzmann H-theorem**

Key concepts and relationships

Probability - Event - Sample space - Random variable - Probability density - Distribution of a random variable - Uniform distribution - Master equation - Maxwell-Boltzmann distribution – Steady state of a dynamical system - Boltzmann's H functional

Contents

A) Preliminary knowledge - Description of the model and the main features of the application

The 2-dimensional ideal gas is consisted by an aggregate of N discrete particles moving in a plane container of dimensions $L \times L$. Each particle has the form of a disk with radius r and mass m. We correspond to each particle an integer j=0,1,2…N-1.

The particles interact with each other and with the walls of the container. The interactions with the walls are elastic collisions. The mutual interactions of the particles take place among

couples of particles. In each interaction the total linear momentum and the energy of the couple are conserved. According to our model, the particles of a couple interact when the distance of their centers is getting less than $s \cdot r$ where s is a coefficient controlling the scope of the interaction (see paragraph "**The items, the graphs, and the tools of the simulation**"). Then, strong repelling forces obeying Newton's third law are exerted on the particles. The duration of each interaction is negligible compared with the time passing among two successive interactions (see paragraph: "**How do the particles interact?**"). Between two successive interactions, each particle moves with constant velocity.

The positions (X_j, Y_j) and the velocities (V_{jx}, V_{jy}) of the particles (the centers of the disks) are random variables(4). They are calculated in the inertial reference frame Oxy: the origin O is the left-down edge of the container and the axes Ox, Oy are parallel to its walls.

The random variables X_j, Y_j fulfill the conditions:

$$r \le X_j \le L - r\,,\ r \le Y_j \le L - r\,,\ j = 0,1,...N-1 \qquad (1)$$

The initial state of the system is determined by the initial positions and velocities of the particles. The initial distribution of the particles' positions is uniform, i.e. the following conditions are fulfilled:

a) The probability of the event(4): "*the x-coordinate of the j-particle takes a value in the infinitesimal interval* $[x, x+\Delta x)$", is calculated by the relationship:

$$p\left(x \le X_j < x + \Delta x\right) = \frac{\Delta x}{L-2r}\text{, for each } x \in [r, L-r] \qquad (2a)$$

b) The probability of the event: "*the y-coordinate of the j-particle takes a value in the infinitesimal interval* $[y, y+\Delta y)$" is calculated by the relationship:

$$p\left(y \le Y_j < y + \Delta y\right) = \frac{\Delta y}{L-2r}\text{, for each } y \in [r, L-r] \qquad (2b)$$

The **probability density**(4) $p_U(u)$ of a random variable U that takes values in an interval I of the real numbers R $(I \subseteq R)$ is defined by the relation:

$$p\left(u \le U < u + \Delta u\right) = p_U(u)\Delta u\,,\ \Delta u \to 0 \qquad (2c)$$

For the case of the uniform distribution, the probability density is constant everywhere in the range of the random variable. Hence, according to 2a and b, the probability densities of the random variables X_j, Y_j are determined by the analytic expressions:

$$p_{X_j}(x) = p_{Y_j}(y) = \frac{1}{L-2r}\,,\ x, y \in [r, L-r] \qquad (3a)$$

The **probability distribution** (or simply: distribution) $P_{X_j}(x)$ of the random variable X_j is defined as the probability of the event: "*the value of the variable X_j is less than x*". Given that the range of X_j is the interval $[r, L-r]$, we right:

$$P_{X_j}(x) = p\left(r \le X_j < x\right)$$

Consider two disjoint sets I_1 and I_2, in the range of the random variable X_j:

$$I_1 \cap I_2 = \varnothing$$

The events: "$X_j \in I_1$" and "$X_j \in I_2$" are mutually independent and the following relation holds:

$$p\left(X_j \in I_1 \cup I_2\right) = p\left(X_j \in I_1\right) + p\left(X_j \in I_2\right)$$

Hence, we can partition the range of X_j in a sequence of successive infinitesimal intervals and express the probability distribution $P_{X_j}(x)$ as follows:

$$P_{X_j}(x) = p\left(r \le X_j < x\right) = p\left(x_0 \le X_j < x_1\right) + p\left(x_1 \le X_j < x_2\right) + ...p\left(x_{M-1} \le X_j < x_M\right)$$

where: $x_{n+1} = x_n + \Delta x_n$, $n = 0,1,...M-1$, $\Delta x_n \to 0$, $M \to +\infty$ and $x_0 = r$, $x_M = x$

Hence, according to 2a and c, we obtain:

$$P_{X_j}(x) = p\left(r \le X_j < x\right) = \int_r^x p_{X_j}(\bar{x})d\bar{x} \qquad (3b)$$

$$P_{X_j}(x) = \int_r^x \frac{1}{L-2r}d\bar{x} = \frac{x-r}{L-2r},\ r \le x \le L-r \qquad (3c)$$

From the last equation, we result that: $P_{X_j}(L-r) = 1$ which agrees with our anticipation.

In our model, the position of each particle at time *t* is independent of the positions of the other particles; the *N* events (*j*=0,1,…*N*-1): "at time *t*, for the j-particle it holds: $X_j \in [x, x+\Delta x)$" are mutually independent. Hence the number of particles $\Delta n(x,t)$, with x-coordinate in the interval $[x, x+\Delta x)$ at time *t*, is calculated by the equations:

$$\Delta n(x,t) = \sum_{j=0}^{N-1} p\left(x \le X_j < x+\Delta x\right) = \sum_{j=0}^{N-1} \frac{\Delta x}{L-2r} = \frac{N}{L-2r}\Delta x \qquad (4a)$$

The number of particles $N(x,t)$ with x-coordinates less than a given value *x* is the "**distribution of the particles' x-position**". Its value arises directly from 3b, 3c and 4a:

$$N_x(x) = \sum_{j=0}^{N-1} P_{X_j}(x) = N\frac{x-r}{L-2r},\ r \le x \le L-r \qquad (4b)$$

The particles' interactions do not cause any change at the analytical expression of the particles' x-position distribution: at every time *t*, the probability densities of the random variables X_j, Y_j, j=0,1,…*N*-1 are given by the expressions 3.
One can easily derive relations similar to 4a and b, for the random variables Y_j, j=0,1,…*N*.

In the environment of the simulation, the initial positions of the particles are determined by using the JavaScript method for generating random numbers. The directions of the initial velocities are chosen so that the gas is homogeneous and isotropic. On the other hand, along any pair-interaction, the particles emerge with velocities with directions completely random, independent of their initial directions. Hence, the homogeneity and the isotropy of the system are not affected.
We shall prove that according to our model, the velocity distribution is changing with time and converges to an equilibrium distribution. The equilibrium distribution is the **Maxwell-Boltzmann distribution** [2,5] (M-B distribution).
We must notice that the system will finally get the M-B distribution, independently of the initial velocity distribution. When the system reaches the M-B distribution, it remains in that state: this state, determined by the M-B distribution, is a stable state of equilibrium. This theoretical prediction is impressively confirmed in the virtual environment of the simulation.

The user is permitted to choose the initial velocity distribution of the system among three alternatives:
1st choice: At *t*=0 the directions of the velocities are random, but their magnitudes have the same value, V_{in}. In that case, consider a partition of the velocity-range in a union of infinitesimal intervals:

$$[0, V_{\max}) = \bigcup_{\mu=0}^{M-1} [v_\mu, v_{\mu+1}) \qquad (5a)$$

$$v_0 = 0 < v_1 = v_0 + \Delta v_0 < v_2 = v_1 + \Delta v_1 < \ldots v_{\mu+1} = v_\mu + \Delta v_\mu < \ldots v_M = V_{\max}$$

We symbolize V_{max} the least upper bound of the velocity magnitude in the simulation environment. So, in the initial state, $V_j \in [0, V_{\max})$ and we can write:

$$p\left(v_\mu \le V_j < v_\mu + \Delta v_\mu\right) = \begin{cases} 0 \text{ για } v_\mu \ne V_{in} \\ 1 \text{ για } v_\mu = V_{in} \end{cases}$$

Hence, the distribution probability of the variable V_j takes the form:

$$P_{V_j}(v) = p\left(0 \le V_j < v\right) = \sum_{v_\mu=0}^{v_\mu=v} p\left(v_\mu \le V_j < v_{\mu+1}\right) = \theta\left(v - V_{in}\right)$$

where: $\theta\left(v - V_{in}\right) = \begin{cases} 0 \text{ for } v < V_{in} \\ 1 \text{ for } v \ge V_{in} \end{cases}$

The particles' velocity-distribution for the initial state of the gas is:

$$N_V(v) = \sum_{j=0}^{N-1} P_{V_j}(v) = \sum_{j=0}^{N-1} p\left(0 \le V_j < v\right) = \sum_{j=0}^{N-1} \theta\left(v - V_{in}\right) = N\theta\left(v - V_{in}\right) \qquad (5b)$$

2nd choice: At t=0 the velocities of the half number of particles are equal to zero. For the other half, the directions of the velocities are random, and their magnitudes have the same value, V_{in}. Hence, the initial velocity distribution is expressed as follows:

The magnitude of the velocity of whichever particle in the aggregate equals 0 with probability 1/2 or V_{in} with probability 1/2 too. The probability of any other value is zero. Consider again a partition of the velocity-range to a union of infinitesimal intervals (see 5a):

$$\left[0, V_{\max}\right) = \bigcup_{\mu=0}^{M-1} \left[v_\mu, v_{\mu+1}\right)$$

Then, the probability of the event "the value of the random variable V_j is in the infinitesimal interval $\left[v_\mu, v_{\mu+1}\right)$ of the partition" is given by the relation:

$$p\left(v_\mu \le V_j < v_\mu + \Delta v_\mu\right) = \begin{cases} \dfrac{1}{2} \text{ for } v_\mu = 0 \\ \dfrac{1}{2} \text{ for } v_\mu = V_{in} \\ 0 \text{ for } v_\mu \ne 0 \text{ and } v_\mu \ne V_{in} \end{cases}$$

We infer that the particles' velocity distribution is calculated by the expression:

$$N_V(v) = \sum_{j=0}^{N-1} P_{V_j}(v) =$$

$$= \sum_{j=0}^{N-1} p\left(0 \le V_j < v\right) = \sum_{j=0}^{N-1} \sum_{v_\mu=0}^{v_\mu=v} p\left(v_\mu \le V_j < v_\mu + \Delta v_\mu\right) =$$

$$= \sum_{j=0}^{N-1} \left(\frac{1}{2}\theta(v) + \frac{1}{2}\theta\left(v - V_{in}\right) \right) = \frac{N}{2}\left(\theta(v) + \theta\left(v - V_{in}\right)\right) \qquad (6)$$

3d choice: At t=0, both the directions of the velocities, and their magnitudes are random. The values of the velocity magnitude for each particle are chosen by the random number generator of JavaScript, in the interval [0, v_{max}). The parameter v_{max} is related to the mean energy of the gas particles and is to be determined as follows:

The velocity magnitude of each particle is chosen by the random-numbers generator in the interval [0,v_{max}). Hence, the probability of the event: "The velocity magnitude V_j of the j-particle is in the infinitesimal interval $\left[v_\mu, v_\mu + \Delta v_\mu\right)$" is given by the equation:

$$p\left(v_\mu \le V_j < v_\mu + \Delta v_\mu\right) = \frac{\Delta v_\mu}{v_{\max}} \qquad (7a)$$

The mean value of the kinetic energy $\bar{E}$ of the j-particle is calculated by the equalities:

$$\bar{E} = \sum_{v_\mu=0}^{v_\mu=v_{\max}} \frac{1}{2} m {v_\mu}^2 p\left(v_\mu \le V_j < v_\mu + \Delta v_\mu\right) = \frac{1}{2} m \sum_{v_\mu=0}^{v_\mu=v_{\max}} {v_\mu}^2 \frac{\Delta v_\mu}{v_{\max}} \to \frac{m}{2 v_{\max}} \int_0^{v_{\max}} v^2 dv = \frac{1}{6} m {v_{\max}}^2$$

In the environment of the simulation, the value of the mean energy is an input parameter, chosen by the user. Hence, the corresponding value of the parameter v_{max} is determined by the equation:

$$v_{\max} = \sqrt{\frac{6\bar{E}}{m}} \qquad (7b)$$

The sequence of the experimental graphs

In the environment of the simulation, the particle-particle interactions cause a gradual variation of the velocity distribution. The theoretical variation of the distribution function with time is determined by equation 20 (see unit B2: How does the particles' velocity probability distribution vary with time?). We can check the theoretical predictions by constructing **a sequence of experimental graphs** depicting the evolution of the actual velocity distribution. To this end, in the simulation program we have determined a sequence of time moments $t_j \in \{0, t_1, \ldots t_J\}$ at which the program counts the number $N_{exp}(v; t_j)$, $j = 0,1 \ldots J-1$ of particles with velocity magnitudes in the intervals:

$$\left[0, v_{\mu_1}\right), \left[0, v_{\mu_2}\right), \ldots \left[0, v_{\mu_{M_{\max}}}\right),\ v_{\mu_1} < v_{\mu_2} < \ldots < v_{\mu_{M_{\max}}} = V_{\max} \qquad (8a)$$

The set of values $\left\{0, v_{\mu_1}, v_{\mu_2}, \ldots v_{\mu_{M_{\max}}} = V_{\max}\right\}$ determines a partition of the velocity range $[0, V_{\max})$:

$$[0, V_{\max}) = \bigcup_{k=0}^{M_{\max}-1} \left[v_{\mu_k}, v_{\mu_{k+1}}\right),\ \left(v_{\mu_0} = 0\,,\ v_{\mu_{M_{\max}}} = V_{\max}\right) \qquad (8b)$$

As a result, we obtain a sequence of **experimental graphs** which depict in **real time** the **actual** variation of the particles' velocity distribution. The max time t_J is determined in the program of the simulation.

How do we have constructed partition (8b) in the program of the simulation?

First, we decide how many points M_{max} will compose each experimental graph. Then, we define the length of each interval $\left[v_{\mu_k}, v_{\mu_{k+1}}\right)$ to be: $\Delta v = \dfrac{V_{\max}}{M_{\max} - 1}$

Hence: $v_{\mu_{k+1}} = v_{\mu_k} + \Delta v$, $k = 0,1, \ldots M_{\max} - 1$

$$v_{\mu_k} = k \frac{V_{\max}}{M_{\max} - 1},\ k = 0,1, \ldots M_{\max} - 1 \qquad (8c)$$

For t=0, the graph $N_{exp}(v;0)$ versus v is identical to the graph of the initial distribution the user has chosen. As time runs, we see that the sequence of the experimental graphs converges with an impressive way to the Maxwell-Boltzmann equilibrium distribution $N_{MB}(v)$ according to the predictions of the Boltzmann theoretical model: $\lim_{t \to \infty} N_{exp}(v;t) = N_{MB}(v)$

How do we have chosen the maximum value $V_{\max}$ appearing in relations 8, in the program of the simulation?

In the unit "D) Equilibrium of the system: The Maxwell-Boltzmann distribution" we shall see that in the equilibrium state of a two-dimensional ideal gas, the particles' velocity distribution is determined by the analytical expression (Maxwell-Boltzmann):

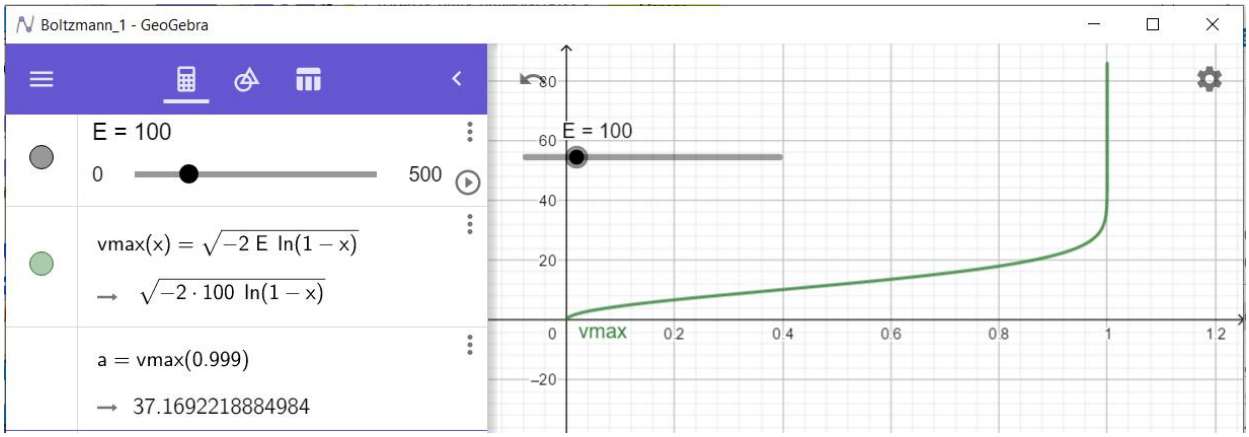
$$N_{MB}(v) = N\left(1 - e^{-\beta \frac{mv^2}{2}}\right) \qquad (9a)$$

Constant β is related to the mean energy $\bar{E}$ of the particles, according to 34: $\bar{E} = \dfrac{1}{\beta}$

From 9a, we result that the fraction $\lambda = N_{MB}(v)/N$ of the particles with velocity magnitude less than v equals $1 - e^{-\beta \frac{mv^2}{2}}$. Conversely: the max value of the velocity magnitude corresponding to a given value of λ is:

$$v_\lambda = \sqrt{-\frac{2}{\beta m}\ln(1-\lambda)} \qquad (9b)$$

The graph of 9b, (in the simulation's system of units $m = 1$, $E = 100$) is depicted in the following figure.



We can see that for $\lambda = 999/1000$, $v_\lambda = 37.17$ i.e. 999 in 1000 particles have velocity magnitude less than 37.17 (simulation-units). Hence, it is a very good approximation to choose the max value of the velocity magnitude V_{max} in relations 8a-c from 9b, for $\lambda = 999/1000$.

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B) The theoretical model of the 2-dimensional ideal gas

B1: *How do the particles interact?*

The virtual gas consists of *N* interacting particles. Each particle has a disk-shape of radius *r* and mass *m*. The system is confined in a 2-dimensional orthogonal container of width *L* and height *L*. The interactions between the particles and the walls of the container (p-w interactions) are elastic collisions.

The particles interact with each-other by pairs (p-p interactions). In every p-p interaction, the linear momentum and the total kinetic energy of the interacting particles are conserved. The directions of the velocities just after every interaction are determined by the conservation-principles and by a random variable (angle) which is independent of the velocities' directions just before the interaction. Between two successive interactions, each particle moves with constant velocity. Finally, the duration of any interaction is negligible, compared with the time between two successive interactions of any particle in the system.

Now, we shall derive the relations of the particles' velocities just before and just after their interaction.

Consider that at time *t*, the j-particle interacts with the k-particle. Let $\vec{r}_j, \vec{v}_j, \vec{r}_k, \vec{v}_k$ be the positions and the velocities of the particles just before their interaction, in the inertial reference frame Oxy, which is fixed to the container (figure 1).

In the virtual gas, the interaction of the j and k-particle happens at any time *t* which is determined by the following two conditions:

a) $\left|\vec{r}_j - \vec{r}_k\right| < s \cdot r$

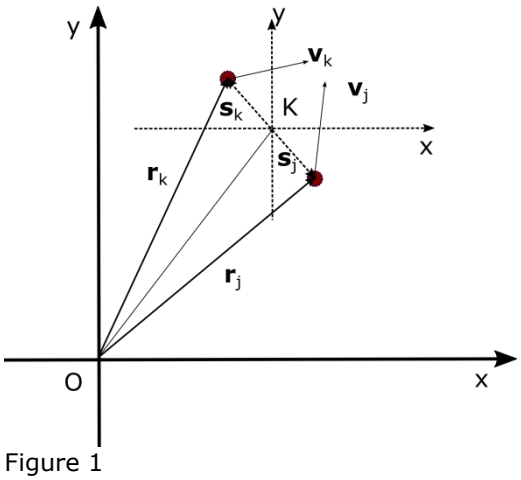

Figure 1

(The parameter s is related with the max permitted distance of the particles' centers to get the interaction triggering and is controlled by the user)

b) $\frac{d}{dt}\left[\left(\vec{r}_j-\vec{r}_k\right)\left(\vec{r}_j-\vec{r}_k\right)\right]<0$ or: $\left(\vec{v}_j-\vec{v}_k\right)\cdot\left(\vec{r}_j-\vec{r}_k\right)<0$

(The two particles are moving so, that in the infinitesimal time interval $\left[t,t+\Delta t\right)$ the distance of their centers decreases)

Let $K_{jk}\equiv K$ be the **center of mass** of the j and k-particle at the time-moment *t* that their interaction begins, and Kxy, their center-of-mass inertial reference frame (figure 1).

We implement the following steps:

1) Find the relations of the velocities in the frames Oxy and Kxy.
2) Calculate the velocities just after the interaction in the center of mass frame Kxy.
3) Calculate the velocities just after the interaction in the frame Oxy.

1) The particles have equal masses. Hence:

$$\overrightarrow{OK}=\frac{1}{2}\left(\vec{r}_j+\vec{r}_k\right),\vec{V}_K=\frac{1}{2}\left(\vec{v}_j+\vec{v}_k\right) \qquad (10a)$$

We symbolize $\vec{V}_K$ the center of mass velocity in Oxy. Let $\vec{u}_j$, $\vec{u}_k$ be the velocities of the j and k-particle, in the Kxy system.

According to figure 2, the following relations are true:

$$\vec{s}_j=\vec{r}_j-\overrightarrow{OK}=\frac{1}{2}\left(\vec{r}_j-\vec{r}_k\right),\ \vec{s}_k=\vec{r}_k-\overrightarrow{OK}=\frac{1}{2}\left(\vec{r}_k-\vec{r}_j\right)=-\vec{s}_j \qquad (10b)$$

$$\vec{u}_j=\frac{1}{2}\left(\vec{v}_j-\vec{v}_k\right),\ \vec{u}_k=\frac{1}{2}\left(\vec{v}_k-\vec{v}_j\right)=-\vec{u}_j \qquad (10c)$$

$$\vec{r}_j=\vec{s}_j+\overrightarrow{OK},\ \vec{r}_k=\vec{s}_k+\overrightarrow{OK} \qquad (10d)$$

$$\vec{v}_j=\vec{u}_j+\vec{V}_K,\ \vec{v}_k=\vec{u}_k+\vec{V}_K \qquad (10e)$$

2) Just after the interaction of the j and k-particle, their velocities $\vec{u}'_j$, $\vec{u}'_k$ in the Kxy frame are calculated from the linear momentum and energy conservation (figure 2):

$$\vec{u}'_j+\vec{u}'_k=\vec{u}_j+\vec{u}_k=0 \qquad (11a)$$

$$u'^2_j+u'^2_k=u_j{}^2+u_k{}^2 \qquad (11b)$$

From 11a and b we imply that:

$$u'^2_j=u'^2_k=u_j{}^2=u_k{}^2 \qquad (11c)$$

We infer that $\vec{u}'_j$, $\vec{u}'_k$ have mutually opposite directions and their magnitudes are the same with the magnitudes of the velocities just before the interaction; but in general, their directions are different from the direction of the velocities just before the interaction. The directions of $\vec{u}'_j$, $\vec{u}'_k$ are determined by a rotation angle θ forming with $\vec{u}_j$, $\vec{u}_k$ respectively (figure 2). In our model, the value of θ is random; in the simulation, it is determined by the JavaScript random values method.

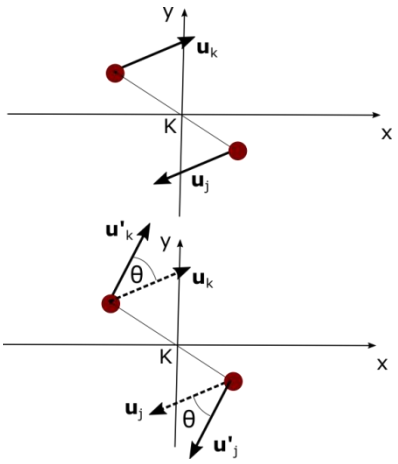

Figure 2

With the help of figure 2, we find that the x and y-components of $\vec{u}'_j$, $\vec{u}'_k$ are related with the x and y-components of the velocities u_j, u_k and the angle θ, according to the equations:

$$\begin{pmatrix}u'_{jx}\\u'_{jy}\end{pmatrix}=\begin{pmatrix}\cos\theta & \sin\theta\\-\sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}u_{jx}\\u_{jy}\end{pmatrix}=\begin{pmatrix}u_{jx}\cos\theta+u_{jy}\sin\theta\\-u_{jx}\sin\theta+u_{jy}\sin\theta\end{pmatrix} \qquad (12a)$$

$$\begin{pmatrix}u'_{kx}\\u'_{ky}\end{pmatrix}=-\begin{pmatrix}u'_{jx}\\u'_{jy}\end{pmatrix} \qquad (12b)$$

3) The velocities $\vec{v}'_j$, $\vec{v}'_k$ of the j and k-particle just after their interaction, in the Oxy reference frame are calculated from 10e, 12a, and b:

$\vec{v}'_j = \vec{u}'_j + \vec{V}_K$, $\vec{v}'_k = \vec{u}'_k + \vec{V}_K$ (13)

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B2: *How does the particles' velocity distribution vary with time?*

A) We assume that every time moment, the range of the velocity magnitude for each particle is a **finite** set: $\Omega_V = \{0, v_1, v_2, ...v_M\}$

The values: $0, v_1, v_2, ...v_M$ are determined by a partition of the interval $[0, v_{\max})$ (paragraph A):

$[0, v_{\max}) = \bigcup_{\mu=0}^{M-1} [v_\mu, v_{\mu+1})$ where: $v_{\mu+1} = v_\mu + \Delta v_\mu$, $v_0 = 0$, $v_M = v_{\max}$

The time moments are defined by the time sequence: $0, Dt, 2Dt, ...q \cdot Dt, ...$ The time interval Dt is determined in the simulation program; its value is selected so that it is much less than the mean time between two successive interactions of any particle.

Let $p_j(t;v)$ be the probability of the event: "At time t, the velocity magnitude of the j-particle equals v, where: $v \in \Omega_V$ ". We call $p_j(t;v)$ "velocity probability function".

It is obvious that:

$\sum_{v \in \Omega_V} p_j(t;v) = 1$

In our model, the analytic expression of the probability $p_j(t;v)$ is independent of j: the probabilities $p_j(t;v)$ are the same for all particles. Hence, we can write:

$p_j(t;v) = p(t;v)$ for any $j = 0,1,...N$ (14a)

Consequently, if we symbolize $n(t;v)$ the number of particles that at time t have velocities with magnitude v, we imply that:

$n(t;v) = \sum_{j=0}^{N-1} p(t;v) = Np(t;v)$ (14b)

As the system evolves from its initial state to the equilibrium state, the probability $p(t;v)$ and the particles' number $n(t;v)$ change with time; this is caused by the p-p interactions.

Let us see how the variation of these functions is expressed mathematically [1,2].

B) Assume two neighboring time moments t and $t+Dt$. The variation of $n(t;v)$ in the time interval $[t, t+Dt)$ is caused by the following reasons:

a) $n(t;v)$ increases by the number of particles that their velocity magnitude at time t was different of v and, because of their interactions, at time $t+Dt$ they emerge with velocity magnitude $V=v$

b) $n(t;v)$ decreases by the number of particles that their velocity magnitude at time t was v and, because of their interactions, at time $t+Dt$ they emerge with velocity magnitude $V \neq v$

We define the compound event $\Gamma_{t \to t+Dt}(v', u' \to v, u)$: "At time t, two particles P1 and P2 have velocities with magnitudes v' and u', respectively – P1 and P2 interact in the time interval $[t, t+Dt)$ and at time $t+Dt$ they emerge with velocity magnitudes v, u."

The event $\Gamma_{t \to t+Dt}(v', u' \to v, u)$ is composed by the following independent events $\Gamma 1$ and $\Gamma 2$:

$\Gamma 1$: "At time t, the velocity magnitudes of P1 is v' and of P2 is u' "

$\Gamma 2$: "P1 and P2 interact in the time interval $[t, t+Dt)$ and at time $t+Dt$ they emerge with velocities of magnitude v and u, respectively"

Let $p_{t\to t+Dt}(u',v'\to u,v)$ be the probability of $\Gamma_{t\to t+Dt}(v',u'\to u,v)$ and $p(\Gamma 1)$, $p(\Gamma 2)$, the probabilities of $\Gamma 1$ and $\Gamma 2$, respectively. Then it holds:

$$p_{t\to t+Dt}(u',v'\to u,v)=p(\Gamma 1)\,p(\Gamma 2) \qquad (15a)$$

In our model, the events: "The velocity magnitude of P1 at t is v" and "The velocity magnitude of P2 at t is u" are independent; hence, we can write (see 14a, b):

$$p(\Gamma 1)=p(t,v')\,p(t,u') \qquad (15b)$$

The probability $p(\Gamma 2)$ of the event $\Gamma 2$ is called "**transition probability**". In our model we have assumed that $p(\Gamma 2)$ is independent of the time moment t; it is proportional to the time length Dt. We write:

$$p(\Gamma 2)=Dt\,\sigma(v',u'\to u,v) \qquad (16)$$

The quantity $\sigma(v',u'\to v,u)$ is a function of the initial and the final mechanical state of the interacting particles. Its analytic expression depends on the type of the p-p interactions. Nevertheless, there are some general properties satisfied by $\sigma(v',u'\to v,u)$ derived by the symmetries we have imposed to our model:

a) The mechanism of the p-p interaction is invertible, i.e. the probabilities of the transitions: $(v',u')\to(v,u)$ and $(v,u)\to(v',u')$ in the same time interval Dt are equal (see paragraph: "How do the particles interact?"):

$$\sigma(v',u'\to v,u)=\sigma(v,u\to v',u') \qquad (17)$$

b) The gas is homogeneous and isotropic. Then, in combination with 17, we infer that:

$$\sigma(v',u'\to v,u)=\sigma(v,u\to v',u')=\sigma(u',v'\to v,u)=\sigma(v',u'\to u,v) \qquad (18)$$

According to 15-18, we deduce the following equations:

$$p_{t\to t+Dt}(v',u'\to v,u)=Dt\,p(t;v')\,p(t;u')\,\sigma(v',u'\to v,u) \qquad (19a)$$

$$p_{t\to t+Dt}(v,u\to v',u')=Dt\,p(t;v)\,p(t;u)\,\sigma(v,u\to v',u')=$$
$$=Dt\,p(t;v)\,p(t;u)\,\sigma(v',u'\to v,u) \qquad (19b)$$

C) *Variation of the particles' number with velocity magnitude v with time*

Let us first see how the probabilities $p(v,t)$ change with time. According to the arguments of paragraph (B), the variation of $p(v,t)$ in the time interval $[t,t+Dt)$ is given by the subsequent equations:

$$p(t+Dt;v)=p(t;v)+\sum_u p_{t\to t+Dt}(v',u'\to u,v)-\sum_u p_{t\to t+Dt}(v,u\to u',v')=$$
$$=p(t;v)+Dt\sum_u \sigma(v',u'\to v,u)\left(p(t;v')\,p(t;u')-p(t;v)\,p(t;u)\right) \qquad (19c)$$

Or:

$$\frac{\partial p(t;v)}{\partial t}=\sum_u \sigma(v',u'\to v,u)\left(p(t;v')\,p(t;u')-p(t;v)\,p(t;u)\right) \qquad (20)$$

By using 20 and 14b, we derive the "master" equation:

$$\frac{\partial n(t;v)}{\partial t}=N\sum_u \sigma(v',u'\to v,u)\left(p(t;v')\,p(t;u')-p(t;v)\,p(t;u)\right) \qquad (21)$$

In 20 and 21, the summations include terms corresponding to any possible transition $(\vec{v}',\vec{u}')\to(\vec{v},\vec{u})$ that is compatible with the linear momentum and energy conservation.

It is worth noticing that 20 or 21 describe the variation of the velocity magnitude distribution of the gas, given that the p-p interaction is determined by the quantity $\sigma(v',u'\to v,u)$. In the case that the particles do not interact, it holds $\sigma(v',u'\to v,u)=0$ for any value of the velocity magnitudes. Then, the initial velocity distribution of the particles is not changing with time.

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C) The Boltzmann H-theorem [7]

In our model, the evolution of the state of the system is described by equation 20 or 21. A steady state of the gas is obtained by any probability function which is independent of time:

$$\frac{\partial p(t;v)}{\partial t} = 0 \qquad (22)$$

We call it "Maxwell-Boltzmann probability function" (MB-probability function); symbolize: $p_{MB}(v)$ and the particles' velocity distribution determined by this, is called "MB-velocity distribution".
From equations 20-22, we imply that $p_{MB}(v)$ must fulfill the condition:

$$p_{MB}(v')\,p_{MB}(u') = p_{MB}(v)\,p_{MB}(u) \qquad (23)$$

In the context of our model, we formulate and demonstrate Boltzmann H-theorem [1,2,7] as follows:

Assume that the macro-state of an isolated ideal gas is determined by a certain initial velocity distribution. The gas passes through a sequence of velocity-distributions which converges to the MB-distribution, independently of its initial distribution. This is due to the p-p interactions that obey conditions 18.

The variation of the probability function $p(t;v)$ with time is given by equation 20.
Define the functional:

$$H[p_t] \underset{def}{=} \sum_v p(t;v)\ln\left(p(t;v)\right),\ p_t(v) \equiv p(t;v) \qquad (24)$$

We shall show that $H[p_t]$ satisfies the conditions of a Lyapunov function[3] for the dynamical system described by equation 20. I.e. for any family of distribution functions $p_t(v) = p(t;v)$ determined by equation 20, the following relations are true:

$$H[p_t] < 0 \qquad (25a)$$

$$\frac{dH[p_t]}{dt} < 0 \qquad (25b)$$

$$\frac{dH[p_{MB}]}{dt} = 0 \qquad (25c)$$

Steps to the proof

a) From relations 14a, b, it is true that: $0 < p(t;v) = \frac{n(t;v)}{N} \le 1$
From this, we imply that: $\ln\left(p(t;v)\right) < 0$ Hence, 25a is true for any probability function $p_t(v) = p(t;v)$

b) From 24, we obtain the equation:

$$\frac{dH[p_t]}{dt} = \sum_v \frac{\partial p(t;v)}{\partial t}\left[\ln\left(p(t;v)\right) + 1\right] \qquad (26)$$

From 20, 26 and the symmetry relations 18, we derive the subsequent equations:

$$\frac{dH[p_t]}{dt} = \sum_v \sum_u \sigma(v',u' \to v,u)\left(p(t;v')p(t;u') - p(t;v)p(t;u)\right)\left[\ln\left(p(t;v)\right) + 1\right]$$

$$\frac{dH[p_t]}{dt} = \sum_v \sum_u \sigma(v',u' \to v,u)\left(p(t;v')p(t;u') - p(t;v)p(t;u)\right)\left[\ln\left(p(t;u)\right) + 1\right]$$

Adding these equations by parts, and using again the symmetry properties of $\sigma(v',u' \to v,u)$, we obtain:

$$2\frac{dH[p_t]}{dt} = \sum_v \sum_u \sigma(v',u' \to v,u)\left(p(t;v')p(t;u') - p(t;v)p(t;u)\right)\left[\ln\left(p(t;v')\right) + \ln\left(p(t;u')\right) + 2\right]$$

$$2\frac{dH[p_t]}{dt} = \sum_v \sum_u \sigma(v',u' \to v,u)\left(p(t;v')p(t;u') - p(t;v)p(t;u)\right)\left[-\ln\left(p(t;v')\right) - \ln\left(p(t;u')\right) - 2\right]$$

Adding by parts:

$$4\frac{dH[p_t]}{dt} =$$

$$= -\sum_v \sum_u \sigma(v',u' \to v,u)\left(p(t;v')p(t;u') - p(t;v)p(t;u)\right)\left[\ln\left(p(t;v')p(t;u')\right) - \ln\left(p(t;v)p(t;u)\right)\right]$$

The logarithm is a monotonically increasing function; hence for any $x,y>0$ it holds:

$$(x-y)(\ln x - \ln y) > 0$$

Besides, the transition probability is a positive quantity. We imply that for any probability function, it is true that:

$$\frac{dH[p_t]}{dt} < 0$$

c) The MB probability function is a stable solution of equation 20; it is determined by 22 and 23. Hence, by using 26, relation 25c is derived.

$H[p_t]$ takes its extreme value for $p_t(v) = p_{MB}(v)$ (see 26). Hence, by following 25a-c, we infer that it is bounded: $H[p_{MB}] \le H[p_t] \le H[p_0] \le 0$ (p_0 is the initial probability function).

For $t \to +\infty$ the function $H[p_t]$ is strictly decreasing with time and has a greatest lower bound $H[p_{MB}]$; we conclude that it converges to $H[p_{MB}]$ and that $\lim_{t\to\infty} p_t(v) = p_{MB}(v)$ independently of the form of the initial probability function p_0.

Any sequence of probability functions $p_k(v) \underset{def}{=} p(k \cdot Dt; v)$, $k = 0,1,\ldots$ determined by the analytic expression 19c converges to the Maxwell-Boltzmann probability function, independently of the initial probability function $p_0(v)$. That is:

$$p_{k+1}(v) = p_k(v) + Dt \sum_u \sigma(v',u' \to v,u)\left(p_k(v')p_k(u') - p_k(v)p_k(u)\right) \qquad (27a)$$

$$\lim_{k\to\infty} p_k(v) = p_{MB}(v) \qquad (27b)$$

When the system reaches the Maxwell-Boltzmann probability function, it does not escape from this: it is in a stable equilibrium state.

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D) Equilibrium of the system: The Maxwell-Boltzmann distribution for a 2-dimensional ideal gas

Which is the analytic expression of the velocity distribution, in the equilibrium state of the two-dimensional gas?

The analytic expression of the probability function $p_{MB}(v)$ is derived from condition 23 and the conservation principles characterizing the p-p interactions. For the case of our two-dimensional gas, linear momentum and kinetic energy are conserved for any p-p interaction. Keeping the formalism of the previous paragraphs, we have:

$$\frac{mv'^2}{2} + \frac{mu'^2}{2} = \frac{mv^2}{2} + \frac{mu^2}{2} \qquad (28)$$

The primed quantities indicate the state of the interacting particles just before their interaction, and the non-primed, just after.

We assume that 28 expresses the **only additive scalar conservation principle**.

The equilibrium condition 23 implies another relation connecting the states of the interacting particles before and after their interaction:

$$p_{MB}(v')p_{MB}(u') = p_{MB}(v)p_{MB}(u)$$

$$\text{Or: } \ln p_{MB}(v') + \ln p_{MB}(u') = \ln p_{MB}(v) + \ln p_{MB}(u) \qquad (29)$$

Condition 29 indicates a new additive scalar conservation principle concerning the velocity magnitudes of the particles before and after their interaction. We presume that 29 must be reduced to 28; i.e.:

$$\ln p_{MB}(v) \propto m\frac{v^2}{2} + const.$$

Hence, we can write:

$$p_{MB}(v) \propto e^{-\beta\frac{mv^2}{2}} \qquad (30)$$

The constant quantity β is to be specified.

To accomplish our calculations, let us consider that the particles' velocity magnitude is a continuous random variable, taking values in the interval $[0,+\infty)$.

In our two-dimensional system, the number $\Delta n(v)$ of particles with velocities in the interval: $[v, v+\Delta v)$, $\Delta v \to 0$ is proportional to the velocity probability $p_{MB}(v)$ and to the number of particles with velocities in the infinitesimal ring with radius *v* and width Δv. We write:

$$\Delta n(v) = n(v \le V < v + \Delta v) = NAe^{-\beta\frac{mv^2}{2}} 2\pi v\Delta v \qquad (31)$$

Where, A is a constant.

By integrating 31 in the range $[0,+\infty)$ of the velocity magnitude, we obtain: $A = \frac{m\beta}{2\pi}$

Hence, 31 takes the form:

$$\Delta n(v) = n(v \le V < v + \Delta v) = Nm\beta e^{-\beta\frac{mv^2}{2}} v\Delta v \qquad (32a)$$

From 32a we can define "the probability density" by the equation:

$$f(v) \underset{def}{=} \frac{1}{N}\frac{\Delta n(v)}{\Delta v},\ \Delta v \to 0$$

In the equilibrium state, for the two-dimensional gas, the probability density takes the analytic expression:

$$f_{MB}(v) = \frac{1}{N}\frac{\Delta n(v)}{\Delta v} = m\beta e^{-\beta\frac{mv^2}{2}} v \qquad (32b)$$

The number of particles with velocity magnitude less than a given value *v* -i.e. the particles' velocity distribution- in the equilibrium state, is calculated by 32b:

$$N(v) = N\int_{v'=0}^{v} f(v')dv'$$

We find:

$$N_{MB}(v) = N\left(1 - e^{-\beta\frac{mv^2}{2}}\right) \qquad (33a)$$

The velocity distribution function is calculated by the relationship: $F(v) = \frac{1}{N}N(v)$

Hence:

$$F_{MB}(v) = \left(1 - e^{-\beta\frac{mv^2}{2}}\right) \qquad (33b)$$

The constant β is related to the mean kinetic energy of the gas particles:

$$\bar{E} = \left\langle \frac{1}{2} m V^2 \right\rangle = \int_0^{+\infty} dv \, \frac{1}{2} m v^2 m \beta e^{-\beta \frac{m v^2}{2}} v = \frac{1}{\beta} \qquad (34)$$

In the environment of the simulation, the constant mean energy of the system is calculated from the initial velocities of the particles, according to the relation:

$$\bar{E} = \frac{1}{N} \sum_{j=0}^{N-1} \frac{1}{2} m v_j^{\,2} \qquad (35)$$

In the equilibrium state, we find:

$$\bar{E} = \frac{1}{N} \sum_{j=0}^{N-1} \frac{1}{2} m v_j^{\,2} = \frac{1}{N} \sum_{v=0}^{v=+\infty} \frac{1}{2} m V^2 \Delta n \left(v \le V < v + \Delta v \right) = \int_{v=0}^{+\infty} dv \, \frac{1}{2} m v^2 m \beta e^{-\beta \frac{m v^2}{2}} v =$$

$$= \frac{m^2}{4} \beta \int_{\zeta=0}^{+\infty} d\zeta \zeta e^{-\beta \frac{m\zeta}{2}} = -\frac{m}{2} \left(\int_{\zeta=0}^{+\infty} \zeta de^{-\beta \frac{m\zeta}{2}} \right) = \frac{m}{2} \left(\int_{\zeta=0}^{+\infty} d\zeta e^{-\beta \frac{m\zeta}{2}} \right) = \frac{1}{\beta}$$

Hence:

$$\beta = \frac{1}{\bar{E}} = \left(\frac{1}{N} \sum_{j=0}^{N-1} \frac{1}{2} m v_j^{\,2} \right)^{-1} \qquad (36)$$

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E) The items, the graphs, and the tools of the simulation

Open the simulation here: **The evolution of a 2-dimensional ideal gas toward the equilibrium state. The Boltzmann H-theorem**

[The system of units is determined in the program of the simulation]

The simulation window: Here, the user can see the motion of N=300 interacting particles of a 2D-gas, in a plane container. Each particle is a disk of radius r=0.1 length-unit and mass m=1 mass-unit. The container is an orthogonal of dimensions LxL, with L=20 length-unit.
One of the particles has been colored red and its path is depicted in the virtual environment of the simulation. So, the user can watch the successive interactions of this specific particle with the other particles and the walls of the container.

The initial position-distribution of the particles is random. The directions of the initial velocities are random too, but the user can select one of three possible initial velocity magnitude distributions:
1st choice, "step_function_1": All particles have the same velocity magnitude.
2nd choice, "step_function_2": Half particles have zero velocity and the rest have the same velocity magnitude.
3d choice, "chaotic": The initial velocity magnitude of each particle is calculated by a random process, but the total energy of the particles is controlled by the user.

The mean energy of the particles is controlled by the user. Hence, the value of β -which has been renamed to "b"- is changed under any specific selection of mean energy.
The user can also control the value of a quantity called "the strength" of the interaction. This quantity is related to the transition probability $Dt \cdot \sigma\left(v', u' \to v, u\right)$ discussed in the paragraph "How does the particles' velocity probability function vary with time". In our model, the transition probability is an increasing function of the least distance which is necessary for two particles to interact. So, the "strength" coefficient, by taking values between 0 and 1.5 controls the least necessary distance for the p-p interaction. For *strength*=0, there is no interaction between the particles, and the user can see that the initial magnitude-velocity distribution is not changing with time.

The graph-windows: In the "Velocity-Distribution" graph, the user can watch in **real-time**, the **experimental** evolution of the particles' velocity distribution caused by the particles' interactions (blue points), and its convergence to the Maxwell-Boltzmann distribution predicted by the theoretical model (red curve). In the "Boltzmann H-functional" graph, the user watches in real-time, the **experimental** variation of the Boltzmann H-functional with time. In the "Measurement of the total energy" graph, the program measures the total energy of the particles at a sequence of time moments, and the user checks the conservation of the energy along the evolution of the system of the interacting particles, which is the basic prerequisite for the Boltzmann H-theorem.

For the composition of the experimental velocity distribution graphs, at the time-moments: $t = 0, \Delta t, 2\Delta t, ...J \cdot \Delta t$, the program counts the number $N(t, v)$ of particles with velocities in a sequence of intervals:

$\left[0, v_{\mu_1}\right), \left[0, v_{\mu_2}\right), ... \left[0, v_{\mu_{M_{max}}}\right),\ v_{\mu_1} < v_{\mu_2} < ... < v_{\mu_{M_{\max}}} = V_{\max}$

[See relations 8a-c, paragraph "The sequence of the experimental graphs"]

For each $t_j = j \cdot \Delta t$, $j = 0, 1, ...J$ the program plots the points $\left(v_{\mu_k}, N\left(t_j, v_{\mu_k}\right)\right), k = 1, 2, ...M_{\max}$ in a system of axes *v*-*N*, and the corresponding experimental graph is accomplished. Every graph $N_j = N\left(t_j, v\right), j = 1, 2, ...J$ appears at the moment t_j and disappears at the moment t_{j+1} of the next set of measurements.

How the experimental graph of the Boltzmann H-functional versus time has been achieved?

H is a functional of the probability function $p(t; v)$ Hence, we must evaluate the experimental values of $p(t; v)$ every time $t = 0, \Delta t, 2\Delta t, ...J \cdot \Delta t$ at the array of magnitude velocity values:

$\left[v_{\mu_1}, v_{\mu_2}, ...v_{\mu_{M_{\max}}}\right]$

Every time moment t_j the program counts the number of particles $\Delta n_{\mu_k}\left(t_j\right)$, $k = 0, 1, ...M_{\max}$ with velocities in the intervals (see relation 8c):

$\left[v_{\mu_k}, v_{\mu_k} + \Delta v\right),\ k = 0, 1, ...M_{\max} - 1,\ \Delta v = \dfrac{V_{\max}}{M_{\max} - 1}$

The experimental values of the probability function $p_{\mu_k}\left(t_j\right) = p\left(t_j, v_{\mu_k}\right)$ are calculated by the relations:

$$p_{\mu_k}\left(t_j\right) = \frac{\Delta n_{\mu_k}\left(t_j\right)}{N}$$

It is noticed that some of the calculated values $p_{\mu_k}\left(t_j\right)$ should be zero, whence the logarithm of $p_{\mu_k}\left(t_j\right)$ is not possible to be calculated. To confront these cases, we choose a small quantity $0 < \varepsilon << 1$ and calculate the experimental value of *H* by the expression:

$$H\left(t_j\right) = \sum_{\mu=1}^{M}\left(\varepsilon + p_\mu\left(t_j\right)\right)\ln\left(\varepsilon + p_\mu\left(t_j\right)\right) \qquad (37)$$

[Notice that: $\lim_{x \to 0^+}\left(x \log x\right) = 0$]

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F) Activities implemented in the virtual environment of the simulation

1. Select the initial distribution "step_function_1" and run the simulation successively by choosing the values:

   $\left[\bar{E} = 200,\ strength = 1\right] - \left[\bar{E} = 400,\ strength = 1\right] - \left[\bar{E} = 400,\ strength = 0\right]$

   $\left[\bar{E} = 300,\ strength = 0.5\right] - \left[\bar{E} = 300,\ strength = 1.5\right]$

a. Watch the motion of the particles and think if it appears to agree with the related descriptions of the theoretical model. Write down your comments.
b. Write down the variations of the theoretical curves you notice when you vary the quantities $\bar{E}$ and "*strength*", and explain them by using the theoretical model.
c. Watch the sequence of the experimental distribution graphs and check if it converges to the Maxwell-Boltzmann distribution, according to the prediction of the Boltzmann H-theorem. How this is related with the energy-graph shown in the environment of the simulation?
d. Estimate the time needed for the system to reach the equilibrium state. How the variation of the quantities $\bar{E}$ and "*strength*" appear to affect the transition time?
e. Repeat actions a-d, for each of the mentioned selection of the quantity "*strength*" but choosing successively the initial distributions "step_function_2" and "chaotic".

2. Select the initial distribution "step_function_1". Run the simulation by selecting successively the values: $\left[\bar{E}=200,\ strength=1\right]$, $\left[\bar{E}=200,\ strength=1.5\right]$ and $\left[\bar{E}=400,\ strength=1\right]$.
   For every case, watch the variation of the Boltzmann H-functional and estimate the time needed to reach its steady value. Write down your conclusions. Compare the results of these activities with the results of the activities 1.

3. Repeat activities 2, by selecting the initial distributions "step_function_2" and "chaotic", successively. Compare the transition times of the system from its initial state to the equilibrium state, by keeping the value of the mean energy constant. Write down your conclusions.

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