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An examination of various postulates of irreversibility

by

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SUMMARY. — Firstly, we recall the need to break the reversible character of the B. B. G. K. Y. system of equations by means of a postulate of irreversibility to obtain a kinetic equation compatible with the second principle of thermodynamics.

Next, three postulates of irreversibility are examined: that of molecular chaos, that of linear relaxation and, finally, that of superposition. Then we determine the corresponding kinetic equations and the expressions for the viscosity coefficient to which they lead. Comparison with experiment is made each time.

Lastly, we attempt to obtain an irreversible kinetic equation without introducing a postulate of irreversibility in the B. B. G. K. Y. system. This consists in adding a complementary irreversible term to the fundamental equation of the dynamics of a particle. The suggested term is of quantum origin and leads to a kinetic equation of the Fokker-Planck type.

RÉSUMÉ. — La nécessité de briser le caractère réversible du système d'équations B. B. G. K. Y. à l'aide d'un postulat d'irréversibilité pour obtenir une équation cinétique compatible avec le second principe de la thermodynamique est tout d'abord rappelée.

Trois postulats d'irréversibilité sont ensuite examinés, celui du chaos moléculaire, celui de la relaxation linéaire et celui de superposition. Les équations cinétiques correspondantes et les expressions du coefficient de viscosité auxquelles elles conduisent sont déterminées. La comparaison avec l'expérience est effectuée chaque fois.

Une tentative en vue d'obtenir une équation cinétique irréversible sans introduction d'un postulat d'irréversibilité dans le système d'équations

B. B. G. K. Y. est alors présentée. Cette tentative consiste à intervenir dans l'équation fondamentale de la dynamique d'une particule en ajoutant un terme complémentaire irréversible. Le terme proposé est d'origine quantique et conduit à une équation cinétique du type Fokker-Planck.

I. INTRODUCTION

The reversible character of the equation of the dynamics of a particle subjected to a force deriving from a potential brings about the reversibility of the fundamental equation of classical statistical mechanics (or the Liouville equation) and of the B. B. G. K. Y. system of equations which is equivalent to the latter.

Such a thing is in compatible with the second principle of thermodynamics which expresses the irreversible character of the evolution of a physical system.

Classical physics rests on two contradictory ideas: on the one hand, the Hamiltonian formalism which is compatible with the first principle of thermodynamics or the conservation of energy principle; on the other hand, the principle of the non-decrease in entropy or the second principle of thermodynamics which is incompatible with the Hamiltonian formalism.

Quantum mechanics does not seem capable of contributing any improvement since its fundamental equation—*i. e.* the Schroedinger equation—is also reversible as a consequence of the link between the Hamiltonian of classical mechanics and the Hamiltonian operator of quantum mechanics. At the end of this article we will show that this is perhaps the case provided that a new idea is introduced.

It is both remarkable and surprising that theoretical physics has been able to develop so deeply despite this intrinsic incoherence. Physicists have surmounted this difficulty on writing Newton's equation for a particle subjected to a force deriving from a potential which, in such conditions, is reversible; on obtaining a phase-space density equation (Liouville's equation) for the treatment of a population of a large number of particles, which is also reversible; on deducing from the latter the B. B. G. K. Y. system of equations which is also reversible, and on breaking the reversibility of this system by means of a postulate or irreversibility which is foreign to dynamics.

Such a postulate leads to a kinetic equation governing the single distribution function from which one determines the expressions for the transport coefficients with a view to making a comparison with experimental results.

In addition, one shows that the entropy, defined from an integral which involves the logarithm of the single distribution function, cannot decrease.

This article is divided into parts. In the first, we proceed to examine

three postulates of irreversibility and the kinetic equations to which they lead. We give the expressions for the corresponding viscosity coefficients and make a comparison with experiment. The three postulates are: that of molecular chaos; that of linear relaxation and that of superposition. The first leads to Boltzmann's kinetic equation and the second and third to a Fokker-Planck type of equation whose coefficients of the collision term contain the moments of the distribution function. This form of the Fokker-Planck equation has been suggested by J. Frey and J. Salmon.

In the second part, we show our attempt to modify Newton's law for a particle subjected to the effect of a potential φ .

The force involved is the sum of the usual term $-\vec{\nabla}\varphi$ and of a complementary irreversible term which contains the Laplacien $\Delta\varphi$ of φ as a factor and consequently vanishes for the potentials in r^{-1} . On the other hand, the potential φ is the sum of the usual potential φ_0 and of a complementary term of quantum origin which, for the potential in r^{-1} negligible at a long distance.

An irreversible kinetic equation is thus obtained in a strictly deductive manner and the entropy increases away from equilibrium, conforming to the second principle of thermodynamics. In the case of a dilute gas, this equation merges with that obtained from the second and third postulates. For each of the suggested equations, the corresponding expression for the kinetic viscosity coefficient is determined and the theoretical values are compared with the experimental values in a temperature range lying between 200 and 1,000° K.

This comparison is fundamental since the best theory is that which, starting from the smallest number of laws, principles and postulates, leads to a correct prediction of the experimental results.

In this connection, let us note that scientific authors use the terms « law », « principle », and « postulate » to qualify an *a priori* imposed relation from which they exactly deduce the theoretical expressions for physical quantities that are able to be compared with experiment, or on introducing justified approximations. A few famous examples are « The fundamental law of dynamics », « The principles of thermodynamics » and « The postulate of irreversibility of the molecular chaos ».

In an effort to simplify language, we suggest that only the term « postulate » be used. The physicist postulates basic equations such as those of Newton and Schroedinger and examines their consequences.

II. THE FIRST TWO POSTULATES OF CLASSICAL STATISTICAL MECHANICS

These are the postulate of the dynamics of a particle approximated by a material point and subjected to a force deriving from a potential and the

postulate of the representation of the behaviour of a large number of particles by means of a function of the time t and the position and velocity vectors, called phase-space density.

The first postulate, or Newton's postulate, asserts that m designating the mass of a particle, \vec{w} its velocity vector, \vec{x} its position vector and \vec{X} the force deriving from a potential φ , these quantities are linked by the equations:

$$m \frac{d\vec{w}}{dt} = \vec{X} \quad (1)$$

$$\vec{X} = - \frac{\partial \varphi}{\partial \vec{x}} \quad (2)$$

The second postulate, or the postulate of the representation by phase-space density, asserts the existence of a function D of the time t and of the $2N$ position and velocity vectors \vec{x}_i et \vec{w}_i of the N particles from which on deduces the macroscopic quantities of interest to the physicist by means of integrals.

These two postulates lead to the Liouville equation which is written on designating the external forces by \vec{X}_i and the interaction forces by \vec{X}_{ij} deriving respectively from the potential φ_i and φ_{ij}

$$\frac{\partial D}{\partial t} + \sum_i \vec{w}_i \cdot \frac{\partial D}{\partial \vec{x}_i} + \frac{1}{m} \sum_i \left[\vec{X}_i + \sum_{i \neq j} \vec{X}_{ij} \right] \cdot \frac{\partial D}{\partial \vec{w}_i} = 0 \quad (3)$$

Let us examine two consequences of this equation.

Let us designate the total energy of the system by E and the element of the phase-space volume by $d\Gamma = dx_1 dw_1 dx_2 dw_2 \dots dx_N dw_N$. The quantity E is given by the integral:

$$E = \int \left[\sum_i \frac{1}{2} m w_i^2 + \sum_i \varphi_i + \sum_{i < j} \varphi_{ij} \right] D d\Gamma \quad (4)$$

and it is easy to show that:

$$\frac{\partial E}{\partial t} = 0 \quad (5)$$

Let us designate by S the entropy of the system defined by the relation suggested by Boltzmann:

$$S = - K_0 \int D \text{Log} D d\Gamma \quad (6)$$

(K_0 is Boltzmann's constant).

We also show that:

$$\frac{\partial S}{\partial t} = 0 \quad (7)$$

From the point of view of thermodynamics, the result relative to the energy is exact and that relative to the entropy is false. The invariance of

the energy is compatible with the first two postulates of classical statistical mechanics and the evolution of the entropy is incompatible with them.

The quantity S , devoid of physical meaning but still interesting is called « statistical entropy » [1]. To overcome this difficulty, we need to introduce a supplementary postulate foreign to dynamics—*i. e.* the postulate of irreversibility. This introduction is made at the level of the B. B. G. K. Y. system. Now we will examine three postulates of irreversibility.

III. THE POSTULATE OF MOLECULAR CHAOS AND BOLTZMANN'S EQUATION [2] [3]

This postulate, which is a little more than a century old, is justly famous, not only for its happy consequences, but also for the polemics that it has raised.

Let us write the first two equations of the B. B. G. K. Y. system which involves the single, double and triple distribution function F_1 , F_{12} and F_{123} :

$$\frac{\partial F_1}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_1}{\partial \vec{x}_1} + \frac{\vec{X}_1}{m} \cdot \frac{\partial F_1}{\partial \vec{w}_1} + \frac{1}{m} \int \vec{X}_{12} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} d\vec{x}_2 d\vec{w}_2 = 0 \quad (8)$$

$$\begin{aligned} & \frac{\partial F_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial F_{12}}{\partial \vec{x}_2} + \frac{(\vec{X}_1 + \vec{X}_{12})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} \\ & + \frac{(\vec{X}_2 + \vec{X}_{21})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_2} + \frac{1}{m} \int \left[\vec{X}_{13} \cdot \frac{\partial F_{123}}{\partial \vec{w}_1} + \vec{X}_{23} \cdot \frac{\partial F_{123}}{\partial \vec{w}_2} \right] d\vec{x}_3 d\vec{w}_3 = 0 \quad (9) \end{aligned}$$

Let us assume the fluid to be dilute and the interaction forces of a particle to be weak *vis-à-vis* the mean free path but, in their domain of action, very intense compared to the external forces.

A certain number of approximations are going to be introduced.

The dilute character of the fluid leads us to neglect the terms in F_{123} in the equation (9), whence:

$$\frac{\partial F_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial F_{12}}{\partial \vec{x}_2} + \frac{(\vec{X}_1 + \vec{X}_{12})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} + \frac{(\vec{X}_2 + \vec{X}_{21})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_2} = 0 \quad (10)$$

This equation takes the form of a reversible, two particles Liouville equation and consequently is not physically justified.

Let us carry out the change of variable:

$$\vec{x}_{12} = \vec{x}_2 - \vec{x}_1 \quad (11)$$

It follows that:

$$\begin{aligned} & \overrightarrow{X}_{12} \cdot \frac{\partial F_{12}}{\partial \overrightarrow{w}_1} \\ &= - \left[\frac{\partial F_{12}}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_1} + (\overrightarrow{w}_2 - \overrightarrow{w}_1) \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_{12}} + \frac{\overrightarrow{X}_1}{m} \cdot \frac{\partial F_{12}}{\partial \overrightarrow{w}_1} + \frac{(\overrightarrow{X}_2 + \overrightarrow{X}_{21})}{m} \cdot \frac{\partial F_{12}}{\partial \overrightarrow{w}_2} \right] \end{aligned} \quad (12)$$

whence, on substituting into (8), the still reversible equation:

$$\begin{aligned} & \frac{\partial F_1}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial F_1}{\partial \overrightarrow{x}_1} + \frac{\overrightarrow{X}_1}{m} \cdot \frac{\partial F_1}{\partial \overrightarrow{w}_1} \\ &= \int_{\text{in}} \left[\frac{\partial F_{12}}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_1} + (\overrightarrow{w}_2 - \overrightarrow{w}_1) \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_{12}} + \frac{\overrightarrow{X}_1}{m} \cdot \frac{\partial F_{12}}{\partial \overrightarrow{w}_1} \right] d\overrightarrow{x}_{12} d\overrightarrow{w}_2 \end{aligned} \quad (13)$$

The symbol \int_{in} signifying that the integration is limited to the interaction domain since \overrightarrow{X}_{12} is zero outside it.

The local and instant character of the collisions and the low value of the external force \overrightarrow{X}_1 *vis-à-vis* the interaction force in the integration domain allow us to conserve only the term in $\frac{\partial F_{12}}{\partial \overrightarrow{x}_{12}}$ in the right-hand side of the equation (13), whence:

$$\frac{\partial F_1}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial F_1}{\partial \overrightarrow{x}_1} + \frac{\overrightarrow{X}_1}{m} \cdot \frac{\partial F_1}{\partial \overrightarrow{w}_1} = \int_{\text{in}} (\overrightarrow{w}_2 - \overrightarrow{w}_1) \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_{12}} d\overrightarrow{x}_{12} d\overrightarrow{w}_2 \quad (14)$$

The vector \overrightarrow{w}_1 being given, let us choose a vector \overrightarrow{w}_2 whence a relative velocity vector \overrightarrow{g}_{12} :

$$\overrightarrow{g}_{12} = \overrightarrow{w}_2 - \overrightarrow{w}_1 \quad (15)$$

The vector \overrightarrow{g}_{12} being determined, it is advisable to integrate with respect to $d\overrightarrow{x}_{12}$.

Let us designate by O the centre of the interaction sphere and by Oxyz a system of axes such that the vector \overrightarrow{g}_{12} and the axis Oz are parallel and in the same direction (fig. 1).

Let us consider a straight line parallel to Oz and lying at a distance b from O. This straight line cuts the sphere at the points A_E and A_S and the plane xOy at the point A of polar coordinates b and ε . In these conditions:

$$\begin{aligned} \int (\overrightarrow{w}_2 - \overrightarrow{w}_1) \cdot \frac{\partial F_{12}}{\partial \overrightarrow{x}_{12}} d\overrightarrow{x}_{12} &= \iint \left[g_{12} \int_{z_E}^{z_S} \frac{\partial F_{12}}{\partial z} dz \right] b db d\varepsilon \\ &= \iint g_{12} [F_{12}(z_S) - F_{12}(z_E)] b db d\varepsilon \end{aligned} \quad (16)$$

The point E corresponds to a state of velocities relative to the beginning

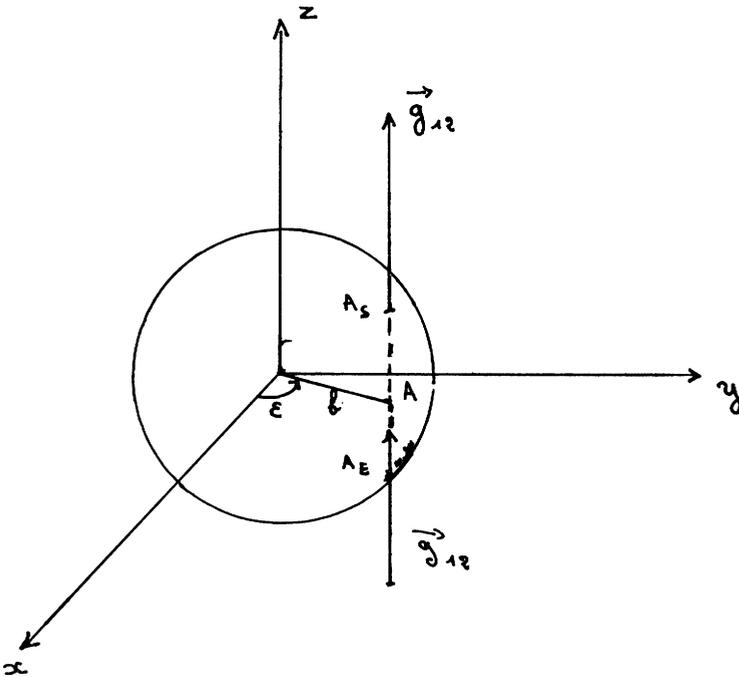


FIG. 1.

of a collision and the point S relative to the end of a collision. The irreversibility is introduced by choosing the direction of the axis Oz. Indeed, the reversal of the velocities and the time, which changes the sign of the first term of the equation (14), does not change the sign of the expression (16). Since Oz changes direction with \vec{g}_{12} , we obtain the difference between the values of F_{12} corresponding to a state after a collision and before a collision. On substituting the expression (16) into the relation (14), we obtain an irreversible kinetic equation if F_{12} can be expressed as a function of F_1 and F_2 .

The postulate of molecular chaos then intervenes to this end. This postulate imposes:

$$z = z_E \quad F_{12} = F_1(\vec{w}_1)F_2(\vec{w}_2) \tag{17}$$

and as a consequence of the conservation of the phase-space density in a collision:

$$z = z_S \quad F_{12} = F_1(\vec{w}'_1)F_2(\vec{w}'_2) \tag{18}$$

\vec{w}'_1 and \vec{w}'_2 designating the velocity vectors at the beginning of a collision which transforms them into \vec{w}_1 and \vec{w}_2 .

Thus Boltzmann's equation is established:

$$\frac{\partial F_1}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_1}{\partial \vec{x}_1} + \frac{\vec{X}_1}{m} \cdot \frac{\partial F_1}{\partial \vec{w}_1} = \int [F'_1 F'_2 - F_1 F_2] b db d\epsilon d w_2. \quad (19)$$

Although the efficacy and prestige of this equation have become undeniable for us, let us try to understand the violent criticism which it provoked in the past.

The reversibility is broken by choosing the direction of the axis Oz in the integration with respect to the volume of the interaction sphere. The axis Oz is in the same direction as the vector \vec{g}_{12} which imposes a time arrow. On the other hand, the reversibility is conserved during the collision which transforms \vec{w}'_1, \vec{w}'_2 into \vec{w}_1, \vec{w}_2 . Therefore, a certain contradiction exists.

From the strictly mechanical point of view, the postulate of molecular chaos is « absurd » since, if the particles 1 and 2 collide with the particle 3 at the moment when they meet, they are correlated by these collisions and are not « in molecular chaos with each other » as desired by the relation (17). But these incoherences are useful since they bring the loss of information which makes Boltzmann's equation compatible with the second principle of thermodynamics.

The entropy S_1 , called thermal entropy as opposed to the statistical entropy S , is defined by the relation:

$$S_1 = -K_0 \int \log F_1 F_1 d w_1 d x_1 \quad (20)$$

and the solution F_1 of Boltzmann's equation satisfies the inequality:

$$\frac{\partial S_1}{\partial t} \geq 0 \quad (21)$$

and supplies good expressions for the transport coefficients in a dilute medium as if this dilution, bringing about an increase of the average time between two collisions, made it easier for the particles to forget between two collisions the correlation due to one collision.

The expression for the viscosity coefficient of a dilute gas is a function of the temperature T and of the inter-particle potential characterized by a depth- $K_0 T_i$ and a value zero at the distance σ .

$$\mu = \frac{5}{16} \frac{(\pi m K_0 T)^{1/2}}{\pi \sigma^2 \Omega^{2,2*}} \left[1 + \frac{3}{196} \left(8 \frac{\Omega^{2,3*}}{\Omega^{2,2*}} - 7 \right)^2 \right] \quad (22)$$

The quantities $\Omega^{l,s*}$ being given by the integrals:

$$\Omega^{l,s*} = \frac{2}{(s+1)!} \left(\frac{T_i}{T} \right)^{s+2} \int_0^\infty \left(\frac{m}{4K_0 T_i} \right)^{s+2} Q_l(g) g^{2s+3} dg \quad (23)$$

$$Q_l(g) = \frac{2}{\left[1 - \frac{1}{2} \left(\frac{1+(-1)^l}{1+l} \right) \right]} \int_0^\infty (1 - \cos^l \chi) \frac{b db}{\sigma^2} \quad (24)$$

$$\chi = \pi - 2b \int_{r_d}^{\infty} \left[1 - \frac{b^2}{r^2} - \frac{4\varphi}{mg^2} \right]^{-1/2} \frac{dr}{r^2} \tag{25}$$

r_d designating the largest root of the denominator.

An effective potential is that given by H. J. M. Hanley and M. Klein [4], [5], [6].

$$\varphi = -K_0 T_i \left[\frac{6 + 2\gamma}{m_0 - 6} \left(\frac{d\sigma}{r} \right)^{m_0} - \frac{[m_0 - \gamma(m_0 - 8)]}{m_0 - 6} \left(\frac{d\sigma}{r} \right)^6 - \gamma \left(\frac{d\sigma}{r} \right)^8 \right] \tag{26}$$

One can easily verify that:

$$r = d\sigma \quad \varphi = -K_0 T_i \quad \frac{d\varphi}{dr} = 0 \tag{27}$$

This potential depends only on the four parameters σ , T_i , m_0 and γ , since d is relinked to the latter by the condition:

$$r = \sigma \quad \varphi = 0 \tag{28}$$

Table I shows the good agreement between theory and practice for argon and krypton. This good agreement especially justifies Boltzmann's boldness. Nevertheless, the need to calculate a triple integral demands the use of a computer. Let us add that the experimental results are those of J. Kestin, W. Wakeham and K. Watanabe [7].

TABLE I. — $K_0 = 1,3804 \cdot 10^{-23} - \mu$ in 10^{-6} poise.

T	Argon $m=6,6355 \cdot 10^{-26}$ kg $T_i=152,8^\circ$ K $\sigma = 3,297 \cdot 10^{-10}$ m $\gamma = 3$ $m_0 = 11$			Krypton $m=13,9152 \cdot 10^{-26}$ kg $T_i=215,8^\circ$ K $\sigma = 3,513 \cdot 10^{-10}$ m $\gamma = 3$ $m_0 = 11$		
	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$
298,16	227,5	226,3	0,5 %	254,3	254,8	0,2 %
373,16	273,5	273,2	0,1	311	312,9	0,7
463,16	323,4	323,1	0,1	376,8	375,6	0,25
573,16	380	377,2	0,8	443,1	442,5	0,25
653,16	415,5	413,3	0,5	495,6	490	1,1
783,16	471,5	468,4	0,6	560,3	557,7	0,5
873,16	507,9	505	0,6	606	602,6	0,5
973,16	546,3	547,7	0,2	654,3	652,6	0,3

We add that to obtain Landau - Fokker-Planck and Balescu - Lennard-Guernsey kinetic equations, it is necessary to use molecular chaos at $t = 0$

$$t = 0 \quad f_{12}(0) = f_1(0)f_2(0)$$

IV. THE POSTULATE OF LINEAR RELAXATION AND THE FREY-SALMON KINETIC EQUATION

This position was suggested by J. Frey and J. Salmon [8], [9], [10], [11], [12], [13] and was also published in the book *Modern developments in Thermodynamics* [14].

The postulate of molecular chaos imposes that between two collisions—*i. e.* almost always—two particles evolve without correlation between each other, thus:

$$F_{12} = F_1 F_2 \quad (29)$$

Now, in equilibrium, there exists a spatial correlation between the two particles, expressed by a function ψ_{12} :

$$F_{12} = F_1^M F_2^M \psi_{12} \quad (30)$$

F^M designating a Maxwellian velocity distribution.

Likewise, and always in equilibrium:

$$F_{123} = F_1^M F_2^M F_3^M \psi_{123} \quad (31)$$

ψ_{123} designating the spatial triple correlation function linked to ψ_{12} by the equation:

$$K_0 T \frac{\partial \psi_{12}}{\partial x_1} = \overrightarrow{X}_{12} \psi_{12} + \int \overrightarrow{X}_{13} n_3 \psi_{123} \underline{dx}_3 - \psi_{12} \int \overrightarrow{X}_{13} n_3 \psi_{13} \underline{dx}_3 \quad (32)$$

n designating the particle density.

It is convenient to write F_{12} and F_{123} in the form:

$$F_{12} = F_1 F_2 \psi_{12} + \chi_{12} \quad (33)$$

$$F_{123} = F_1 F_2 F_3 \psi_{123} + \chi_{123} \quad (34)$$

ψ_{12} and ψ_{123} corresponding to a local equilibrium defined from the average temperature and particle density values at the considered points.

It is possible to put the first two B. B. G. K. Y. equations in the following form:

$$\widehat{D}_1 F_1 = \widehat{G}_1 F_{12} = \widehat{G}_1 F_1 F_2 \psi_{12} + \widehat{G}_1 \chi_{12} \quad (35)$$

$$\widehat{D}_{12} F_{12} = \widehat{G}_{12} F_{123} = \widehat{G}_{12} F_1 F_2 F_3 \psi_{123} + \widehat{G}_{12} \chi_{123} \quad (36)$$

\widehat{D}_1 , \widehat{D}_{12} , \widehat{G}_1 , \widehat{G}_{12} designating the operators.

$$\widehat{D}_1 = \frac{\partial}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial}{\partial \overrightarrow{x}_1} + \frac{\overrightarrow{X}_1}{m} \cdot \frac{\partial}{\partial \overrightarrow{w}_1} \quad (37)$$

$$\widehat{D}_{12} = \frac{\partial}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial}{\partial \overrightarrow{x}_1} + \overrightarrow{w}_2 \cdot \frac{\partial}{\partial \overrightarrow{x}_2} + \frac{(\overrightarrow{X}_1 + \overrightarrow{X}_{12})}{m} \cdot \frac{\partial}{\partial \overrightarrow{w}_1} + \frac{(\overrightarrow{X}_2 + \overrightarrow{X}_{21})}{m} \cdot \frac{\partial}{\partial \overrightarrow{w}_2} \quad (38)$$

$$\widehat{G}_1 = -\frac{1}{m} \int \overrightarrow{X}_{12} \cdot \frac{\partial}{\partial w_1} \dots \underline{dx_2 dw_2} \quad (39)$$

$$\widehat{G}_{12} = -\frac{1}{m} \int \left[\overrightarrow{X}_{13} \frac{\partial}{\partial w_1} + \overrightarrow{X}_{23} \frac{\partial}{\partial w_2} \right] \dots \underline{dx_3 dw_3} \quad (40)$$

The postulate of linear relaxation imposes that the local equilibrium term, being considered as dominating the irreversibility, can be obtained on imposing a relation of linear relaxation on the action of an integral operator \widehat{G} on a divergence function at the local equilibrium.

IV.a) The Vlasov-B. G. K. equation

The postulate of linear relaxation applied to the function χ_{12} is written:

$$\widehat{D}_1 \chi_{12} = \frac{F_1^M - F_1}{\tau_1} \quad (41)$$

τ_1 designating the average value of the time interval between two collisions. Thus a kinetic equation is obtained containing a term identical to that of Vlasov to roughly the factor ψ_{12} , as well as the B. G. K. collision term [15]:

$$\frac{\partial F_1}{\partial t} + \overrightarrow{w_1} \cdot \frac{\partial F_1}{\partial x_1} + \frac{\left[\overrightarrow{X}_1 + \int \overrightarrow{X}_{12} n_2 \psi_{12} dx_{12} \right]}{m} \cdot \frac{\partial F_1}{\partial w_1} = \frac{F_1^M - F_1}{\tau_1} \quad (42)$$

IV.b) The Frey-Salmon kinetic equation in isothermal conditions

Assuming the temperature T to be uniform, the postulate of linear relaxation imposes the relation of closure and irreversibility.

$$\widehat{G}_{12} \chi_{123} = \frac{F_1 F_2 \psi_{12} - F_{12}}{\tau_2} \quad (43)$$

τ_2 designating the average value of the relative velocities and the impact parameters of the collision time between two particles. This collision time is taken to be equal to the duration of the crossing time of the reduced particle of mass through the repulsive zone of the interaction potential. Whereas the postulate of molecular chaos asserts that the loss of information responsible for the irreversibility takes place between the collisions, the postulate of linear relaxation applied to χ_{123} asserts that this loss takes place during the crossing time through the repulsive zone of the interaction potential.

On using the relation (43), the second B. B. G. K. Y. equation becomes:

$$\widehat{D}_{12} F_{12} = \widehat{G}_{12} F_1 F_2 F_3 \psi_{123} + \frac{F_1 F_2 \psi_{12} - F_{12}}{\tau_2} \quad (44)$$

whence:

$$F_{12} = [1 + \tau_2 \widehat{D}_{12}]^{-1} [F_1 F_2 \psi_{12} + \tau_2 \widehat{G}_{12} F_1 F_2 F_3 \psi_{123}] \quad (45)$$

On setting $t = \tau_1 \tilde{t}$ we may write a development as a function of the small parameter $\frac{\tau_2}{\tau_1}$ whence, to the first order:

$$F_{12} = F_1 F_2 \psi_{12} - \tau_2 [\widehat{D}_{12} F_1 F_2 \psi_{12} - \widehat{G}_{12} F_1 F_2 F_3 \psi_{123}] \quad (46)$$

thus, on developing:

$$\begin{aligned} F_{12} &= F_1 F_2 \psi_{12} \\ &- \frac{\tau_2}{m} F_2 \frac{\partial F_1}{\partial w_1} \cdot \left[\overrightarrow{X}_{12} \psi_{12} + \int \overrightarrow{X}_{13} n_3 \psi_{123} dx_3 - \psi_{12} \int \overrightarrow{X}_{12} n_2 \psi_{12} dx_2 \right] \\ &- \frac{\tau_2}{m} F_1 \frac{\partial F_2}{\partial w_2} \cdot \left[\overrightarrow{X}_{21} \psi_{12} + \int \overrightarrow{X}_{23} n_3 \psi_{123} dx_3 - \psi_{12} \int \overrightarrow{X}_{21} n_1 \psi_{12} dx_1 \right] \\ &- \tau_2 F_1 F_2 \left[\frac{\partial \psi_{12}}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial \psi_{12}}{\partial x_1} + \overrightarrow{w}_2 \cdot \frac{\partial \psi_{12}}{\partial x_2} \right] \end{aligned} \quad (47)$$

As:

$$\int \overrightarrow{X}_{12} n_2 \psi_{12} dx_2 = \int \overrightarrow{X}_{13} n_3 \psi_{13} dx_3. \quad (48)$$

The use of the relation (32) allows us to simplify the expression (47), whence:

$$\begin{aligned} F_{12} &= F_1 F_2 \psi_{12} - \tau_2 \left[F_1 F_2 \frac{\partial \psi_{12}}{\partial t} + F_2 \frac{\partial \psi_{12}}{\partial x_1} \cdot \left(\overrightarrow{w}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial w_1} \right) \right] \\ &- \tau_2 \left[F_1 \frac{\partial \psi_{12}}{\partial x_2} \cdot \left(\overrightarrow{w}_2 F_2 + \frac{K_0 T}{m} \frac{\partial F_2}{\partial w_2} \right) \right] \end{aligned} \quad (49)$$

F_{12} is now a functional of F_1 and F_2 . On substituting this expression into the first B. B. G. K. Y. equation, we obtain the F-S kinetic equation:

$$\begin{aligned} &\frac{\partial F_1}{\partial t} + \overrightarrow{w}_1 \cdot \frac{\partial F_1}{\partial x_1} + \frac{1}{m} \frac{\partial F_1}{\partial w_1} \cdot \left[\overrightarrow{X}_1 + \int \overrightarrow{X}_{12} n_2 \psi_{12} dx_2 \right] \\ &= \tau_2 \int n_2 \frac{\overrightarrow{X}_{12}}{m} \cdot \frac{\partial}{\partial w_1} \left[\frac{\partial \psi_{12}}{\partial t} + \frac{\partial \psi_{12}}{\partial x_1} \cdot \left(\overrightarrow{w}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial w_1} \right) + \frac{\partial \psi_{12}}{\partial x_2} \cdot \overrightarrow{v}_2 F_1 \right] dx_2 \end{aligned} \quad (50)$$

Let us assume that the particle density and the average velocity vary little enough within the interaction sphere for it to be possible to identify n_2 and n_1 as well as \overrightarrow{v}_2 and \overrightarrow{v}_1 . ψ_{12} becomes an isotropic function and the kinetic equation (44) is simplified.

On omitting the index I which is no longer useful, it follows that:

$$\frac{\partial F}{\partial t} + \overrightarrow{w} \cdot \frac{\partial F}{\partial x} + \frac{\overrightarrow{X}}{m} \cdot \frac{\partial F}{\partial w} = \frac{n K_0 T}{2m} \tau_2 B \left[3F + (\overrightarrow{w} - \overrightarrow{v}) \cdot \frac{\partial F}{\partial w} + \frac{K_0 T}{m} \Delta_w F \right] \quad (51)$$

$$\frac{\partial F}{\partial t} + \vec{w} \cdot \frac{\partial F}{\partial \vec{x}} + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{w}} = \frac{nK_0T}{2m} \tau_2 \mathbf{B} \left[\frac{\partial}{\partial \vec{V}} \cdot \left(\vec{V}F + \frac{K_0T}{m} \frac{\partial F}{\partial \vec{V}} \right) \right]$$

$$\vec{V} = \vec{w} - \vec{v} \tag{52}$$

\mathbf{B} designating the integral:

$$\mathbf{B} = - \frac{8\pi}{3K_0T} \int_0^\infty \frac{d\varphi}{dx} \frac{d\psi}{dx} x^2 dx. \tag{53}$$

IV.c) The Frey-Salmon kinetic equation in non-isothermal conditions

The temperature T is no longer considered to be uniform. Nevertheless, its spatial variations are considered to be small enough for one to be justified in writing on the scale of the interaction sphere:

$$T(\vec{x}_2) = T(\vec{x}_1) + (\vec{x}_2 - \vec{x}_1) \cdot \frac{\partial T}{\partial \vec{x}_1} \tag{54}$$

The heat flow vector is \vec{q} :

$$\vec{q} = \int \frac{1}{2} m V^2 \vec{V} F dV \tag{55}$$

The postulate of linear relaxation imposes:

$$\widehat{G}_{12} \chi_{123} = \frac{\left[F_1 F_2 + \frac{\eta}{n_1 m} \vec{q}_1 \cdot \frac{\partial F_1}{\partial \vec{w}_1} \Delta_{w_2} F_2 + \frac{\eta}{n_2 m} \vec{q}_2 \cdot \frac{\partial F_2}{\partial \vec{w}_2} \Delta_{w_1} F_1 \right] \psi_{12} - F_{12}}{\tau_2}$$

and after long calculations, it follows that:

$$\frac{\partial F}{\partial t} + \vec{w} \cdot \frac{\partial F}{\partial \vec{x}} + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{w}} = \frac{\tau_2 \mathbf{B} n K_0 T}{2m} \left[3F + (\vec{w} - \vec{v}) \cdot \frac{\partial F}{\partial \vec{w}} + \frac{K_0 T}{m} \Delta_w F + \frac{\eta}{nm} \vec{q} \cdot \frac{\partial}{\partial \vec{w}} \Delta_w F \right] \tag{57}$$

η designating a coefficient equal to $-1/3$ for a monoatomic gas and $-2/5$ for a diatomic gas.

The equation (57) shows that the postulate of linear relaxation leads to kinetic equation of the Fokker-Planck type. The collision term is shown as a development as a function of F and its derivatives whose coefficients are expressed in a simple manner as a function of the moments of the distribution function F .

IV.d) Expressions for the transport coefficients

Let us designate by p_{kl} the components of the kinetic tensor:

$$p_{kl} = \int m V_k V_l F dV. \tag{58}$$

$$p = nK_0T = \frac{1}{3}p_{KK}. \quad (59)$$

and choose for F the approximation of the thirteen moments suggested by Grad [16]:

$$F = n \left(\frac{m}{2\pi K_0 T} \right)^{3/2} e^{-\frac{mV^2}{2K_0 T}} \left[1 + \frac{(p_{ij} - p\delta_{ij})mV_i V_j}{p} \frac{1}{2K_0 T} - \frac{mq_i V_i}{pK_0 T} \left(1 - \frac{mV^2}{5K_0 T} \right) \right] \quad (60)$$

By suitable integrations we deduce from (57) and (60) the following system of the equations of fluids mechanics:

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x_j} (nv_j) = 0 \quad (61)$$

$$nm \left[\frac{\partial v_K}{\partial t} + v_j \frac{\partial v_K}{\partial x_j} \right] - nX_K + \frac{\partial p_{Kj}}{\partial x_j} = 0 \quad (62)$$

$$\begin{aligned} \frac{\partial p_{Kl}}{\partial t} + \frac{\partial}{\partial x_j} (v_j p_{Kl}) + p_{Kj} \frac{\partial v_l}{\partial x_j} + p_{lj} \frac{\partial v_K}{\partial x_j} \\ + \frac{2}{5} \left[\frac{\partial q_K}{\partial x_l} + \frac{\partial q_l}{\partial x_K} + \frac{\partial q_j}{\partial x_j} \delta_{Kl} \right] + \frac{\tau_2 B n K_0 T}{m} [p_{Kl} - nK_0 T \delta_{Kl}] = 0 \end{aligned} \quad (63)$$

$$\begin{aligned} \frac{\partial q_K}{\partial t} + v_j \frac{\partial q_K}{\partial x_j} + \frac{7}{5} \left[q_K \frac{\partial v_j}{\partial x_j} + q_j \frac{\partial v_K}{\partial x_j} \right] + \frac{2}{5} q_j \frac{\partial v_j}{\partial x_K} + \frac{7}{2} \frac{K_0}{m} p_{Kj} \frac{\partial T}{\partial x_j} \\ + \frac{2K_0 T}{m} \frac{\partial p_{Kj}}{\partial x_j} - \frac{K_0^2 T}{m} \left[T \frac{\partial n}{\partial x_K} + 2n \frac{\partial T}{\partial x_K} \right] - \frac{1}{nm} p_{Kl} \frac{\partial p_{lj}}{\partial x_j} \\ + \frac{\tau_2 B n K_0 T}{2m} (3 + 5n) q_K = 0 \end{aligned} \quad (64)$$

and the expressions for the viscosity coefficient μ and the thermal conductivity coefficient λ :

$$\mu = \frac{m}{\tau_2 B} \quad (65)$$

$$\lambda = \frac{5K_0}{\tau_2 B (3 + 5n)} \quad (66)$$

λ and μ satisfying the relation:

$$\lambda = \frac{5}{3 + 5\eta} \frac{K_0 \mu}{m} \quad \eta = -\frac{1}{3} \quad \lambda = \frac{15}{4} \frac{K_0 \mu}{m} \quad (67)$$

The Sutherland potential allows us to obtain a very simple expression for μ (fig. 2).

$$r < \sigma \quad y = \infty \quad r = \sigma \quad \varphi = -E_i = -K_0 T_i \quad r > \sigma \quad \varphi = \varphi_a(r) \quad (68)$$

The discontinuity in $r = \sigma$ brings difficulties in calculation which can be overcome on considering the potential between 0 and σ as the limit of a

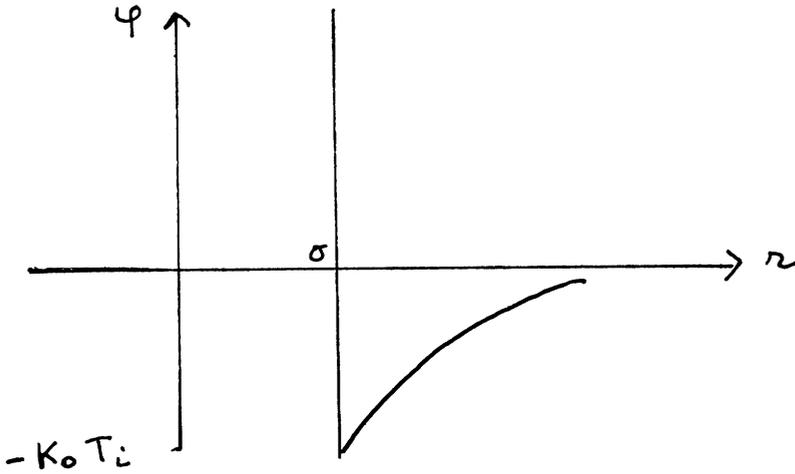


FIG. 2.

potential having a linear variation with a slope equal to $-\frac{E_m}{\sigma}$ which is made to bend to infinity with E_m :

$$0 < r < \sigma \quad \varphi = -E_m \left(\frac{r}{\sigma} - 1 \right) - E_i \quad r > \sigma \quad \varphi = \varphi_a(r). \quad (69)$$

For a dilute gas, the ψ function has the usual form and the expression for B is:

$$\psi = e^{-\frac{\varphi}{K_0 T}} \quad (70)$$

$$B = -\frac{8\pi}{3K_0 T} \int_0^\infty \frac{d\psi}{dx} \frac{d\varphi}{dx} x^2 dx = \frac{8\pi}{3K_0^2 T^2} \int_0^\infty \left(\frac{d\varphi}{dx} \right)^2 e^{-\frac{\varphi}{K_0 T}} x^2 dx \quad (71)$$

thus, for the potential (69):

$$B = \frac{8\pi\sigma}{3} \left[\frac{K_0 T}{E_m} e^{-\frac{(E_m - E_i)}{K_0 T}} \left[e^{\frac{E_m}{K_0 T}} \left(\frac{E_m^2}{K_0^2 T^2} - 2 \frac{E_m}{K_0 T} + 2 \right) - 2 \right] + \frac{8\pi}{3K_0^2 T^2} \int_0^\infty \left(\frac{d\varphi_a}{dx} \right)^2 e^{-\frac{\varphi_a}{K_0 T}} x^2 dx \right] \quad (72)$$

When the slope of the straight line tends to infinity with E_m B tends to infinity according to the asymptotic form:

$$E_m \rightarrow \infty \quad B = \frac{8\pi}{3} \sigma \frac{E_m}{K_0 T} e^{\frac{E_i}{K_0 T}} \quad (73)$$

The relaxation time τ_2 is to roughly a scaling coefficient the average duration of the crossing time trough the repulsive zone of the potential during a collision.

Figure 3 shows the path of the reduced particle of mass $m/2$ corresponding to an impact parameter b and to a velocity g relative to infinity.

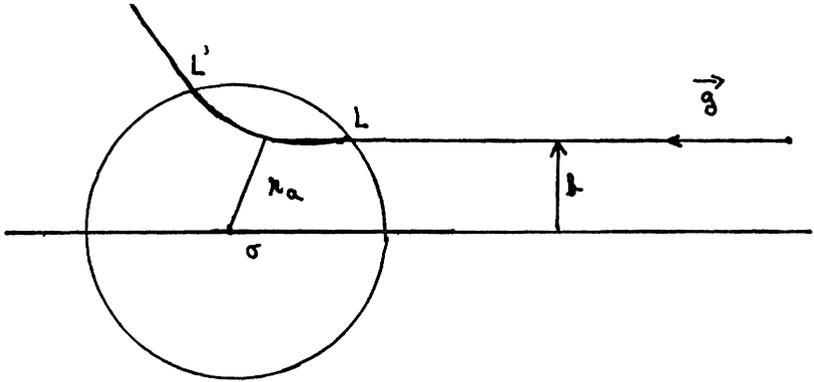


FIG. 3.

The crossing time within the sphere of radius σ is $\Delta\tau(b, g)$.

$$\Delta\tau(b, g) = 2 \int_{r_a}^{\sigma} \left[g^2 \left(1 - \frac{b^2}{r^2} \right) - \frac{4}{m} \left(-E_i + E_m \left(1 - \frac{r}{\sigma} \right) \right) \right]^{-1/2} dr \quad (74)$$

r_a designating the root of the quantity between brackets.

Since E_m is very large, r_a is very close to σ and $\frac{b^2}{r^2}$ may be merged with $\frac{b^2}{\sigma^2}$ while on the other hand, as the potential varies very fiercely its expression must be entirely conserved. It follows that:

$$\Delta\tau(b, g) = \frac{m\sigma}{E_i} \left[g^2 \left(1 - \frac{b^2}{\sigma^2} \right) + \frac{4E_i}{m} \right]^{1/2} \quad (75)$$

τ_2 is the average value of $\Delta\tau(b, g)$ taken over the distribution function $f(b)$ of the impact parameters and the Maxwellian distribution $F^M(g)$ of the relative velocities:

$$0 < b < \sigma \quad f(b)db = \frac{2\pi b db}{\pi\sigma^2} \quad \sigma < b \quad f(b) = 0$$

$$F^M(g) = \left(\frac{m}{4\pi K_0 T} \right)^{3/2} e^{-\frac{mg^2}{4K_0 T}} 4\pi g^2 \quad (76)$$

On introducing the scaling coefficient α , it follows that:

$$\tau_2 = \alpha \frac{m\sigma}{E_m} \frac{16}{3\sqrt{\pi}} \left(\frac{K_0 T}{m} \right)^{1/2} \left[\int_0^\infty \left[\left(\lambda^2 + \frac{T_i}{T} \right)^{3/2} - \left(\frac{T_i}{T} \right)^{3/2} \right] e^{-\lambda^2} d\lambda \right] \quad (77)$$

The function $G_{3/2}(x)$ being defined by the integral:

$$b_{3/2}(x) = 2 \int_0^\infty (\lambda^2 + x)^{3/2} e^{-\lambda^2} d\lambda. \tag{78}$$

For the product $\tau_2 B$, we obtain an expression from which E_m disappears:

$$\tau_2 B = \frac{64}{9} \alpha \pi \sigma^2 \left(\frac{m}{\pi K_0 T} \right)^{1/2} \left[G_{3/2} \left(\frac{T_i}{T} \right) - \sqrt{\pi} \left(\frac{T_i}{T} \right)^{3/2} \right] e^{\frac{T_i}{T}} \tag{79}$$

The expression for the viscosity coefficient of the dilute gas is:

$$\mu = \frac{m}{\tau_2 B} = \frac{9(\pi m K_0 T)^{1/2}}{64 \pi \alpha \sigma^2 \left[G_{3/2} \left(\frac{T_i}{T} \right) - \sqrt{\pi} \left(\frac{T_i}{T} \right)^{3/2} \right] e^{\frac{T_i}{T}}} \tag{80}$$

Thus for $\frac{T}{T_i}$ very much higher than unity the formula of Sutherland:

$$\mu = \frac{A \sqrt{T}}{1 + \frac{5}{2} \frac{T_i}{T}} \tag{81}$$

Table II shows the good agreement with experiment.

TABLE 2. — μ in 10^{-6} poise.

T	Argon $T_i=61,2^\circ \text{ K}$ $\sigma=3,405 \cdot 10^{-10}$ $\alpha=0,3352$			Krypton $T_i=84^\circ \text{ K}$ $\sigma=3,61 \cdot 10^{-10}$ $\alpha=0,34$		
	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$
298,16	227,7	226,3	0,4 %	254,9	254,8	0,04 %
373,16	273,6	273,2	0,4	313	312,9	0,03
463,16	322,6	323,1	0,3	375,7	375,6	0,03
573,16	376	377,2	0,3	444,2	442,5	0,01
653,16	411,3	413,3	0,5	489,8	490	0,04
783,16	464	468,4	1	557,8	557,7	0,02
873,16	497,7	505	1	601,3	602,6	0,2
973,16	532,9	547,7	3	646,8	652,6	1

This result is very satisfactory. It involves two parameters: $\alpha \sigma^2$ and T_i . The formula is simple whereas another potential requires the calculation of a triple integral. The comparison between the results obtained from the formula deriving from Boltzmann's equation and from that derived from

the Frey-Salmon equation has been made by P. Hoffmann in the case of a Lennard-Jones potential [17]. The agreement with experiment is also good with the two formulæ.

The weak point of the postulate of linear relaxation is the need to determine τ_2 phenomenologically. Therefore, we are going to suggest a new postulate from which we deduce the Frey-Salmon kinetic equation and the expression for τ_2 at the same time.

V. THE POSTULATE OF SUPERPOSITION [18]

This postulate was suggested by J. Frey, J. Salmon and M. Valton. It imposes on the triple distribution function F_{123} the form:

$$\begin{aligned}
 F_{123} = & F_1 F_2 F_3 \psi_{123} \\
 & + \left[\frac{F_3}{n_3} [F_{12} - F_1 F_2 \psi_{12}] \left[\psi_{13} \psi_{23} n_3 \right. \right. \\
 & \left. \left. + \alpha_0 \left(\frac{m}{K_0 T} \right)^{1/2} \left(\frac{(\vec{w}_1 - \vec{w}_3) \cdot \vec{X}_{13} + (\vec{w}_2 - \vec{w}_3) \cdot \vec{X}_{23}}{\sigma^3 X_m} \right) \right] \right] \\
 & + \left[\begin{array}{c} 1 \leftrightarrow 2 \\ 2 \leftrightarrow 3 \\ 3 \leftrightarrow 1 \end{array} \right] + \left[\begin{array}{c} 2 \leftrightarrow 3 \\ 3 \leftrightarrow 1 \\ 1 \leftrightarrow 2 \end{array} \right] \quad (82)
 \end{aligned}$$

α_0 designating a coupling coefficient and X_m the average value of the interaction force.

In equilibrium, we recover the desired relations $F_{12} = F_1 F_2 \psi_{12}$ and $F_{123} = F_1 F_2 F_3 \psi_{123}$.

In equilibrium and away from equilibrium, when the particle 3 is very distant from the particles 1 and 2, we have:

$$F_{13} = F_1 F_3 \quad F_{23} = F_2 F_3 \quad \psi_{13} = \psi_{23} = 1 \quad \vec{X}_{13} = \vec{X}_{23} = 0 \quad (83)$$

and on substituting into the equation (82) we have the relation:

$$F_{123} = F_{12} F_3 \quad (84)$$

The relation (82) contains position correlation terms and velocity correlation terms.

The latter are proportional to the quantities of the type $(\vec{W}_1 - \vec{W}_3) \cdot \vec{X}_{13}$ which express the power involved by the interaction force. It seems reasonable that they intervene.

Let us substitute the relation (82) into the second B. B. G. K. Y. equation. It follows that:

$$\begin{aligned}
 & \frac{\alpha_0 [F_{12} - F_1 F_2 \psi_{12}] \int [X_{13}^2 + X_{23}^2] dx_3}{(mK_0T)^{1/2} \sigma^3 X_m} = \\
 & - \left[\frac{\partial F_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial F_{12}}{\partial \vec{x}_2} + \frac{(\vec{X}_1 + \vec{X}_{12})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} + \frac{(\vec{X}_2 + \vec{X}_{21})}{m} \cdot \frac{\partial F_{12}}{\partial \vec{w}_2} \right] \\
 & - \int \left[\frac{\vec{X}_{13}}{m} \cdot \frac{\partial}{\partial \vec{w}_1} + \frac{\vec{X}_{23}}{m} \cdot \frac{\partial}{\partial \vec{w}_2} \right] [F_1 F_2 F_3 (\psi_{123} - 3\psi_{12}\psi_{23}\psi_{31}) \\
 & + F_{12} F_3 \psi_{13} \psi_{23} + F_{23} F_1 \psi_{12} \psi_{13} + F_{13} F_2 \psi_{12} \psi_{23}] dx_3 dw_3 \\
 & - \frac{\alpha_0}{(mK_0T)^{1/2} \sigma^3 X_m} \int [(\vec{w}_1 - \vec{w}_3) \cdot \vec{X}_{13} (\vec{w}_2 - \vec{w}_3) \cdot \vec{X}_{23}] \\
 & \left[\vec{X}_{13} \cdot \frac{\partial}{\partial \vec{w}_1} + \vec{X}_{23} \cdot \frac{\partial}{\partial \vec{w}_2} \right] [F_{12} - F_1 F_2 \psi_{12}] \frac{F_3}{n_3} dx_3 dw_3 \\
 & - \frac{\alpha_0}{(mK_0T)^{1/2} \sigma^3 X_m} \int \left[\vec{X}_{13} \cdot \frac{\partial}{\partial \vec{w}_1} + \vec{X}_{23} \cdot \frac{\partial}{\partial \vec{w}_2} \right] \\
 & \left[[(\vec{w}_1 - \vec{w}_2) \cdot \vec{X}_{12} + (\vec{w}_1 - \vec{w}_3) \cdot \vec{X}_{13}] [F_{23} - F_2 F_3 \psi_{23}] \frac{F_1}{n_1} \right. \\
 & \left. + [(\vec{w}_2 - \vec{w}_3) \cdot \vec{X}_{23} + (\vec{w}_1 - \vec{w}_2) \cdot \vec{X}_{12}] [F_{13} - F_1 F_3 \psi_{13}] \frac{F_2}{n_2} \right] dx_3 dw_3 \tag{85}
 \end{aligned}$$

This expression is again written:

$$F_{12} - F_1 F_2 \psi_{12} = \tau_2 A(F_1, F_2, F_3, F_{12}, F_{23}, F_{13}). \tag{86}$$

A designating the right-hand side of (85) and τ_2 a homogeneous quantity to a time whose expression is:

$$\frac{1}{\tau_2} = \frac{2\alpha_0}{(mK_0T)^{1/2} \sigma^3 X_m} \int X_{13}^2 dx_{13} \tag{87}$$

Let us solve the equation (86) by iteration... *i. e.* by replacing F_{ij} by $F_i F_j \psi_{ij}$ in the right-hand side. It follows that:

$$F_{12} = F_1 F_2 \psi_{12} - \tau_2 [\hat{S}_{12} F_1 F_2 \psi_{12} - \hat{G}_{12} F_1 F_2 F_3 \psi_{123}] \tag{88}$$

Whence the kinetic equation:

$$\frac{\partial F}{\partial t} + \vec{w} \cdot \frac{\partial F}{\partial \vec{x}} + \frac{\vec{X}}{m} \cdot \frac{\partial F}{\partial \vec{w}} = \frac{1}{\tau_0} \left[3F + (\vec{w} - \vec{v}) \cdot \frac{\partial F}{\partial \vec{w}} + \frac{K_0 T}{m} \Delta_w F \right] \tag{89}$$

with:

$$\frac{1}{\tau_0} = - \frac{n\sigma^3}{2\alpha_0} \left(\frac{K_0 T}{m} \right)^{1/2} X_m \frac{\int_0^\infty \frac{d\varphi}{dx} \frac{d\psi}{dx} x^2 dx}{\int_0^\infty \left(\frac{d\varphi}{dx} \right)^2 x^2 dx} \tag{90}$$

The expression for the viscosity coefficient is:

$$\mu = \frac{nK_0T}{2} \tau_0 \quad (91)$$

thus, for a Sutherland potential and a dilute gas with $X_m = \frac{E_m}{\sigma}$ and the crossing at the limit:

$$\mu = \frac{\alpha_0}{3\sigma^2} (mK_0T)^{1/2} e^{-\frac{T_i}{T}} \quad (92)$$

Table III shows the satisfactory agreement with experiment. Let us state that a formula of this type was suggested in 1919 by Reigenbaum from phenomenological reasoning. The postulate of superposition justifies it.

TABLE III. — μ in 10^{-6} poise.

T	Argon $T_i=126,7^\circ \text{ K}$ $\sigma=3,115 \cdot 10^{-10}$ $\alpha_0=0,602$			Krypton $T_i=152,6^\circ \text{ K}$ $\sigma=3,513 \cdot 10^{-10}$ $\alpha_0=0,649$		
	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$	μ_{Th}	μ_{exp}	$\Delta\mu/\mu$
298,16	223,3	226,3	1,5 %	251,6	254,8	1 %
373,16	272,16	273,2	0,3	311,95	312,9	0,3
463,16	323,89	323,1	0,2	376,3	375,6	0,3
573,16	379,73	377,2	0,6	445,9	442,5	0,6
653,16	416,49	413,3	0,7	491,8	490	0,4
783,16	470,98	468,4	0,5	559,8	557,7	0,4
873,16	505,67	505	0,1	603,1	602,6	0,1
973,16	541,86	547,7	1,2	648,2	652,6	0,7

VI. INTERNAL POSTULATES

The postulates used previously may be qualified as external postulates in the sense that the B. B. G. K. Y. system of equations established by means of the Hamiltonian formalism being reversible, this reversibility is broken from the exterior by means of postulates that arbitrarily impose certain relations on the distribution functions. Thus for a gas dilute enough for the triple interactions to be neglected, Newton's equation in a field of forces deriving from the interaction potential.

$$m \frac{d\vec{w}_1}{dt} = - \frac{\partial \varphi}{\partial \vec{x}_1} \quad (93)$$

leads to the reversible equation of the double distribution function :

$$\frac{\partial F_{12}}{\partial t} + w_1 \cdot \frac{\partial F_{12}}{\partial x_1} + w_2 \cdot \frac{\partial F_{12}}{\partial x_2} - \frac{1}{m} \frac{\partial \varphi}{\partial x_1} \cdot \frac{\partial F_{12}}{\partial w_1} - \frac{1}{m} \frac{\partial \varphi}{\partial x_2} \cdot \frac{\partial F_{12}}{\partial w_2} = 0 \quad (94)$$

This equation is compatible with the first principle of thermodynamics or the conservation of energy principle. As the latter is defined by the relation:

$$E = \frac{1}{2} m (w_1^2 + w_2^2) + \varphi. \quad (95)$$

we show that:

$$\frac{\partial}{\partial t} \int E F_{12} dx_1 dw_1 dx_2 dw_2 = 0 \quad (96)$$

On the other hand, this equation is incompatible with the second principle of thermodynamics since the entropy being defined by the usual relation:

$$S_2 = - K_0 \int \text{Log } F_{12} F_{12} dx_1 dw_1 dx_2 dw_2 \quad (97)$$

we have a result contradicted by experiment away from equilibrium:

$$\frac{\partial S_2}{\partial t} = 0 \quad (98)$$

S_2 is a statistical entropy and not a thermal entropy. Boltzmann's postulate of molecular chaos $F_{12} = F_1 F_2$ associated with approximations justified by the neutral and dilute character of the gas, allows us to establish a kinetic equation such that the thermal entropy S_1 defined by:

$$S_1 = - K_0 \int F_1 \text{Log } F_1 dx_1 dw_1 \quad (99)$$

increases away from equilibrium:

$$\frac{\partial S_1}{\partial t} \geq 0 \quad (100)$$

A coherent physics would be based upon an equation for the evolution of F_{12} such that S_1 and S_2 increase away from equilibrium but such a physics assumes that Newton's law (or postulate), related to the movement of a particle in a field of force, be revised. The internal postulates are modifications of Newton's postulate making it irreversible with the aim of deducing from it a result that is correct for the entropy.

A first attempt, due to J. Salmon, is based on the following postulates.

a) The movement equation of a particle in interaction with another by means of a potential φ is:

$$\begin{aligned} m \frac{d\vec{w}_1}{dt} &= \vec{X}_{12} = - \frac{\partial \varphi}{\partial \vec{x}_1} + \tau \Delta \varphi (\vec{w}_2 - \vec{w}_1) \\ m \frac{d\vec{w}_2}{dt} &= \vec{X}_{21} = - \frac{\partial \varphi}{\partial \vec{x}_2} + \tau \Delta \varphi (\vec{w}_1 - \vec{w}_2) \end{aligned} \quad (101)$$

τ designating the average duration of the crossing time through the repulsive zone of the interaction potential and $\Delta \varphi$ the Laplacien of φ . On the usual gradient term of φ is superposed an irreversible term containing a factor τ expressing a collective effect and the Laplacien $\Delta \varphi$ which vanished for the potentials in $1/r$.

b) A potential φ_0 deriving from the positions engenders a potential of quantum origin φ_q such that:

$$\varphi_q = - \frac{\hbar^2}{2m} \frac{\Delta \mathcal{A}}{\mathcal{A}} \quad (102)$$

\hbar designating Planck's constant divided by 2π and \mathcal{A} the modulus of the wave function Ψ which is the solution of Schroedinger's equation. The potential φ to be introduced into the equation (101) is not the usual potential φ_0 but the sum:

$$\varphi = \varphi_0 + \varphi_q \quad (103)$$

Thus an attractive potential in $-1/r$ engenders a potential φ_q such that the potential $\varphi = \varphi_0 + \varphi_q$ becomes repulsive at short distances (see Appendix 1).

For the solar system, the average distance between planets is so great that the influence of φ_q is negligible. φ merges with and the irreversible term $\Delta \varphi$ vanishes. Therefore the mechanics of the solar system remains unchanged.

On the other hand, for a fully ionized plasma, the term φ_q plays an essential role and allows the electric conductivity to remain finite. The equation (102) is a very old one and due to Madelung. In a neutral gas, the interaction potential between molecules is of quantum origin and its non-zero Laplacien operator contributes to the introduction of the irreversibility. Therefore, the latter is linked to the quantum character of the interactions.

Liouville wrote his equation for the forces which could depends on the positions and velocities:

$$\frac{\partial \mathbf{F}_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial \mathbf{F}_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial \mathbf{F}_{12}}{\partial \vec{x}_2} + \frac{\partial}{\partial w_1} \cdot (\vec{X}_{12} \mathbf{F}_{12}) + \frac{\partial}{\partial w_2} \cdot (\vec{X}_{21} \mathbf{F}_{12}) = 0 \quad (104)$$

thus within the framework of the equations (101):

$$\begin{aligned} \frac{\partial F_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial F_{12}}{\partial \vec{x}_2} - \frac{1}{m} \frac{\partial \varphi}{\partial \vec{x}_1} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} - \frac{1}{m} \frac{\partial \varphi}{\partial \vec{x}_2} \cdot \frac{\partial F_{12}}{\partial \vec{w}_2} \\ = \frac{\tau \Delta \varphi}{m} \left[\frac{\partial}{\partial \vec{w}_1} \cdot (\vec{w}_1 - \vec{w}_2) F_{12} + \frac{\partial}{\partial \vec{w}_2} \cdot (\vec{w}_2 - \vec{w}_1) F_{12} \right] \end{aligned} \quad (105)$$

This equation is irreversible but in equilibrium does not have the exact solution.

Now we will discuss a second attempt. This conserves the postulate (b) and modifies the postulate (a) on bringing in the idea of fine entropy due to J. Fronteau [19], [20], [21].

The equation of movement is now written:

$$m \frac{d\vec{w}_1}{dt} = - \frac{\partial \varphi}{\partial \vec{x}_1} + \tau \Delta \varphi \left[(\vec{w}_2 - \vec{v}_2) - (\vec{w}_1 - \vec{v}_1) + \frac{K_0 T}{m} \left(\frac{\partial}{\partial \vec{w}_2} - \frac{\partial}{\partial \vec{w}_1} \right) \text{Log } F_{12} \right] \quad (106)$$

$$m \frac{d\vec{w}_2}{dt} = - \frac{\partial \varphi}{\partial \vec{x}_2} + \tau \Delta \varphi \left[(\vec{w}_1 - \vec{v}_1) - (\vec{w}_2 - \vec{v}_2) + \frac{K_0 T}{m} \left(\frac{\partial}{\partial \vec{w}_1} - \frac{\partial}{\partial \vec{w}_2} \right) \text{Log } F_{12} \right] \quad (107)$$

The fine entropy is $\log F_{12}$ and its presence shows that the state of the population of particles reacts on the equation of movement. The term in $\log F_{12}$ accentuates the collective effect previously introduced by τ .

Liouville's equation becomes:

$$\begin{aligned} \frac{\partial F_{12}}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_{12}}{\partial \vec{x}_1} + \vec{w}_2 \cdot \frac{\partial F_{12}}{\partial \vec{x}_2} - \frac{1}{m} \frac{\partial \varphi}{\partial \vec{x}_1} \cdot \frac{\partial F_{12}}{\partial \vec{w}_1} - \frac{1}{m} \frac{\partial \varphi}{\partial \vec{x}_2} \cdot \frac{\partial F_{12}}{\partial \vec{w}_2} \\ = \frac{\tau \Delta \varphi}{m} \left[\frac{\partial}{\partial \vec{w}_1} \cdot \left[(\vec{w}_1 - \vec{v}_1) F_{12} - (\vec{w}_2 - \vec{v}_2) F_{12} + \frac{K_0 T}{m} \left(\frac{\partial F_{12}}{\partial \vec{w}_1} - \frac{\partial F_{12}}{\partial \vec{w}_2} \right) \right] \right] \\ + \frac{\tau \Delta \varphi}{m} \left[\frac{\partial}{\partial \vec{w}_2} \cdot \left[(\vec{w}_2 - \vec{v}_2) F_{12} - (\vec{w}_1 - \vec{v}_1) F_{12} + \frac{K_0 T}{m} \left(\frac{\partial F_{12}}{\partial \vec{w}_2} - \frac{\partial F_{12}}{\partial \vec{w}_1} \right) \right] \right] \end{aligned} \quad (108)$$

and has the exact solution in equilibrium.

If only two particles are in presence and not a population of particles, one may consider that their velocity distribution functions are Maxwellian distributions at zero temperature... *i. e.* they are Dirac distributions. The irreversible term disappears and the movement of the two particles is traditional.

Now let us return to the case of a population of particles and on the right-hand side of the equation (108) replace F_{12} by the approximation:

$$F_{12} = F_1 F_2 e^{-\frac{\varphi}{K_0 T}} \quad (109)$$

This approximation is valid if the term (109) is dominant in the development of F_{12} as a function of F_1 , F_2 , and their derivatives. This fact has been previously established. In addition, let us admit that the function F_1 and F_2 vary little in position within the interaction sphere. We shall obtain two results. Firstly, on multiplying the equation (108) by $\underline{dx_1 dx_2 dw_1 dw_2}$ and on taking account of the relation:

$$\int_0^\infty \Delta\varphi e^{-\frac{\varphi}{K_0 T} x^2} dx = \frac{1}{K_0 T} \int_0^\infty \left(\frac{d\varphi}{dx}\right)^2 e^{-\frac{\varphi}{K_0 T} x^2} dx \quad (110)$$

we recover the Frey-Salmon kinetic equation on integration:

$$\begin{aligned} \frac{\partial F_1}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_1}{\partial \vec{x}_1} + \frac{\vec{X}_1}{m} \cdot \frac{\partial F_1}{\partial \vec{w}_1} &= \frac{nK_0 T \tau B}{2m} \frac{\partial}{\partial \vec{V}_1} \cdot \left[\vec{V}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial \vec{V}_1} \right] \\ \vec{V}_1 &= \vec{w}_1 - \vec{v}_1 \end{aligned} \quad (111)$$

with, for the single S_1 entropy defined by the relation:

$$S_1 = -K_0 \int F_1 \text{Log } F_1 \underline{dx_1 dw_1} \quad (112)$$

the correct relation:

$$\frac{\partial S_1}{\partial t} \geq 0 \quad (113)$$

Indeed, the change of function:

$$F_1 = F_1^M h_1 \quad (114)$$

leads to the inequality (see Appendix II):

$$\frac{\partial S_1}{\partial t} = \frac{nK_0^3 T^2}{2m^2} \tau B \int \left(\frac{\partial h_1}{\partial w_1}\right)^2 \frac{F_1^M}{h_1} dw_1 dx_1 \geq 0 \quad (115)$$

Secondly, the double entropy S_2 also satisfies the inequality:

$$\frac{\partial S_2}{\partial t} = \frac{\partial}{\partial t} \left(-K_0 \int \text{Log } F_{12} F_{12} \underline{dx_1 dw_1 dx_2 dw_2} \right) \geq 0 \quad (116)$$

since on setting:

$$F_1 = F_1^M h_1 \quad F_2 = F_2^M h_2 \quad (117)$$

it follows that:

$$\begin{aligned} \frac{\partial S_2}{\partial t} &= \frac{4\pi K_0 \tau}{m^2} \int F_1^M F_2^M \left[\frac{h_2}{h_2} \left(\frac{\partial h_1}{\partial w_1}\right)^2 + \frac{h_1}{h_2} \left(\frac{\partial h_2}{\partial w_2}\right)^2 \right] \\ &\quad \left[\int_0^\infty \left(\frac{d\varphi}{dx}\right)^2 e^{-\frac{\varphi}{K_0 T} x^2} dx \right] \underline{dx_1 dw_1 dw_2} \end{aligned} \quad (118)$$

The two entropies S_1 and S_2 are thermal entropies satisfying the required inequality at one and the same time.

CONCLUSION

The physics of dilute fluids is based traditionally on Newton's postulate for an interaction potential and on Boltzmann's postulate, thus on the Hamiltonian formalism and the postulate of molecular chaos.

We have shown that other ways exist.

On the one hand, it is possible to substitute for the postulate of molecular chaos the postulate of linear relaxation or that of superposition but the irreversibility in these three cases is introduced from the exterior.

On the other hand, it is possible to modify the postulate of dynamics in an interaction potential in such a way that the irreversibility be obtained by means of two new postulates. The first modifies the traditional equation of dynamics on adding a term proportional to the Laplacian operator of the potential $\Delta\varphi$. The second asserts that a term of quantum origin φ_q should be added to the usual potential φ_0 .

Thus two particles exchanging information in $1/r$ exchange additional information of quantum origin. The resulting potential has a Laplacian operator which is non-zero except at very long distances where the potential in $\frac{1}{r}$ is preponderant. Therefore the reversibility of the solar system is linked to the very low value of the ratio between the diameters and the distances of the planets.

On the contrary, a totally ionized plasma exhibits irreversible phenomena because the quantum correction of the potential engenders a potential with a non-zero Laplacian operator at short distances. The transport phenomena in the gases result also from the existence of an irreversible term proportional to the Laplacian operator of the potential in the equation of movement. The form of the potential is the consequence of quantum effects. To summarize: within the perspective of this article the irreversibility is of quantum origin.

But the price to pay has been heavy because we have had to introduce collective effects linked to the state of the population of particles and especially the Fine entropy. The basic postulates of the Hamiltonian formalism have therefore been rejected as a consequence of their failure with respect to the second principle of thermodynamics.

Two new postulates govern the movement of the particles in such a way that the second principle of thermodynamics be a consequence of these postulates.

APPENDIX I

Let us consider a nucleus of positive charge Ze and an electron of mass m and of charge $-e$ which comes from infinity with an energy E in the direction Oz .

The potential φ_0 is:

$$\varphi_0 = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (1)$$

let us set:

$$K = \frac{(2mE)^{1/2}}{\hbar} \quad (2)$$

$$\gamma = \frac{mZe^2}{4\pi\epsilon_0\hbar^2 K} \quad (3)$$

$$u = K(r - z) \quad (4)$$

The expression for the wave function near the origin is:

$$\psi = e^{iKz} \left[\left(1 - \gamma u + \frac{\gamma^2 u^2}{4} \right) - i \frac{\gamma}{4} u^2 \right] \quad (5)$$

whence:

$$\mathcal{A} = (\psi\psi^+)^{1/2} = 1 - \gamma u + \frac{\gamma^2 u^2}{4} \quad (6)$$

and:

$$\varphi_q = -\frac{\hbar^2}{2m} \frac{\Delta\mathcal{A}}{\mathcal{A}} = \frac{K\gamma\hbar^2}{mr} \left(1 - \frac{1}{4}\gamma^2 u^2 \right) \quad (7)$$

The total potential φ is:

$$\varphi = \varphi_0 + \varphi_q = -\frac{Ze^2\gamma^2 K^2}{16\pi\epsilon_0} \frac{(r - z)^2}{r} \quad (8)$$

and for $r \simeq 0$ becomes repulsive and linear.

APPENDIX II

The equation (111) is again written:

$$\frac{\partial F_1}{\partial t} + \vec{w}_1 \cdot \frac{\partial F_1}{\partial \vec{x}_1} + \frac{\vec{X}_1}{m} \cdot \frac{\partial F_1}{\partial \vec{w}_1} = a^2 \frac{\partial}{\partial \vec{V}_1} \cdot \left[\vec{V}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial \vec{V}_1} \right]$$

$$\vec{V}_1 = \vec{w}_1 - \vec{v}_1 \quad a^2 = \frac{n K_0 T}{2m} \tau B$$

Let us show that:

$$\frac{\partial S_1}{\partial t} \geq 0 \quad S_1 = -K_0 \int F_1 \text{Log } F_1 d\Gamma_1 \quad d\Gamma_1 = \underline{dV_1 dx_1}$$

It follows that:

$$\frac{\partial S_1}{\partial t} = -K_0 \frac{\partial}{\partial t} \left[\int F_1 \text{Log } F_1 d\Gamma_1 \right] = -K_0 a^2 \int \text{Log } F_1 \frac{\partial}{\partial \vec{V}_1} \cdot \left[\vec{V}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial \vec{V}_1} \right] d\Gamma_1$$

Let us set:

$$F_1 = n_1 \left(\frac{m}{2\pi K_0 T} \right)^{3/2} e^{-\frac{mV_1^2}{2K_0 T}} \quad h_1 = F_1^M h_1$$

It follows that:

$$\frac{\partial S_1}{\partial t} = -K_0 a^2 \left[\int -\frac{mV_1^2}{2K_0 T} \frac{\partial}{\partial \vec{V}_1} \cdot \left[\vec{V}_1 F_1 + \frac{K_0 T}{m} \frac{\partial F_1}{\partial \vec{V}_1} \right] d\Gamma_1 \right. \\ \left. + \int \frac{K_0 T}{m} \text{Log } h_1 \frac{\partial}{\partial \vec{V}_1} \cdot \left(F_1^M \frac{\partial h_1}{\partial \vec{V}_1} \right) d\Gamma_1 \right]$$

By integrating by parts we obtain:

$$\frac{\partial S_1}{\partial t} = K_0 a^2 \left[\int \left(3 - \frac{mV_1^2}{K_0 T} \right) F_1 d\Gamma_1 + \frac{K_0 T}{m} \int \frac{F_1^M}{h_1} \left(\frac{\partial h_1}{\partial \vec{V}_1} \right)^2 d\Gamma_1 \right] \\ = \frac{K_0^2 a^2 T}{m} \int \frac{F_1^M}{h_1} \left(\frac{\partial h_1}{\partial \vec{V}_1} \right)^2 d\Gamma_1 \geq 0$$

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