

Citation:

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was to be observed in all cases, did not become clear to me, still I will not pass in silence the fact of the constant appearance of this granulation.

As the summary of my results, I find that after onesided lesion of the spinal cord an ascending degeneration is observed in the following systems:

1. The homo-lateral posterior columns, where it may be traced as far as into the nuclei of GOLL and BURDACH.
2. The lateral fasciculi to the cerebellum,
 - a. the dorsal portion almost without exception only on the operated side,
 - b. the antero-lateral portion on both sides, but still principally on the operated side.
3. The fasciculus longitudinalis dorsalis on both sides.
4. The corpus trapezoides on both sides (?)

The descending degeneration is represented in figures 21, 22, 23 and 24. It includes:

1. The anterior columns, principally on the operated side, probably centrifugal fibres from the fasc. long. dors.
2. The pyramidal lateral fasciculus on the operated side.
3. The tractus rubro-spinalis, in the lateral columns (VAN GEHUCHTEN).
4. De tractus vestibulo-spinalis, frontal of the anterior horn (EDINGER).
5. Fibres in the posterior columns, being situated partly along the sulcus longitudinalis posterior, and partly along the entering posterior roots, to all probability presenting a homologon to the oval area and the comma of SCHULTZE.

Physics. — *“Motion of molecule-systems on which no external forces act.”* By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the Meeting of November 30, 1907).

§ 1. Up till now two ways have been mainly followed to show that a gas mass left to itself, on which no external forces act, in consequence of the collisions of the molecules will finally pass into a state, in which the molecules are probably about uniformly distributed over the vessel and possess MAXWELL'S distribution of velocities.

The first is the method of BOLTZMANN, who assuming that the density all through the vessel is already the same, and further starting from the assumption that there is no regular arrangement of the molecules as regards the velocity, demonstrates that a certain

FIG. I. HEMISECTIO. MEDULLA OBL.

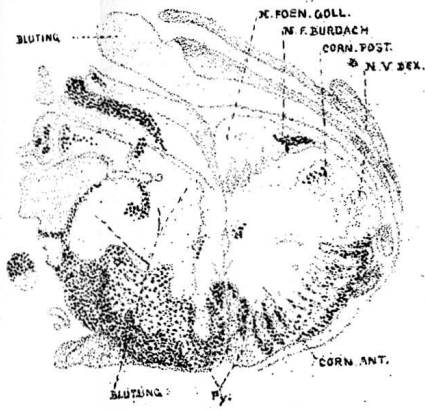


FIG. II. HEMISECTIO. IN C. 7



FIG. III. LAESIO CENTR. IN D. 4.



FIG. IV. HEMISECTIO IN C. 4.

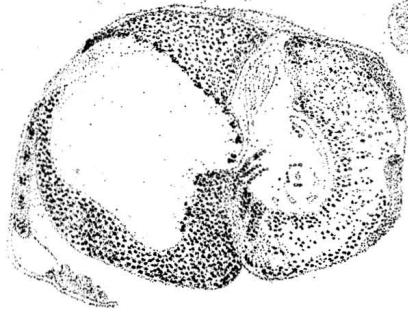


FIG. V

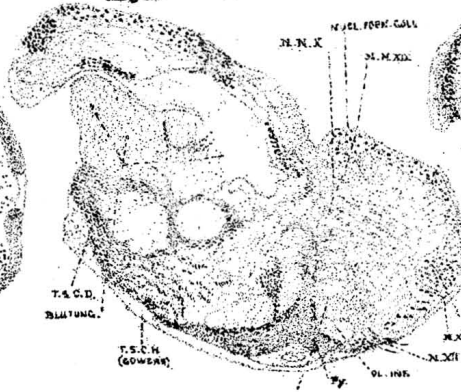


FIG. VI

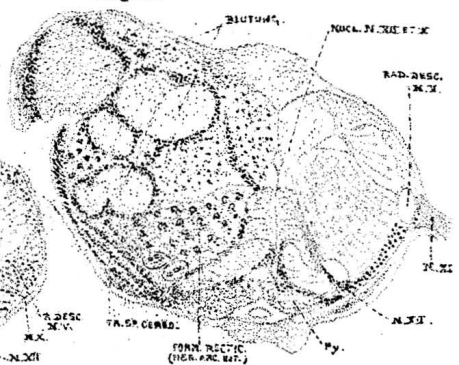


FIG. VII.

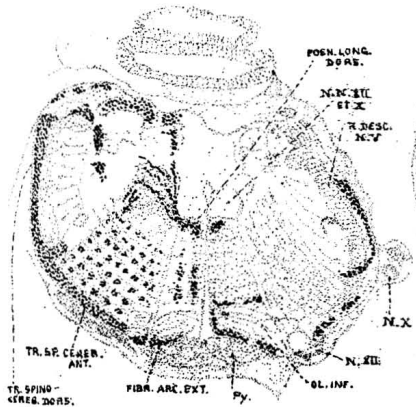


FIG. VIII

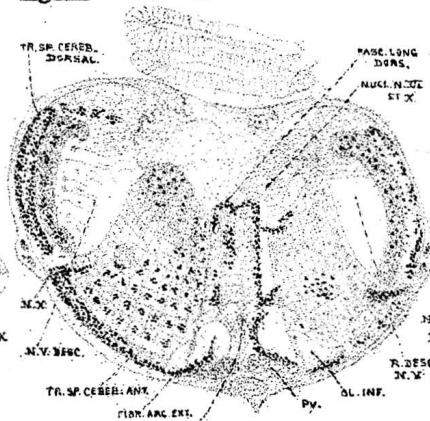


FIG. IX

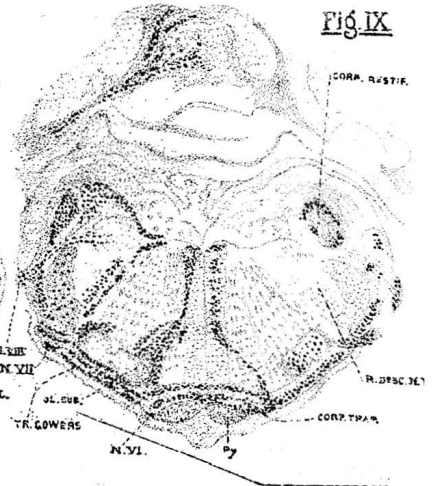


FIG. X

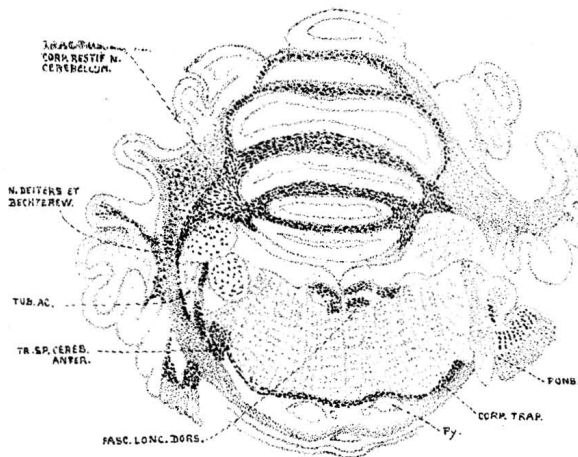


FIG. XI

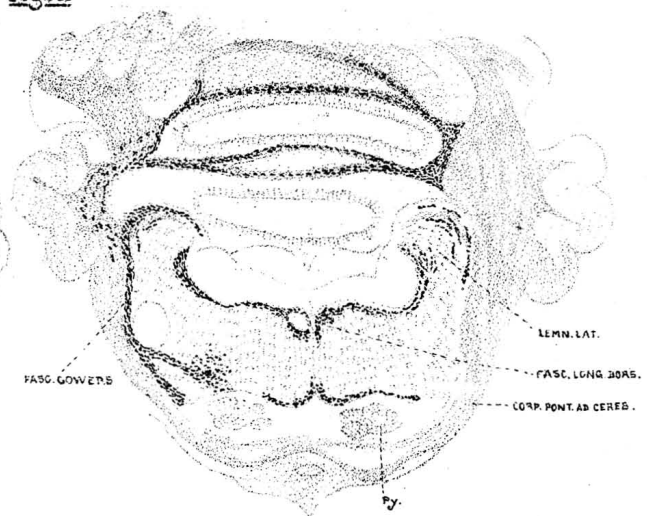


Fig. XII.



Fig. XIII.



Fig. XIV.



Fig. XV.



Fig. XVI. CORPUS TRAPEZOIDES.



Fig. XVII.

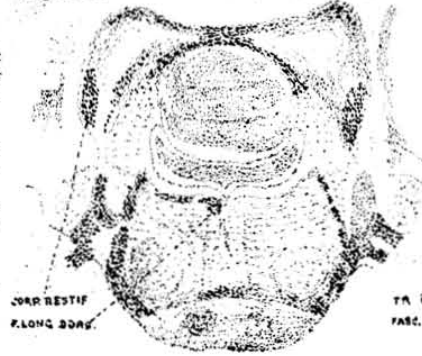


Fig. XVIII.

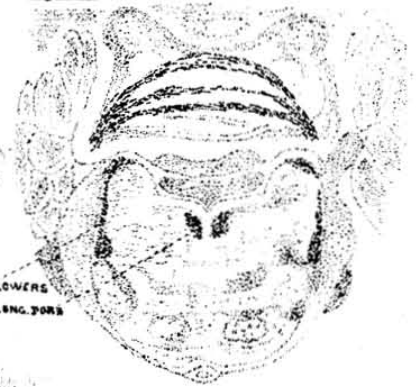


Fig. XIX.

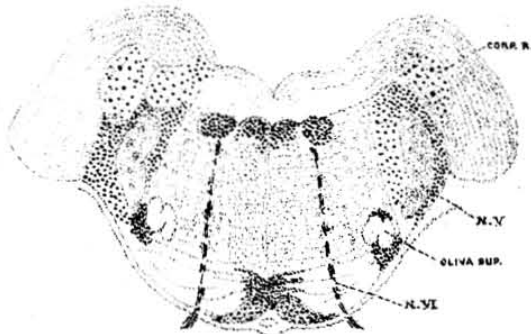


Fig. XX.



Fig. XXI.



Fig. XXII.



Fig. XXIII.



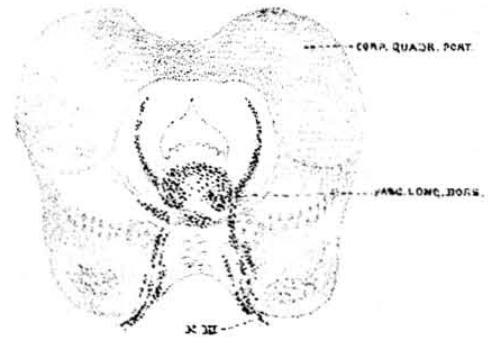
Fig. XXIV.



Fig. XXV.



Fig. XXVI.



quantity $H = \int f \cdot l f \cdot d\omega$ constantly decreases by the collisions till the stationary state is reached, with which, as appears, MAXWELL'S distribution of velocities exists.

The second is the method half followed by BOLTZMANN, and entirely by JEANS, by which it is demonstrated that on certain hypotheses the state with uniform density and that with Maxwell's distribution of velocities are the most probable. These hypotheses are, as regards the distribution of place, that every time there would be an equal chance to any place in the vessel for every molecule; with regard to the distribution of velocities that there would every time be an equal chance that the point of velocity of a molecule would get into any arbitrarily chosen volume-element, in which we should finally have to reckon with the fact that the total energy has a certain definite value.

I have tried to show¹⁾ that there is something contradictory in this, which might be avoided by assuming that the gasmass is arbitrarily chosen from a microcanonical ensemble, of which all the systems possess the energy which the gasmass must have. For in this all the combinations of place and all the combinations of velocities with the same energy are equally numerous, and so we have the same chance to hit upon them for the system chosen.

So another proof for the above mentioned result is furnished, when we show that an arbitrary ensemble of systems with the same energy, left to itself, passes into a microcanonical ensemble. GIBBS endeavours to demonstrate this in the XIIth Chapter of his "Statistical Mechanics"; the reasoning is made clearer by LORENTZ²⁾, though the latter goes no further than calling the assumption that we should finally get a microcanonical distribution, very plausible.

However in a recent paper³⁾ POINCARÉ called attention to a property in the light of which, in my opinion, the above reasoning is no longer tenable. There POINCARÉ shows, namely, that the quantity

$$S = \int P \log P dx_1 \dots dx_n \quad (\text{in which } x_1 \dots x_n \text{ represent the variables}$$

which determine every system of a certain ensemble, and $P = \frac{D}{N}$

the coefficient of probability, the integration being extended over the

¹⁾ These Proc. Febr. 21, 1906 and Jan. 24, 1907.

²⁾ "Über den zweiten Hauptsatz der Thermodynamik"; Abhandlungen über Theoretische Physik, Leipzig 1906, p. 289.

³⁾ "Réflexions sur la Théorie cinétique des gaz"; Journal de Physique, 1906, p. 369.

whole region occupied by the ensemble) is constant if the external circumstances are unchanged and the relation $\sum \frac{\partial X_i}{\partial x_i}$ exists (for which $X_i = \frac{dx_i}{dt}$). In this POINCARÉ takes as variables the coordinates and velocity-components of the molecules; so the quantity referred to above differs from the quantity $\bar{\eta}$ introduced by GIBBS only by a constant factor.

GIBBS shows that in a canonical ensemble $-\bar{\eta}$ has the properties of the entropy, POINCARÉ calls the quantity S itself entropy, also for an arbitrary ensemble. Hence this quantity will have to decrease, where $-\bar{\eta}$ increases.

The property in question may be derived as follows: P has the properties of a density, so:

$$\frac{\partial P}{\partial t} = - \sum \frac{\partial P X_i}{\partial x_i} = - \sum X_i \frac{\partial P}{\partial x_i} \left(\text{as } \sum \frac{\partial X_i}{\partial x_i} = 0 \right).$$

Now, an arbitrary function of P will also behave as a density. Namely:

$$\begin{aligned} \frac{\partial f(P)}{\partial t} &= f'(P) \frac{\partial P}{\partial t} = -f'(P) \sum X_i \frac{\partial P}{\partial x_i} = -f'(P) \sum X_i \frac{\partial P}{\partial x_i} - f(P) \sum \frac{\partial X_i}{\partial x_i} = \\ &= - \sum X_i f'(P) \frac{\partial P}{\partial x_i} - \sum f(P) \frac{\partial X_i}{\partial x_i} = - \sum \frac{\partial [X_i f(P)]}{\partial x_i}. \end{aligned}$$

So the $f(P)$ also satisfies an equation of the same form as the P itself, which equation represents the extension of the wellknown equation from hydrodynamics:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} + \frac{\partial \rho w}{\partial z} = 0$$

to a space of n dimensions.

Now $S = \int P \log P d\tau$, (in which $d\tau = dx_1 \dots dx_n$) $= \int f(P) d\tau$, is the integral of such an $f(P)$, integrated over the whole extension occupied by the ensemble. To ascertain the change of S with the motion of the ensemble, we must every time integrate over the variable space (though constant in size), over which the phases extend or where P and also $f(P)$ have values. So we can perfectly compare $\frac{dS}{dt}$ with the increase in time of a quantity of liquid, taken over all the places where it is. This increase, however, is equal to zero.

However, when $S = \int P \log P dx_1 \dots dx_n$ is constant, the ensemble cannot move in the direction to the microcanonical distribution. For then P would become constant all over the phase-extension in course of time, and so the integral would get a minimum value.

Now, however, the question suggests itself: when the function S or $\bar{\eta}$ is constant, is there not another quantity characterising the ensemble, which by its variation in a certain direction indicates the motion of the ensemble in the direction of the uniform distribution of place and MAXWELL'S distribution of velocities? For this motion is hardly open to doubt, and in a special case such a function has been found for one system by BOITZMANN in the quantity H .

POINCARÉ supposes he has found such a function in his "entropie grossière", a quantity of the same form as S , but in which the elements of the area over which the summation is made, are not taken infinitely small, but so small that practically we cannot distinguish between systems lying within the same element. This quantity may, therefore, be represented by $\sum \Pi \log \Pi \cdot \delta$, in which δ represents the element and Π the mean density in it. In contradistinction with this entropy S is called the "entropie fine", and it may easily be shown that the "entropie grossière" is always smaller than the "entropie fine". It is less easy to see that the "entropie grossière" gradually decreases, nor does POINCARÉ prove this. For it is not easy to see that the quantity $S = \iint P \log P dl d\omega$, of which he tries to prove in some cases that it has decreased, represents an "entropie grossière", while the proof too rests on an assumption which is unjustified in my opinion. It is true that we shall demonstrate further on, that there are quantities of this form which decrease, but for them the name of "entropie grossière" is not very appropriate, as the elements of the extension over which the summation is made are just as well infinitely small, though of lower order of magnitude than the original elements.

§ 2. A very suitable introduction in the theory of gases is supplied by the *problem of the small planets*¹⁾ repeatedly treated by POINCARÉ. There the problem is discussed what in course of time the distribution along the ecliptic will become of a number of small planets, which at some time were placed in their orbit in such a way that chance has decided at least the distribution of the velocities. POINCARÉ shows

¹⁾ Cf. l. c. and also: "Calcul des Probabilités", Paris 1896 and "La Science et l'Hypothèse" Paris 1904.

that if the number is large, and the planets do not interfere with each other, in the long run the planets will most likely get about uniformly scattered over the ecliptic.

If we should wish to treat the problem in exactly the same way as GIBBS, we should have to consider an ensemble of systems each consisting of n planets. As, however, the planets do not interfere with each other, we may also take an ensemble of systems of only one planet, in which case the ensemble represents all possibilities which may occur in the placing of a planet. When now such an ensemble, satisfying certain simple conditions, gradually spreads uniformly over the ecliptic, there is for every planet chosen at random from this ensemble, finally an equal chance to any place of the ecliptic, so that, if we have to choose a planet from such an ensemble n times, they will most probably be distributed about uniformly over the ecliptic, if n is large.

It is assumed that the orbits are circular, and lie in the plane of the ecliptic, so that every planet is determined by the variables l (length) and ω (angular velocity), in which ω is constant, and $l = l_0 + \omega t$, if also larger angles than 2π are admitted. The function S (POINCARÉ'S entropic fine) is, accordingly, here $\iint P \log P dl d\omega$ integrated over all the phases.

As X_1 corresponding to l is equal to ω , and X_2 corresponding to ω is equal to 0, here $\sum \frac{\partial X_i}{\partial x_i} = \frac{\partial \omega}{\partial l} = 0$, so the function S remains constant.

Yet the ensemble approaches uniform distribution over the ecliptic, which, however, is an altogether different thing from the density P becoming constant. Then S would, of course, decrease (it must be observed that $\iint P dl d\omega$ and $\iint dl d\omega$ remain also constant). This approach to uniform distribution is perhaps most readily seen, when we consider only that part of the ensemble that had originally a length between l_0 and $l_0 + dl_0$, the angular velocities lying between ω_1 and ω_2 . This part of the ensemble, being originally found in one point of the ecliptic, will get disintegrated by the different velocities, and gradually spread over the ecliptic, till finally the ecliptic is taken up a very large number of times. At a definite point of the ecliptic there are now parts, which were originally spread over a large number of elements of the extension, always at equal distances from each other, and it is easy to see, that if the function representing the original density, and its derivative are finite and continuous, the

density along the ecliptic will finally be the same everywhere¹⁾. The adjoined fig. 1 represents the motion of the ensemble. Every point of the originally horizontal elementary area moves upwards in a vertical direction with constant velocity, so that the extension always occupies a slanting area with an inclination determined by $t\gamma\alpha = t$.

The horizontal areas at distances 2π from each other indicate the parts of the extension, which are in the same point of the ecliptic. Originally these parts have been in parts of the original area at equal distances from each other. These distances become smaller and smaller, the surface elements becoming more numerous and at the same time smaller.

Instead of the constant quantity $S = \iint P \log F dl d\omega$ (l thought to be continuous) we get a variable, when we immediately take together the

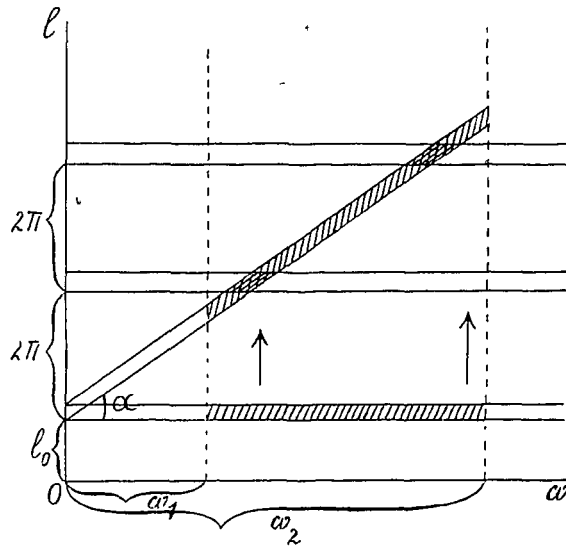


Fig. 1.

surface elements which come to the same thing with respect to the place in the ecliptic. So we get the quantity $S_p = \int_0^{2\pi} P' \log P' dl$, in

which P' represents the quantity found per unit of length in the conjoint areas, of a width dl and at distances 2π apart, which give the same placing in the ecliptic. So in the case referred to, that originally a horizontal area whose width is dl_0 was occupied, $P' dl = \sum P_i dl_0 dl \cot \alpha = \sum P_i \frac{dl_0 dl}{t}$ so $P' = \frac{dl_0}{t} \sum P_i$, in which P_i re-

¹⁾ Cf. POINCARÉ l.c.

presents the density in each of the points of the original area which now come to the same thing.

Now this P' becomes, as we saw, in course of time a constant and so S_p minimum. This quantity might be called *entropy of place*; "entropie grossière" seems less appropriate, because the elements of extension are infinitely small. This final approach to a minimum must not be taken as a continual decrease. It is easy to see that the original function of density might be chosen in such a way that there are also times, at least in the beginning, at which the densities P' rather diverge than draw nearer to each other. Then the quantity S_p would increase; so $\frac{dS_p}{dt}$ is not like BOLTZMANN'S $\frac{dH}{dt}$ negative all through.

If, however, we compare times, in which first an angle 2π , then 4π etc. is occupied, we may say with a pretty high degree of certainty, that S_p has always diminished. If now instead of a horizontal area an arbitrarily chosen ensemble is considered, the above reasoning may be applied for every horizontal elementary area from it. So now too the ensemble is finally uniformly spread over the ecliptic, and the quantity $S_p = \int_0^{2\pi} P' \log P' dl$ becomes minimum. Now, however,

$P' dl = \Sigma \int P dl d\omega$ or $P' = \Sigma \int P d\omega$, every time integrated over all ω 's which fall within the horizontal area determined by dl . This P' becomes finally constant. The motion of the ensemble in this more general case is expressed by fig. 2.

The above mentioned inaccuracy in POINCARÉ'S reasoning is this: he considers the quantity $S = \iint P \log P dl d\omega$, in which he integrates with regard to l from 0 to 2π . So the P from this formula has evidently arisen by summation for the different values of l which come to the same thing, but not by integrating with respect to ω . Hence this P is the sum of the densities of the elements obtained by taking a definite ω , and then successively $l, l + 2\pi$ etc. In fig. 2 these elements are cross-hatched for one value of ω . However, POINCARÉ assumes further that finally for $t = \infty$ this P , or rather this ΣP no longer depends on l , but only on ω ¹⁾. This seems to me incorrect. For then for every vertical elementary area in fig. 2 the sum of the densities in the elements, which are every

¹⁾ Réflexions sur la Théorie cinétique des gaz; p. 381, p. 385 etc.

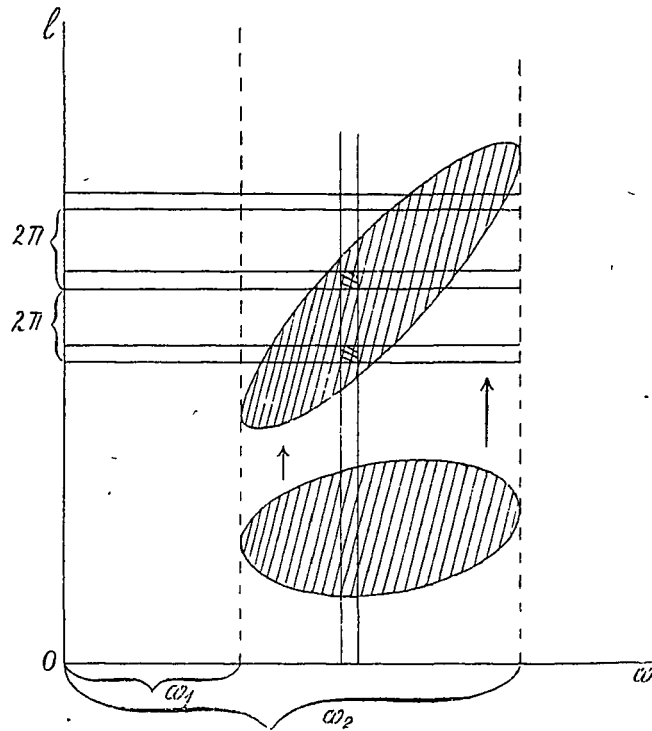


Fig. 2.

time at a distance 2π from each other, would finally have to become constant. This, however is only possible if the number of terms of this sum becomes at last infinitely large, which is by no means the case. Every vertical distance within the extension remains, namely, of the same length, so that the number of elements within each vertical area which are to be taken together, remains always finite. Only when the occurring ω 's extend over a finite distance, the number of terms of the sum for $t = \infty$ can also become infinitely large.

A second partial entropy, that *with regard to the velocities* is obtained by taking these elements of the extension together which give the same velocity. So this is here $S_s = \int_{\omega_1}^{\omega_2} P'' \log P'' d\omega$, in which

$P'' = \int P dl$ is integrated along the vertical areas. This entropy, is indeed, also smaller than the "entropie fine", but the difference remains constant, and so also S constant.

§ 3. A transition case from that of the planets to that of the gas molecules is furnished by the case of a gas of one dimension. By this POINCARÉ understands a gas, all the molecules of which move

parallel to each other to and fro between two parallel walls normal to the direction of motion of the molecules. We assume that perfectly elastic collision takes place, and that the dimensions of the molecules may be neglected. Now if we trace the whole way always in one direction, and introduce the distance to one of the walls as variable l , further consider the velocity ω as constantly positive, this case is identical with the preceding one, if we call the distance between the walls π , only with this difference, that now the distances $l, 2\pi - l, 2\pi + l$ etc. come to the same thing as regards the placing of the molecules. So twice as many areas must be taken together as before, and now we have only to integrate from 0 to π . Just as before we have now a quantity $S_p = \int_0^\pi P' \log P' dl$, which decreases

because $P' = \Sigma \int P d\omega$ becomes at last a constant¹⁾.

Such molecules not interfering with each other in their motion, the case of a continuous ensemble of systems of one molecule each, and that of a real gas of n molecules is pretty much the same, just as for the planets. For a gas of three dimensions this is in general no longer the case in consequence of the collisions.

We meet with another transition case in an ensemble of systems consisting of n planets each. The "entropic fine" is now:

$$S = \int P \log P dl_1 \dots dl_n d\omega_1 \dots d\omega_n,$$

the S_p is given by

$$S_p = \int_0^{2\pi} \dots \int_0^{2\pi} P' \log P' dl_1 \dots dl_n,$$

in which $P' = \Sigma \int P d\omega_1 \dots d\omega_n$, integrated with respect to $\omega_1 \dots \omega_n$

and summed over all the combinations from l_1 to l_n which give the same arrangement of the planets. These combinations are obtained by combining the values $l_1, 2\pi + l_1$ etc. with the values $l_2, 2\pi + l_2$ etc. to $l_n, 2\pi + l_n$ etc. in all ways possible. The number of these combinations, so the number of terms in the summation increases indefinitely during the motion, just as in the preceding cases; so P' becomes constant, and S_p approaches the minimum value. If

¹⁾ Here we might also have taken the coordinate x varying from 0 to π as variable instead of the continuous l . Then the ω shifts every time from + to - and vice versa, and we get the same terms $\int P d\omega$, but now at the same height x .

instead of the planets we imagine molecules moving in a one-dimensional motion, we get: $S_p = \int_0^\pi \int_0^\pi P' \log P' dl_1 \dots dl_n$ in which $l_1, 2\pi - l_1, 2\pi + l_1$ etc. must be taken together in the calculation of P' .

We meet with still another transition case when we consider an ensemble of systems of one molecule each, moving freely in a vessel having the shape of a right-angled parallelepiped with the edges a, b and c . This motion may be thought as composed of three motions parallel to the edges, which we may each treat as in the first transition case. If we call the coordinates with respect to the sides x, y and z , the combinations of $x, 2a-x, 2a+x$ etc. with $y, 2b-y, 2b+y$ etc. and $z, 2c-z, 2c+z$ etc. come to the same thing with regard to place. So we now get the P' by integrating for the P with regard to the components of the velocity, and by then summing for all these combinations.

The $S_p = \int_0^a \int_0^b \int_0^c P' \log P' dx dy dz$ decreases again

till the minimum value is reached. A molecule chosen at random from the ensemble will have an equal chance to any place in the vessel. When the dimensions of the molecules are not neglected planes take the place of the walls of the vessel at a distance r parallel to them.

If we may disregard the collisions of the molecules inter se of a gas mass, we might always consider each of the n molecules as chosen arbitrarily from such an ensemble, and hence at last these n molecules would probably be distributed over the vessel about uniformly.

§ 4. Finally we shall consider an ensemble of systems consisting of n molecules moving in a vessel having the shape of a right-angled parallelepiped. If we take the coordinates with regard to the side faces as variables, the components of the velocities may also be negative and the representing point of a system may occupy any place within the space

$$\int_r^{a-r} dx_1 \dots dx_n \int_r^{b-r} dy_1 \dots dy_n \int_r^{c-r} dz_1 \dots dz_n \int_{-\infty}^{+\infty} d\xi_1 \dots d\xi_n \int_{-\infty}^{+\infty} d\eta_1 \dots d\eta_n \int_{-\infty}^{+\infty} d\zeta_1 \dots d\zeta_n$$

in which we need only take into consideration that during the motion the kinetic energy or also the Σv^2 remains constant. So we shall now have to examine which parts of the phase extension will give the same arrangement of the molecules, and which the same molecular

velocities, and to ascertain whether the P integrated and summed over these spaces becomes constant in course of time.

It stands to reason that here the problem of the distribution of velocities will be the simplest, because it is modified directly by the impact, and the distribution of place only indirectly.

In agreement with § 2 where we considered an area from the original extension lying between l_0 and $l_0 + dl_0$ in order to examine the placing, we shall take here a part from the extension determined by limits of velocity lying infinitely near each other, but covering a finite part of the $3n$ -dimensional space of coordinates. In connection with the condition that $\Sigma v^2 = C$, we take from the $3n$ -dimensional space of velocities an element of a spherical shell, whose radius is $\sqrt{\Sigma v^2}$. To this corresponds a prismatic or cylindrical part of the extension, the base of which is represented by the element in question. With regard to the distribution of velocities the points from these and similar prismatic or cylindrical tubes come to the same thing. The elements of the spherical shell represent the projection of the tubes on the space of velocities. Now it remains to investigate whether the quantity of substance, which originally is found above the element mentioned in a given tube, will not finally have spread uniformly over all the tubes, so that the same quantity will be found above every element of the same size. If so, $S_i = \int P' \log P' d\tau$ will again become minimum, if $d\tau$ represents the size of such an element, and $P' d\tau$ the quantity which is projected in $d\tau$.

We may also call the points from the element of the spherical shell the points of velocity of the systems, and the vector, which joins the origin with such a point of velocity, represents all the velocities of the system both with regard to magnitude and to direction; the projections of the vector on the $3n$ axes of the space are the components of the molecular velocities.

The best way of setting forth the gradual uniform dispersion of these points over the mentioned hypersphere is perhaps by availing ourselves of BOREL's mode of representation, and by partially following his method.¹⁾

BOREL imagines that in the same $3n$ -dimensional space in which the coordinates of the molecules are laid out (so that we get in this way a point representing the total arrangement for every system) also the components of velocity are projected starting from the representing point mentioned. The vector then obtained represents the velocity

¹⁾ "Sur les Principes de la Théorie cinétique des gaz" par EMILE BOREL. Annales de l'Ecole Normale Supérieure IIIe Série, 1906, N^o. 1, p. 9.

of the representing point, and we may now examine what takes place with this vector during the motion. It is now obvious that the representing point moves in a space inclosed by surfaces and spaces as $x_1 = r$, $x_1 = a - r$ etc. with which it collides when one of the molecules of the system strikes against a wall of the vessel. When two molecules collide, the representing point strikes against a surface, the equation of which has the form :

$$(x_m - x_n)^2 + (y_m - y_n)^2 + (z_m - z_n)^2 = 4r^2.$$

Now BOREL shows that for this impact the same rules hold as for ordinary collisions, so that the lines along which the point moves before and after impact, lie in the same plane as the normal, the normal dividing the angle of the first two lines into two equal parts. The velocity, too, remains the same. According to the above we must now imagine a finite space filled with such representing points, an infinitely small pencil of vectors of velocity starting from each point, mutually equal, and also equal for all the points. Now a number of these representing points strikes against one of the above mentioned surfaces, e.g. with equation

$$(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 = 4r^2;$$

this implies then that for these systems the first and the second molecule collide. This surface is that of a cylindre of revolution of the $3n-3^{\text{th}}$ degree, against the outside of which the points strike.¹⁾ The base of the cylindre is a sphere, the descriptive lines have here become descriptive spaces, namely plane spaces of $3n-3$ dimensions.

In the collision referred to, the extension from which the points come being large compared to the dimensions of the section of the cylindre (or at least of the same order) the infinitesimal pencil will extend in the directions of the perpendicular section of the cylindre, so here in 3 dimensions, to a pencil of finite width. If from this we take again an infinitesimal part, it comes from a definite point of each section of the sphere, and so from the points of a descriptive space of the cylindre.²⁾ Part of this strikes again against another cylindre (which e.g. involves collision of the 1st and the 3rd molecule), and the infinitely narrow pencil extends again to finite width; etc.

The representing points which have not taken part in these collisions strike again against another surface, and the pencil extends every time to one an infinite number of times wider, but every time in other

¹⁾ If the new coordinates $\xi, \xi', \eta, \eta', \zeta$ and ζ' determined by $\xi = \frac{1}{2}(x_1 - x_2) \sqrt{2}$, $\xi' = \frac{1}{2}(x_1 + x_2) \sqrt{2}$ etc. are introduced, the equation of the surface becomes $\xi^2 + \eta^2 + \zeta^2 = 2r^2$.

²⁾ Properly speaking a narrow region in the direction of this descriptive space.

spaces. However, when in a system the same molecule has had a great number of collisions, the extension has had a projection on the space determined by the axes of the coordinates of the 1st molecule for each of these collisions. So when every molecule has had a great number of collisions the above mentioned vector of velocity has passed round the sphere on which the points of velocity lie, a great many times in every direction. The points of velocity which originally covered an element of the spherical shell, will now occupy the whole spherical surface many times. As, however, the points of the sphere, where a point of velocity is after one, two etc. revolutions in a certain direction, come to the same thing with respect to the distribution of the velocities of the molecules, as in all the preceding cases we may again assume that finally the density is the same all over the spherical surface.

For the rest of the elements of the same spherical shell originally occupied the same reasoning holds. If there are also systems in the ensemble with another kinetic energy, the points disperse also here homogeneously in spherical layers: as, however, one kind cannot pass into another, the density may be different for the layers. It is the same as in the distribution of place when the gas masses are in different vessels. ¹⁾

Now the problem of the placing of the molecules. For this purpose we consider a part of the phase-extension, originally determined with regard to place by limits lying indefinitely near each other, but occupying a finite part of the space of velocities. Now we have to demonstrate

¹⁾ Also without BOREL's way of representation the above mentioned dispersion may be imagined to a certain extent. In each of a number of systems the molecules have the same velocities, but different places. Now it will entirely depend on the mutual situation e.g. of the molecules 1 and 2 in connection with their velocities, what the direction of the normal becomes in the collision, and so up to a certain extent, what the final velocities will be. In any case we get an infinitely large number from a single pair of velocities. Whereas we had before infinitely narrow limits between which the components of velocity had to lie, now we get a finite region. If we have chosen a definite one from the pairs of final velocities so also a definite velocity of the 1st molecule, this molecule may have all kinds of positions with regard to the 3rd molecule, against which it will presently strike, so also the normal of collision can have all kinds of directions, and so the limits thought infinitely narrow are again removed to a finite distance, etc. If we now take as variables the angles of the general vector of velocity with the axes of velocity instead of the components of velocity, the moving apart of the limits will yield a larger amount of occupied angles, so that finally there is occupied an amount of a large number of times 2π . If we now take into account, that increase of such an angle by an amount 2π has no effect, we arrive at considerations and results of quite the same nature as in the problems treated above.

that finally this ensemble will be uniformly scattered over all the combinations of place. In this case there will again be a partial entropy S_p which has become minimum.

We may try to make use of BOREL's way of representation also here, and shall take as introductory case an ensemble of systems consisting of 2 molecules moving along the same line perpendicular to two parallel walls between these walls.

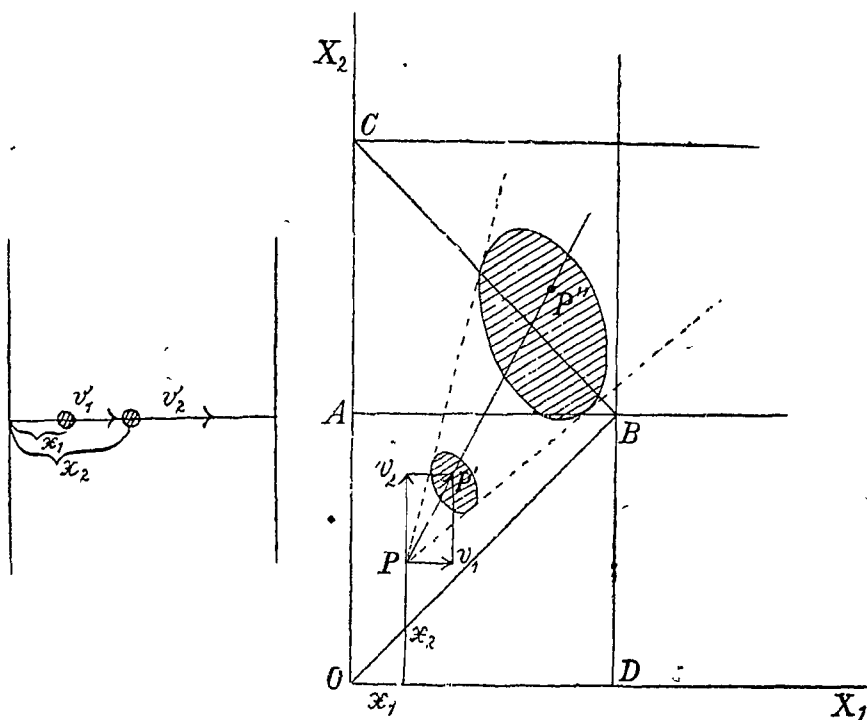


Fig. 3a

Fig. 3b

Fig. 3^a represents one system from the ensemble, fig. 3^b the motion of the whole ensemble, when the dimensions of the molecules are disregarded. Originally all the systems are in an element placed at $P(v_1, x_2)$, the points of velocity lying within an arbitrary figure. Here the representing points will be found after 1 sec., whereas they would occupy a continually extending figure if there was no collision. Collision of the molecules with the walls is here represented by collision of the representing points with the lines OA and AB , collision of the molecules inter se by collision with the line OB .

Now, however, we may also think the motion after the collision e.g. with AB continued past AB , if the triangle ABO which

would then be passed through for the second time with the velocity after impact is thought to be turned over along AB . Now the point pursues its course uninterrupted. A following collision with OB now becomes collision with BC ; now we may proceed again in the same way. The pencil then goes on without any disturbance, but we must take into account that the elements of surface, which in this way proceed from each other, represent the same placing of the two molecules. The continually extending figure of the representing points will finally contain a very large number of elements of surface of every kind coming to the same thing, or a very large number of turned over triangles, so that finally the points will be uniformly distributed over the sums of the elements of surface. So every situation of the two molecules represented by a point in ABO , occurs equally frequently. A point of BDO , however, is never reached: so every situation in which the 2nd molecule is on the right of the 1st is equally probable, but the 2nd cannot get to the left side of the 1st.

Now we should have to extend this reasoning to the case of more than two dimensions. The reflection against the walls does not affect our reasoning. The striking of the molecules against each other, however, is now represented by striking against a cylindrical surface. Though this obstructs the way, it no longer shuts off a part of the space. The case may be compared with that of fig. 3, if the line OB is replaced by a circle. I have not succeeded in solving the problem for this general case. However, it seems very plausible that the finite number of cylindres will not be able to prevent that the uniform distribution of the representing points over the sums of the elements of volume which come to the same thing, which distribution would finally come about as we saw in § 3 if there was no collision, will be established also now. So all the combinations of place of the molecules would then occur equally frequently.

§ 5. Finally it may still be shown that when all the combinations of place and all the combinations of velocity occur with equal frequency, it follows from this that for the great majority of the systems the molecules are distributed about uniformly over the vessel, and have MAXWELL'S distribution of velocities. So far we have always distinguished between the individual molecules, now we shall have to take into consideration, that exchange of the molecules does not affect the *distribution* of place or velocity, so far as we can know it. So all the combinations which arise from each other by exchange of molecules, now come to the same thing. Hence if of s molecules s_1 are in the first element of volume, s_2 in the 2nd etc., there are

$\frac{s!}{s_1! s_2! \dots s_n!}$ combinations yielding the same distribution of place. As BOLTZMANN has shown, the denominator may be represented by $ce^{\int f(xyz) \log f(xyz) dx dy dz}$ by approximation, in which $f(xyz)$ represents the function of distribution of the molecules over the vessel. The integral is minimum if $f(xyz) = C$, so the number of combinations is then maximum, or the uniform distribution is the most frequently occurring one. To show that the deviation from this distribution is not large as a rule, we may examine how many combinations yield a distribution, in which instead of $\frac{s}{n}$ molecules, $\frac{s}{n} + x_1, \frac{s}{n} + x_2$ etc. molecules occur in the elements. This number is:

$$\frac{s!}{\left(\frac{s}{n} + x_1\right)! \left(\frac{s}{n} + x_2\right)! \dots \left(\frac{s}{n} + x_n\right)!}$$

By putting $s! = s^{s+\frac{1}{2}} e^{-s} \sqrt{2\pi}$ etc., we get for this, taking into account that $x_1 + x_2 + \dots + x_n = 0$:

$$\frac{n^{s+\frac{n}{2}}}{(\sqrt{2\pi s})^{n-1} \left(1 + \frac{nx_1}{s}\right)^{\frac{s}{n} + x_1 + \frac{1}{2}} \dots \left(1 + \frac{nx_n}{s}\right)^{\frac{s}{n} + x_n + \frac{1}{2}}}$$

Now by approximation

$$\log \left(1 + \frac{nx_1}{s}\right)^{\frac{s}{n} + x_1 + \frac{1}{2}} = \left(\frac{s}{n} + x_1 + \frac{1}{2}\right) \left(\frac{nx_1}{s} - \frac{n^2 x_1^2}{2s^2} + \dots\right) = x_1 + \frac{nx_1}{2s} + \frac{nx_1^2}{2s} \dots$$

So the *log* of the denominator (with the exception of the first factor) is by approximation:

$$\sum x + \frac{n \sum x}{2s} + \frac{n}{2s} \sum x^2 = \frac{n}{2s} \sum x^2.$$

The number of combinations becomes now:

$$\frac{n^{s+\frac{n}{2}}}{(\sqrt{2\pi s})^{n-1}} e^{-\frac{n}{2s} \sum x^2};$$

if we put $\sum x^2 = nu^2$, the chance, that the mean deviation is smaller than u , may be represented by:

$$c \frac{n^{s+\frac{n}{2}}}{(\sqrt{2\pi s})^{n-1}} \int_0^u e^{-\frac{u^2}{2s}} \frac{1}{n^2} du = \frac{2}{\sqrt{\pi}} \int_0^{\frac{u}{\sqrt{2s}}} e^{-t^2} dt.$$

Very soon, however, this value is very large, when u is only a few times $\frac{1}{n}\sqrt{2s}$ as yet; then u or the mean x , however, is still small compared to $\frac{s}{n}$, the mean number of molecules per volume element.

In a similar way the problem of the distribution of velocities may be treated. Here the denominator of the expression $\frac{s!}{s_1! \cdot s_2! \dots s_N!}$

may be reduced to $Ce^{\int f(\xi\eta\zeta) \log f(\xi\eta\zeta) d\xi d\eta d\zeta}$, in which $f(\xi\eta\zeta)$ represents the function of distribution of the points of velocity. The integral is minimum, taking into consideration that $\sum v^2$ is constant, when $f(\xi\eta\zeta) = ae^{-b(\xi^2+\eta^2+\zeta^2)}$. Now it remains to investigate what is the chance to a given deviation from this distribution. We may define this deviation by the figures $x_1, x_1' \dots x_2, x_2' \dots$ etc. indicating the relative surplus of points of velocity in the elements of volume, respectively with the velocities v_1, v_2 etc. In the first element is then the quantity $s_1 = ae^{-bv_1^2}(1+x_1)^{s_1}$, in the second $s_2 = ae^{-bv_2^2}(1+x_1')$ etc., so that the number of combinations to be taken together:

$$\frac{s!}{[ae^{-bv_1^2}(1+x_1)]! [ae^{-bv_2^2}(1+x_1')]! \dots [ae^{-bv_2^2}(1+x_2)]! \dots}$$

The first factor of the denominator is equal to (by approximation):

$$(ae^{-bv_1^2})^{ae^{-bv_1^2}(1+x_1)+\frac{1}{2}} \times (1+x_1)^{ae^{-bv_1^2}(1+x_1)+\frac{1}{2}} \times e^{-ae^{-bv_1^2}(1+x_1)} \times \sqrt{2\pi} =$$

$$= C_1 (ae^{-bv_1^2})^{ae^{-bv_1^2}x_1} \times (1+x_1)^{ae^{-bv_1^2}(1+x_1)+\frac{1}{2}} \times e^{-ae^{-bv_1^2}x_1}.$$

If we multiply by the other factors, the latter part vanishes, as $\sum ae^{-bv_1^2}x_1 = 0$. So we keep:

$$C (ae^{-bv_1^2})^{ae^{-bv_1^2}x_1} (1+x_1)^{ae^{-bv_1^2}(1+x_1)+\frac{1}{2}} \times (ae^{-bv_1^2})^{ae^{-bv_1^2}x_1'} \\ (1+x_1')^{ae^{-bv_1^2}(1+x_1')+\frac{1}{2}} \times \text{etc.}$$

If we take the Nep. log. the former part vanishes, as also $\sum ae^{-bv_1^2}x_1 \cdot v_1^2 = 0$, so that log. denominator:

$$= \sum [ae^{-bv_1^2}(1+x_1) + \frac{1}{2}] \log(1+x_1) + C.$$

1) This u is equal to the above one multiplied by $d_\xi d_\eta d_\zeta$.

This is by approximation :

$$ae^{-bv_1^2} \left\{ x_1 + \frac{x_1^2}{1.2} + \dots \right\} + ae^{-bv_2^2} \left\{ x_2 + \frac{x_2^2}{1.2} + \dots \right\} + \text{etc.} + C$$

or

$$ae^{-bv_1^2} \frac{\sum x_1^2}{1.2} + ae^{-bv_2^2} \frac{\sum x_2^2}{1.2} + \dots + C,$$

so that the whole form may be represented by

$$C_e \left[ae^{-bv_1^2} \frac{\sum x_1^2}{1.2} + ae^{-bv_2^2} \frac{\sum x_2^2}{1.2} + \dots \right]$$

or if we denote the most probable quantities per element by a_1, a_2 etc. :

$$C_e \left[a_1 \frac{\sum x_1^2}{1.2} + a_2 \frac{\sum x_2^2}{1.2} + \dots \right]$$

This exponent agrees perfectly with that obtained for the preceding problem. We may reduce the latter to the form $-\sum \left(\frac{ax}{\sqrt{2a}} \right)^2$,

and the former to the form $-\sum \left(\frac{x}{\sqrt{\frac{2s}{n}}} \right)^2$; now they represent

the negative sum of the squares of the absolute deviations divided by the root from twice the normal number. Just as in the preceding problem the chance to a combination of deviations for which the root from this latter sum does not amount to more than a few times unity is now very large. If we now take as measure

for the deviation the mean relative deviation or $\sqrt{\frac{\sum x^2}{N}}$, we see

that this value is very small compared to $\sqrt{\sum \frac{ax^2}{2}}$, so that this mean deviation will be very slight¹⁾.

To conclude we may still remark that in order to get in the end both uniform distribution of the molecules over the vessel and MAXWELL'S distribution of velocities, originally both a finite part of the space of velocities and of the space of coordinates must have been occupied. Or there must be such an uncertainty as to the original situation and velocities of the molecules that we must consider possible a finite whole of combinations with regard to both. This finite whole of possible combinations constitutes the ensemble, which we follow in its course instead of the system unknown within certain limits.

¹⁾ It having been assumed in the calculation that a considerable number of points of velocity still occur in every element, we must not think of the whole of the space of velocities when estimating the number of elements N .