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AN INVESTIGATION OF THE MAXWELL-HYPOTHESIS THROUGH
METHODS FROM EXPERIMENTAL STOCHASTICS

Abstract

The validity of the Maxwell-Hypothesis concerning the velocity distribution of the micro-constituents of a gas is examined here by methods from 'Experimental Stochastic', i.e. respective stochastic models are built on the computer in order to investigate effects of the dynamic computer model applying statistical tools.

The method developed allows to treat this phenomenon of velocity distribution in a non-real world context.

Keywords: Computer-experiment, Experimental Stochastics, collision dynamics of molecules, velocity distribution, Maxwell-Hypotythesis, kernel density estimator, non-real physics.

1. Introduction.

The phenomenon to be treated here is the velocity distribution of gas molecules, i.e. the validity of the Maxwell-Hypothesis. As the movement of gas molecules is not observable, a direct confirmation of the Maxwell-Hypotheses is not possible in physics. On the other hand the computer opens possibilities to investigate phenomena by virtual experiments. These phenomena may be from the real world, possibly not easily accessible, or even non-real phenomena, i.e. phenomena, which have no counterpart in the real world.

The method to be applied here is what we call 'Experimental Stochastics', i.e. we build a stochastic dynamic model on the computer- here of collisions of molecules determined by the Newtonian axioms in order to investigate effects of the dynamic computer model by means of statistical methods, cf. [Moeschlin et al. 1998].

These statistical methods may be understood- in correspondence to real laboratory experiments- as a virtual laboratory mounting measuring devices.

Although, as well the design of the stochastic, dynamic model on the computer, as also the statistical evaluation of effects of it, may be based on deeply lying mathematical methods; the act of recognition is not a mathematical one, it belongs to the realm of empirical sciences. The insights reveal themselves through an experiment of a virtual laboratory, as which we want to understand a computer-experiment.

In section 4 the Maxwell-Hypothesis (James Clerk Maxwell 1831-1879) concerning the velocity distribution of the micro-constituents of a gas, cf. [Sklar 1993], p.30/31, is examined by a computer experiment. The methods developed may even be applied to study this phenomenon in a non-real world context, Section 5.

These both section are preceded by two section, Section 2 and 3, having a preparatory character. In Section 2 a Newtonian dynamic is developed to be implemented on the computer while in Section 3 we are describing the kernel density estimator, acting as the virtual laboratory mounting device.

To avoid technicalities we switch fairly freely between random variables and their realizations.

2. Kinetic Dynamics.

In this section we describe a dynamic to be implemented on the computer, which is based on the Newtonian axioms. The outcome of a collision between molecules is determined by the laws of conservation of momentum and energy. As within the

experiments the molecules are represented by discs it is sensible to restrict ourselves exclusively to translation movements, i.e. the transformation from kinetic translation energy to rotational energy does not take place. In the following we consider a 2-dimensional container B , which is modelled as a not necessarily convex subset of the Euclidean plane: $B \subset \mathbf{R}^2$; furthermore, we assume that the boundary ∂B of B is a piecewise differentiable curve such that with the exception of a subset $N \subset \partial B$ of Lebesgue measure 0 at every point $x \in \partial B \setminus N$ there is an uniquely determined direction which is orthogonal to the wall ∂B .

The container B is filled with N molecules; the molecules are represented by non-overlapping discs of radius $\lambda > 0$ and mass $m > 0$. Let

$$(x(0); v(0)) := (x^{(1)}(0), \dots, x^{(N)}(0); v^{(1)}(0), \dots, v^{(N)}(0)) \in B^N \times \mathbf{R}^{2N}$$

be an initial (microscopic) state of the system, where $x^{(i)}(0)$ denotes the position and $v^{(i)}(0)$ the velocity of the i^{th} molecule at the time instant $t = 0$ ($i = 1, \dots, N$). The microscopic state of the system at time $t > 0$ is given by

$$(x(t); v(t)) = (x(0) + tv(0); v(0)),$$

if no collisions between the molecules and no reflections of a molecule off a wall have taken place during the time interval $[0; t]$.

The time t_i , $1 \leq i \leq N$ of a potential reflection of the i^{th} disc off a wall can be computed as the smallest positive solution of the equation

$$d(x^{(i)}(0) + tv^{(i)}(0), \partial B) = \lambda,$$

where d denotes the Euclidean distance on \mathbf{R}^2 and the expression $d(y, \partial B)$ is defined by

$$d(y, \partial B) := \inf \{d(y, a) \mid a \in \partial B\}$$

for $y \in \partial B$.

The time t_{ij} , $1 \leq i < j \leq N$, of a potential collision of between the molecules i and j is the smallest positive solution of the (quadratic) equation

$$d(x^{(i)}(0) + tv^{(i)}(0), x^{(j)}(0) + tv^{(j)}(0)) = 2\lambda. \quad (2.1)$$

If (2.1) has no real or no positive solutions, then the molecules i and j will not collide with one another before the next collision or reflection has occurred. The time \bar{t} of the next collision or reflection in the system is defined as

$$\bar{t} := \min \left(\{t_i \mid 1 \leq i \leq N\} \cup \{t_{ij} \mid 1 \leq i < j \leq N\} \right).$$

If the i^{th} molecules reflects off the wall of the container (such a reflection is interpreted as an instantaneous action, i.e. an action whose time duration has Lebesgue measure 0) at time \bar{t} , then the velocity vector $v^{(i)}(\bar{t})$ is reversed at the tangent to ∂B at the point of reflection.

If, however, a collision between the i^{th} and j^{th} molecule occurs at the time \bar{t} , then the direction of momentum exchange is given by

$$\bar{e} := \frac{1}{2\lambda} (x^{(i)}(\bar{t}) - x^{(j)}(\bar{t})).$$

Under the assumption that the molecules have the same mass, conservation of momentum implies

$$v^{(i)} = v^{(i)}(\bar{t}) + \lambda \bar{e},$$

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$$v^{(j')} = v^{(j)}(\bar{r}) - \lambda \bar{e}$$

with $v^{(j')}$ and $v^{(j)}$ the velocities after the collision and λ are determined by the condition

$$\langle v^{(j)}(\bar{r}), v^{(j)}(\bar{r}) \rangle + \langle v^{(j')}(\bar{r}), v^{(j')}(\bar{r}) \rangle = \langle v^{(j)}, v^{(j)} \rangle + \langle v^{(j')}, v^{(j')} \rangle$$

(conservation of energy).

According to theorem 4.2.1 of [Cercignani et al. 1994] the iterative application of the described procedure yields a trajectory $(x(t); v(t))_{t \in \mathbb{R}_+}$ in $B^N \times \mathbf{R}^{2N}$ for Lebesgue-almost all initial conditions $(x(0); v(0)) \in B^N \in \mathbf{R}^{2N}$.

3. The kernel density estimator.

In Section 4 and 5 we have to estimate distributions being defined by its Lebesgue densities, which gives rise to recall the concept of kernel density estimators.

Let λ denote the Lebesgue measure on $(\mathbf{R}, \mathcal{B})$. Furthermore, let

$$K(x) := \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}x^2\right), \quad x \in \mathbf{R}. \quad (3.1)$$

Let $\mathcal{L}^1(\lambda)$ denote the set of the Lebesgue integrable functions. If $n \in \mathbf{N}$ and $h > 0$, then the value of the mapping $S_{n,h} : \mathbf{R}^n \rightarrow \mathcal{L}^1(\lambda)$ at (x_1, \dots, x_n) is the function

$$S_{n,h}[x_1, \dots, x_n] : \mathbf{R} \rightarrow \mathbf{R}_+, \\ S_{n,h}[x_1, \dots, x_n] := \frac{1}{nh} \sum_{i=1}^n K\left(\frac{t-x_i}{h}\right).$$

$S_{n,h}$ is the kernel density estimator (for the sample size n and band-width h).

Let Q be a probability measure on $(\mathbf{R}, \mathcal{B})$, $f \in \mathcal{L}^1(\lambda)$ its Lebesgue density function, and $(X_n)_{n=1}^\infty$ a sequence of independent random variables on a probability space $(\Omega, \mathcal{A}, \mathcal{P})$ distributed according to Q . Now let $(h(n))_{n=1}^\infty$ be a sequence of positive numbers with

$$\lim_{n \rightarrow \infty} h(n) = 0 \quad \text{and} \quad \lim_{n \rightarrow \infty} nh(n) = \infty. \quad (3.2)$$

It follows (cf. [Devroye, Györfi 1985], chap.3, sec.1, Theorem 1):

$$\lim_{n \rightarrow \infty} \int S_{n,h(n)}[X_1, \dots, X_n](t) \cdot f(t) d\lambda(t) = 0 \quad P\text{-a.s.}, \quad (3.3)$$

i.e. the sequence of estimators $S_{n,h(n)}$ converges in terms of the variational distance P -a.s. to the Lebesgue density function f of Q .

To analyze the experiments, we use the kernel density estimator $S_{n,h(n)}$ with

$$h(n) := c \cdot n^{-1/3} \quad (n \in \mathbf{N}). \quad (3.4)$$

This choice of $(h(n))_{n=1}^\infty$ is motivated from theorem 4.9 in [Wertz 1978]; notice that the sequence defined in (3.4) fulfills the condition in (3.2).

The statement of consistency (3.3) is formulated in terms of the variational distance between the estimator and the (density) function to be estimated, which means convergence with respect to the strong topology; by experience one knows that the estimates of a kernel density estimator generate a dispersion, which leads to a significantly positive variational distance.

4. The examination of the Maxwell-Hypothesis within a virtual experiment.

4.1. The Maxwell-Hypothesis.

The hypothesis of Maxwell says that the velocity distribution of the constituents of a gas in a three-dimensional space follows a centered normal distribution

$$N(0, \sigma^2) \otimes N(0, \sigma^2) \otimes N(0, \sigma^2) = N(0_3, \sigma^2 I_3)$$

over \mathbf{R}^3 , the variance σ^2 being determined up to a multiplicative constant by the temperature in [K] (Kelvin)

$$\sigma^2 := \frac{k_B T}{m}, \quad (4.1)$$

where 0_3 denotes the 0-vector in \mathbf{R}^3 , I_3 the (3×3) -identity matrix, $k_B = 1.38 \cdot 10^{-23} [J/K]$ the Boltzmann constant and m the mass of the molecule.

In the virtual experiment considered here, we have to reduce the dimensionality, i.e. instead of a three-dimensional normal velocity distribution over \mathbf{R}^3 a corresponding two-dimensional velocity distribution over \mathbf{R}^2 is considered.

Confirmation for this hypothesis can be given in (Experimental) Physics only indirectly, i.e. through checking results out of theories, basing on this hypothesis.

In Theoretical Physics one proves, that the velocity distribution of the constituents of a gas follows a normal distribution, appealing to the principle of maximization of entropy, which of course is a principle created by the brains of men, and which itself also can be confirmed only indirectly. The maximization of entropy is not a causal argument. To prove the one hypothesis, i.e. the one of Maxwell, one bases on an another one, i.e. the one of maximization of entropy. The phenomenon, which is subject to the Maxwell-Hypothesis, is evidently a statement about an ergodic equilibrium, as a consequence out of the ruling dynamics determining the movement of molecules. This consequence of course is not accessible to direct observation in a laboratory experiment- but in a computer experiment. In the following we show by a computer experiment, that the molecular dynamics in mind entails, that the ergodic velocity distribution indeed is a normal distribution.

4.2. The design of the experiment.

We consider a 2-dimensional circular container B with radius $R > 0$:

$$B := \{(x_1, x_2) \in \mathbf{R}^2 \mid x_1^2 + x_2^2 \leq R^2\} \quad (4.2)$$

on the computer. We inject uniformly N non-overlapping molecules of mass m and radius λ into B . The intention of the experiment is to show computer-experimentally, that the velocity distribution of our molecules follows- independently of any prevailing starting velocity distribution- in equilibrium, i.e. large \bar{t} , a centered normal distribution

$$N(0, \sigma^2) \otimes N(0, \sigma^2) = N(0_2, \sigma^2 I_2), \quad (4.3)$$

σ^2 being determined by the second moment μ^2 of the starting velocity distribution. The equality $\sigma^2 = \mu^2$ is a consequence out of the law of conservation of energy, saying that the total kinetic energies $E_N(0)$ and $E_N(\bar{t})$ at $t=0$ and $t=\bar{t}$ are equal.

The conclusion follows, as by the strong law of large numbers, we have

$$\frac{1}{mN} E_N(0) = \frac{1}{2N} \sum_{i=1}^N \langle v^{(i)}(0), v^{(i)}(0) \rangle \xrightarrow{p.a.s.} \mu^2 \text{ for } N \rightarrow \infty \quad (4.4)$$

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and

$$\frac{1}{mN} E_N(\vec{r}) = \frac{1}{2N} \sum_{i=1}^N \langle v^{(i)}(\vec{r}), v^{(i)}(\vec{r}) \rangle \xrightarrow{p\text{-a.s.}} \sigma^2 = \frac{1}{mn} \mathbf{E}(E_n(\vec{r})) \quad (n \in \mathbf{N}) \quad (4.5)$$

for $N \rightarrow \infty$; the latter in case of a centered normal distribution, $\mathbf{E}(E_n(\vec{r}))$ denoting the expectation of $E_n(\vec{r})$. $\langle \dots \rangle$ denotes the standard scalar product.

Remark 4.6. One recognizes from (4.1) and (4.5), that the quadratic form

$$\hat{T} := \frac{m}{2Nk_B} \sum_{i=1}^N \langle v^{(i)}(\vec{r}), v^{(i)}(\vec{r}) \rangle = \frac{1}{Nk_B} E_N(\vec{r}) \quad (4.6)$$

is an consistent estimator for the temperature T :

$$\lim_{N \rightarrow \infty} \hat{T} = \lim_{N \rightarrow \infty} \frac{1}{Nk_B} E_N(\vec{r}) = T = \frac{1}{nk_B} \mathbf{E}(E_n(\vec{r})) \quad (n \in \mathbf{N}). \quad (4.7)$$

Standard argumentation from normal-distribution statistics delivers, that \hat{T} is biasfree and as a consequence of the theorem of Lehmann-Scheffé it follows, that it is even of minimal variance. The result opens possibilities for the thermal interpretation of virtual systems of molecules, cf. Section 5.

Remark 4.9. One notices, moreover, that (4.8) is a stochastic formulation of Boltzmann's result saying that the temperature T in $[K]$ is up to multiplication by a constant equal to the total kinetic energy.

The dynamics describes in Section 2 is imposed on the system. In order to compare the evolution of the velocity distribution of the molecules with the equilibrium distribution postulated by Maxwell, the velocity distribution is estimated basing on a kernel density estimator (and displayed) at regular time intervals.

By reasons of visualization and as our data basis, using a PC only, is too limited, we substitute the estimation of the 2-dimensional velocity distribution in equilibrium based on 2-dimensional kernel density estimator by technique applying 1-dimensional kernel density estimator only: let (V_1, V_2) be a vector valued random variable distributed according to $N(0, \sigma^2) \otimes N(0, \sigma^2)$ (cf. (4.1)) over \mathbf{R}^2 equipped with a standard orthonormal coordinate system. Let a linear subspace L_φ of \mathbf{R}^2 be determined by the angle φ between the first component of the elements of \mathbf{R}^2 and L_φ ; then the orthogonal projection $V_1 \cos(\varphi) + V_2 \sin(\varphi)$ of (V_1, V_2) onto L_φ follows the normal distribution $N(0, \sigma^2)$ over L_φ . This is a consequence of the fact that the family of normal distributions is closed under the convolution operation. But this is only a necessary condition for (V_1, V_2) to be distributed according to $N(0, \sigma^2) \otimes N(0, \sigma^2)$; being fulfilled for every angle $0 \leq \varphi \leq 2\pi$ this condition is also sufficient which follows from the proof of the Cramer-Wold theorem (cf. [Billingsley 1995], p.383).

4.3. The experiment.

In an experiment available through internet the experimentator can select one of three predetermined one-dimensional velocity distributions. The measure-theoretic second power of the chosen distribution is taken as two-dimensional starting distribution of the velocities of the molecules.

Moreover, the experimentator can fix two linear subspaces L_1 and L_2 related with angles φ_1 and φ_2 resp.

Basing on the velocity data (micro-data) of the (running) molecules, sampled at regular time intervals, the velocity distribution of the projection of (V_1, V_2) onto L_1 and L_2 resp. Is estimated by kernel density estimators, V_1 and V_2 being random variables modeling the first and the second component of the velocity vector resp.

The velocity distributions estimated over L_1 and L_2 are compared- according to the Maxwell-Hypothesis- with $N(0, \mu^2) = N(0, \sigma^2)$.

Independently of the chosen starting distribution and the fixed subspaces L_1 and L_2 the estimates approximate the $N(0, \sigma^2)$, which proves experimentally the distributional aspect of the Maxwell-Hypothesis.

We renounced applying the Kolmogorov- Smirnov goodness-of-fit test; instead of this we calculated the variational distance between the estimates and $N(0, \sigma^2)$, i.e. the distance generating the strong topology on the set of probability measures over L_1 and L_2 resp. The whole experiment is available in the internet under www.fernuni-hagen.de/WTHEORIE/online-dokumente.html
Choose: Examination of the Maxwell-Hypothesis: Experiment 1.

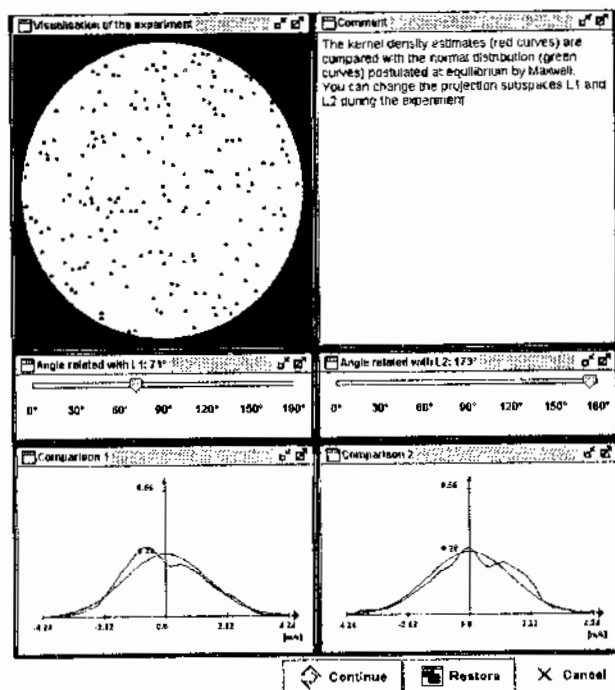


Fig. 1. Examination of the Maxwell- Hypothesis. Experiment1.

The experiment was carried out with 200-400 molecules. According to our experience, the approximation of the normal distribution by the estimated distribution improves when the number of molecules is increased. This observation prompted us to complete these experiments on the vector computer VPP 300 at the Technical University

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of Aachen / Germany with 5000 molecules. The data, which were obtained in a total computation time of ninety hours, were used to produce three digital videos, each approximately one minute in length. These videos confirm our observation described here.

5. One-way-permeable membranes- an example of non-real physics.

5.1. The specification of the problem context.

An advantage of computer experimentation is that even non-real phenomena can be treated. This prompted us to discuss the thermal velocity distribution of molecules in the context of a non-real physics (computer-) experiment.

We again consider a system of molecular constituents following, as before, the Newtonian dynamics, cf. Section 2, imposing now a thermodynamically non-real behavior. In detail, we consider a ring-shaped box with molecules, which is divided into two parts by two membranes, which can be passed by the molecules only in the mathematically positive way. This, of course, contradicts nature: one-way-permeable membranes for micro-constituents do not exist in reality.

The tangential direction is obviously distinguished among all other directions with respect to the average velocity of the micro-constituents, which gives rise to analyze the thermodynamical behavior of the system, e.g. the validity of the equipartition theorem under the prevailing conditions. The latter states, that the thermodynamics kinetic energy is uniformly distributed over all degrees of freedom.

We treat this question in a more general way, as we check the Maxwell-Hypothesis the latter entailing the validity of the equipartition theorem. The methods applied are, essentially, the ones of Section 4.

5.2. The course of analysis.

In a ring-shaped box B we consider a system of N molecules of mass $m > 0$ and radius $\lambda > 0$, on which the dynamics from Section 2 is imposed. The ring-shaped box is divided into two parts by two one-way-permeable membranes, i.e. the molecules can pass the membranes in only the mathematically positive way. This, of course, contradicts nature.

A momentary micro-state of the system at time t is described by the $4N$ -tuple

$$(x^{(1)}(t), \dots, x^{(N)}(t); v^{(1)}(t), \dots, v^{(N)}(t)),$$

$x^{(i)}(t)$ describing the positions and $v^{(i)}(t)$ the velocities of the molecules at time t . The initial positions $x^{(i)}(0)$ and the initial velocities $v^{(i)}(0)$ are generated according to the uniform distribution over B and according to the normal distribution $N(0, \sigma^2(0)) \otimes N(0, \sigma^2(0))$ over \mathbf{R}^2 with $\sigma^2(0) > 0$, resp. By the generation of the initial state of the system the mechanical energy of it is 0 at time $t = 0$, while the thermal energy is given by the total kinetic energy of the micro-constituents:

$$E_{th}(0) = Nm\sigma^2(0). \quad (5.1)$$

For an immediate reference we define the tangential and the radial component of $v^{(i)}(t)$:

$$v_r^{(i)}(t) := \langle v^{(i)}(t), e_r(x^{(i)}(t)) \rangle \quad (5.2)$$

and

$$v_R^{(i)}(t) := \langle v^{(i)}(t), e_R(x^{(i)}(t)) \rangle, \quad (5.3)$$

$e_T(x^{(i)}(t))$ and $e_R(x^{(i)}(t))$ denoting the unit vector in the tangential and the radial direction at $x^{(i)}(t)$ resp., $i=1, \dots, N$. Moreover, we denote the Euclidean norm of $x^{(i)}(t)$ by $r^{(i)}(t)$, $i=1, \dots, N$.

As demonstrated in a first experiment, the system of molecules (medium) enters into a rotational movement in the mathematically positive sense. The angular velocity $\omega(t)$ increases as function of time, which can be quantified by solving the LS-ansatz:

$$\sum_{i=1}^N (v_T^{(i)}(t) - \omega(t)r^{(i)}(t))^2 \rightarrow \min \tag{5.4}$$

with respect to $\omega(t)$ at regular time intervals.

The whole experiment is available in the internet under www.fernuni-hagen.de/WTHEORIE/online-dokumente.html
Choose: One-way-permeable Membranes: Experiment 1.

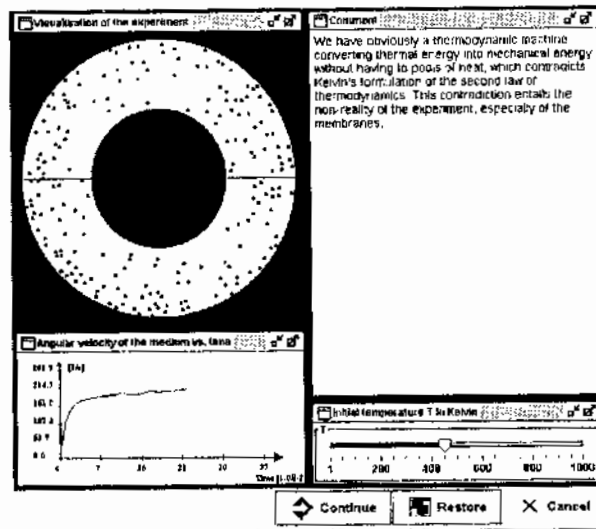


Fig. 2. One-way-permeable Membranes. Experiment 1.

In the first experiment we obviously have a thermodynamic machine which converts heat, i.e. disordered energy, into mechanical kinetic energy, of course, without having two pools of heat!

Provided the Maxwell-Hypothesis remains valid even in this context, the thermal velocity

$$\begin{pmatrix} v_{th1}^{(i)}(t) \\ v_{th2}^{(i)}(t) \end{pmatrix} = \begin{pmatrix} v_T^{(i)}(t) - \omega(t)r^{(i)}(t) \\ v_R^{(i)}(t) \end{pmatrix}, \tag{5.5}$$

$i=1, \dots, N$, at time t being a realization of a random variable distributed according to $N(0, \sigma^2(t)) \otimes N(0, \sigma^2(t))$ with

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$$\sigma^2(t) := \sigma^2(0) - \frac{1}{mN} E_{rot}(t) \quad (5.6)$$

with

$$E_{rot}(t) := \frac{1}{2} m \sum_{i=1}^N \omega(t)^2 r^{(i)}(t)^2, \quad (5.7)$$

which will be proved in a second experiment basing on the same technique, as developed in Section 4.

L_1 is now fixed as the linear space of the tangential direction, while L_2 can be determined in the experiment by the experimentator by fixing the angle φ , $0 \leq \varphi \leq \pi$, between L_1 and L_2 .

Analogously to Section 4, $(v_{th1}(t), v_{th2}(t))$ (instead of (V_1, V_2) in section 4) is projected at regular time intervals onto L_1 and L_2 . The distributions of these projections are given with same arguments as in Section 4 by $N(0, \sigma^2(t))$. One notices that σ^2 defined by (5.6) is a decreasing function of time. In the experiment again the estimates of the distribution densities may be compared with the ones of the theoretically correct distributions. The experiment proving the validity of the Maxwell-Hypothesis under these special conditions is available in the internet under

www.fernuni-hagen.de/WTHEORIE/online-dokumente.html

Choose: One-way-permeable Membranes: Experiment 2.

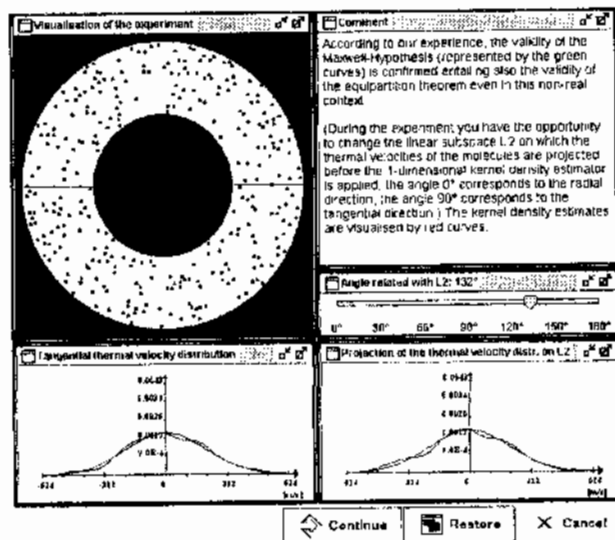


Fig.3. One-way-permeable Membranes: Experiment 2

Notice thereby: In the present experiment we are making only snapshots of the thermal velocity distribution at different time instants; the variance of the velocity distribution being decreasing as function of time. By contrast, in Experiment 1 of Section 4 we intended to have an estimate of the velocity distribution as precise as possible. In

Section 4 the initial velocity distribution was an arbitrary one; in the present section we fixed special normal distributions.

5.3. Conclusions.

The angular velocity of the medium increases; as an immediate consequence we get together with (4.1) and (5.6) that the temperature of the medium decreases.

The increases of $\omega(t)$ is limited, as a consequence of the law of conservation of energy. the theoretically maximal angular velocity cannot be assumed in the experiment, nor does the temperature reach 0 [K]. As the angular velocity of the medium increases, the molecules are concentrated more and more at the periphery of the ring-shaped box, but the ideal concentration at the periphery of B cannot be reached. This is a consequence of the technical data of the experimental plant, especially of λ being positive.

Of course, the design of the experiment defines a thermodynamic machine, having only one pool of heat, which means a perpetum mobile of second kind, contradicting Kelvin's formulation of the second law of thermodynamics, cf. [Reif 1965], sec. 5.11. this irreality could also be confirmed by showing, that the entropy of the medium is decreasing as function of time. Although, the Maxwell-Hypothesis, cf. Section 4.1 and 4.2, remains valid and with it also the equipartition theorem.

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