GENERALIZATION OF BOLTZMANN NONLINEAR EQUATION USING SUBDYNAMICS APPROACH

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Universal law of time irreversibility introduces an arrow of the time, making us always alder.

Macroscopic and microscopic approaches concerning irreversible processes are paradoxically different.

As all experiments show, macroscopic systems irreversibly evolve towards the thermodynamics equilibrium, maximizing the entropy, independently of their initial conditions.

In contradistinction, fundamental equations of mechanics are reversible.

Newton's second law does not change under the transformation ***t*** -> ***-t***

$$\frac{\partial^2 x}{\partial t^2} = -kx \quad \text{since} \quad (-t)(-t) = t^2$$

BOLTZMANN EQUATION

In order to solve this contradistinct, Boltzmann introduced a semi-phenomenological nonlinear integro-differencial irreversible equation for the one-particle velocity distribution function. His famous H-theorem, statistical mechanics analog of entropy, unfortunately holds only for dilute gases.

Binary collisions of particles are represented by two-particle distribution function. It is factorized into the nonlinear product of one-particle distribution functions, only in dilute gases. Particles have to enter in collision as uncorrelated, in order to be represented by independent one-particle distribution functions. Recollisions are forbidden. This is assumption of molecular chaos.

$$\partial_t f_\alpha(x_\alpha, v_\alpha; t) + v_\alpha \nabla_\alpha f_\alpha(x_\alpha, v_\alpha; t) = \int dx_b \int dv_b \, \Psi \cdot$$

$$\cdot \, \delta(x_\alpha - x_b) \, f_\alpha(x_\alpha, v_\alpha; t) \, f_b(x_b, v_b; t)$$

BOLTZMANN'S ASSUMPTION

Boltzmann obtained, using this equation, the famous $\mathcal{H}$-theorem for the quantity $\mathcal{H}$, the analog of entropy in statistical mechanics. However, in the (intuitive) derivation of the Boltzmann equation two kinds of concepts are mixed, mechanical and probabilistic one [1]. Indeed, the assumption of the molecular chaos restricts the choice of the initial conditions for the Boltzmann equation. Hence the velocity inversion "experiment", for instance, cannot be correctly described (numerical computations confirms this).

[1] L. Boltzmann, Wien, Ber, **66**, 275 (1872).

SUBDYNAMICS

Aiming to obtain the relationship between the dynamical and thermodynamical descriptions of large systems, Prigogine George, and Henin, have introduced the concept of subdynamics [2]. The dynamics of the homogeneous system is decomposed into two subdynamics using the projection superoperators $\overset{(0)}{\Pi}$ and $\overset{(\wedge)}{\Pi}$ ($\overset{(0)}{\Pi} + \overset{(\wedge)}{\Pi} = 1$) [2]. The subdynamics in the subspace $\overset{(0)}{\Pi}$ corresponds to the contributions of the pole $z = 0$ of the resolvent. All other poles contribute to the $\overset{(\wedge)}{\Pi}$ subdynamics. The projectors $\overset{(0)}{\Pi}$ and $\overset{(\wedge)}{\Pi}$ respectively split the vacuum component into $\overset{(0)}{\rho}_0$ and $\overset{(\wedge)}{\rho}_0$ and the correlation components into $\overset{(0)}{\rho}_c$ and $\overset{(\wedge)}{\rho}_c$. In the subspace $\overset{(0)}{\Pi}$ the evolution is given by the generalized kinetic equation for the projection of the vacuum component $\overset{(0)}{\rho}_0$.

[2] I. Prigogine, C. George, F. Henin, and L. Rosenfeld, Chemica Scripta, **4**, 5-32 (1973).

DECOMPOSITION INTO SUBDINAMICS

The complete irreversible description of the dissipative systems is based on this decomposition into subdynamics and on a change of representation through a non-unitary transformation [2] .

The star-unitary transformation generalizes for the dissipative systems the usual unitary transformation (which in quantum mechanics diagonalizes the Hamiltonian). The Liouville equation, which is the starting point in the development of this theory, has Lt symmetry, i.e. it does not change when $L \longrightarrow -L$ and $t \longrightarrow -t$. On the other hand the Lt symmetry of the equations in the new physical representation is broken because of the presence of the even collision superoperator, ϕ

LAPLACE TRANSFORMATION OF LIOUVILLE FORMAL SOLUTION

$$\rho(\underline{q}, \underline{v}; t) = e^{-it\{L_0 + \lambda \delta L\}} \rho(\underline{q}, \underline{v}; 0)$$

Using the Laplace transformation, one gets :

$$\rho(\underline{q}, \underline{v}; t) = \frac{1}{2\pi i} \int_C dz \, e^{-izt} \frac{1}{z - L_0 - \lambda \delta L} \rho(\underline{q}, \underline{v}; 0)$$

FORMAL SOLUTION OF LIOUVILLE EQUATION

$$\rho_{\{k\}}(v;t) = \frac{1}{2\pi i}\int_C dz\, e^{-izt} \sum_{\{k'\}} \sum_{n=0}^{\infty} \langle\{k\}| \frac{1}{z-L_0} \cdot$$

$$\left[\lambda \delta L \frac{1}{z-L_0}\right]^n |\{k'\}\rangle \rho_{\{k'\}}(v;0)$$

This is the infinite series of the "propagators" (the diagonal matrix elements) and the interaction "vertices" (off-diagonal elements) which follow each other alternatively.

DIAGRAMMATIC REPRESENTATION

The dynamic of correlations can be expressed using diagrams /6,14/. The propagators of the K-vacuum of inhomogeneous correlations is represented as one line (Fig.I.2).

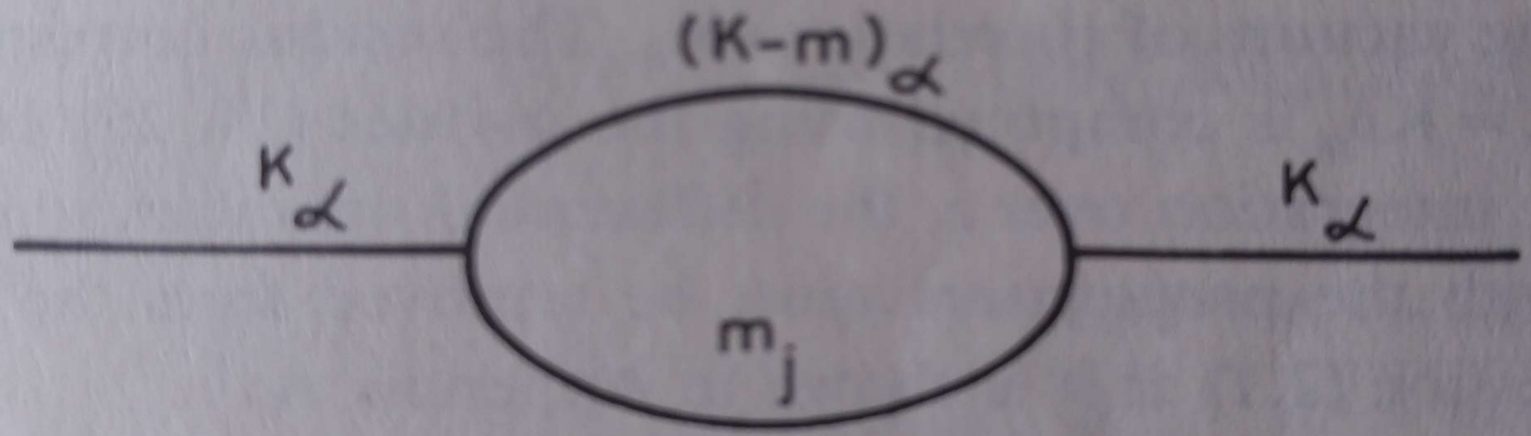
K_α

Fig.I.2.

Considering binary forces, only two wave vectors can change in a single interaction, and this may be done in six different ways.

COLLISION DIAGRAM

Consider the diagonal diagrams with only one line in the repeating state (the diagonal vacuum of correlation state). The possible non-negligible transitions from the K-vacuum of correlation state to the identical one, up to the second order (λ^2) are represented in fig. 1. The



a)

K

Named particle alpha is associated to the inhomogeneous vacuum of correlations, the wave vector K

COLLISION DIAGRAM FORMAL SOLUTION

$$\varrho_{K_\alpha}(v_\alpha, \ldots; t) \doteqdot -\sum_m \sum_j \frac{8\pi^3\lambda^2}{2\pi i \Omega M} \int dz e^{-izt} \frac{1}{z - Kv_\alpha} V_{|-m|}(-m_\alpha).$$

$$\frac{\partial}{\partial v_{\alpha j}} \frac{1}{z - Kv_\alpha + mv_{\alpha j}} V_{|m|} m_\alpha \frac{\partial}{\partial v_{\alpha j}} \frac{1}{z - Kv_\alpha} \varrho_{K_\alpha}(v_\alpha, \ldots; 0) \tag{2.1}$$

using the following short notations :

$$mv_{\alpha j} = m(v_\alpha - v_j)$$

$$\frac{\partial}{\partial v_{\alpha j}} = \frac{\partial}{\partial v_\alpha} - \frac{\partial}{\partial v_j} \tag{2.2}$$

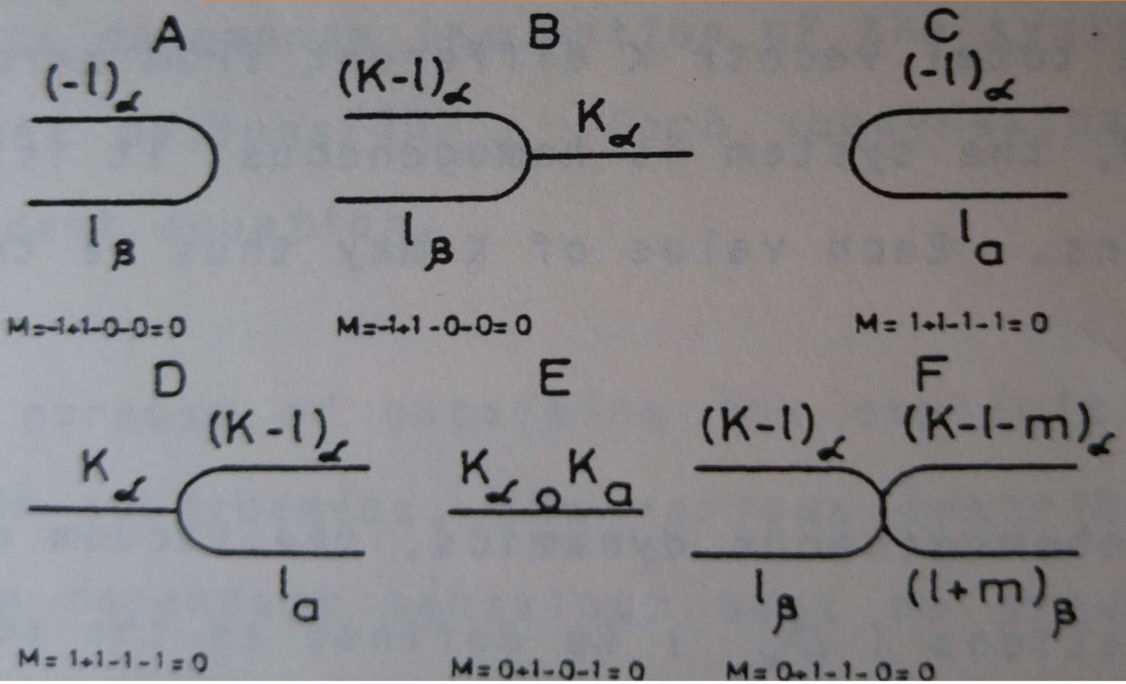
$$-\sum_m F_m = \sum_m \left(\frac{8\pi^3}{\Omega M}\right)^2 V_{-m} V_m (-m)_\alpha \cdot m_\alpha$$

where M is the mass of the particle and V is the central potential.

TOPOLOGIC THEOREM OF FACTORIZATION

6 different ways, because of the conservation law [2]. Consequently any change in a Fourier component of the distribution function, due to the interaction, is represented by use of an elementary vertex

[3] V. Skarka, Bull. Acad. Roy. Belg. Cl. Sci. **64**, 578 and 795 (1978).
[4] V. Skarka, Contribution to the statistical mecanics of irreversible processes in inhomogeneous gases through the subdynamics approach, Thesis, U.L.B. Brussels (1981).



DIAGRAMS NEGLIGIBLE IN THERMODYNAMIC LIMIT

As a whole, a given diagram is of order of magnitude $\frac{N^X}{\Omega^Y}$ where X and Y are integers to be determined by inspection. In order to see whether this ratio is finite or zero in the thermodynamic limit, it is necessry to take into account (i) the difference of degree of correlations between the initial and the final state $\underline{D} = \underline{D}_o - \underline{D}_t$, ii) the number of vertices (V) as well as iii) the number of the novel (i.e. involved in the diagram) "field" particles (β) and "integrating" wave vectors (α). We obtain in this way the order of magnitude ratio :

DIAGRAMS NEGLIGIBLE IN THERMODYNAMIC LIMIT

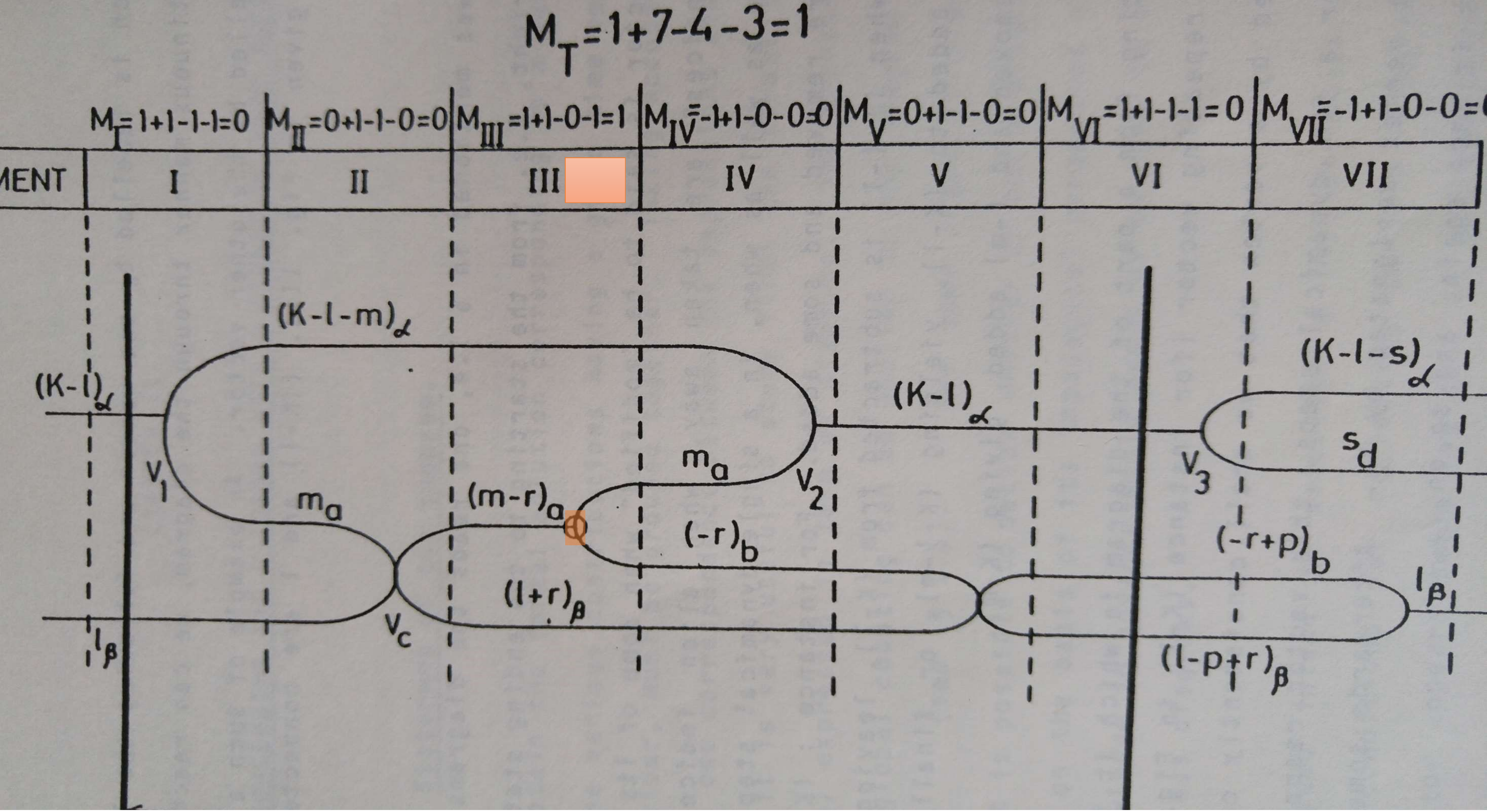
$$\frac{N^{\beta}}{\Omega^{\Delta \underline{D}+V-\alpha}} = \frac{C^{\beta}}{\Omega^{\Delta \underline{D}+V-\alpha-\beta}} = \frac{C^{\beta}}{\Omega^{M}} \qquad (I.23)$$

which provides us with the following criterion in terms of the expression /41/ :

$$M = \Delta \underline{D} + V - \alpha - \beta \qquad (I.24)$$

"A diagram is negligible in thermodynamic limit if

$$M > 0 \qquad (I.25a)$$



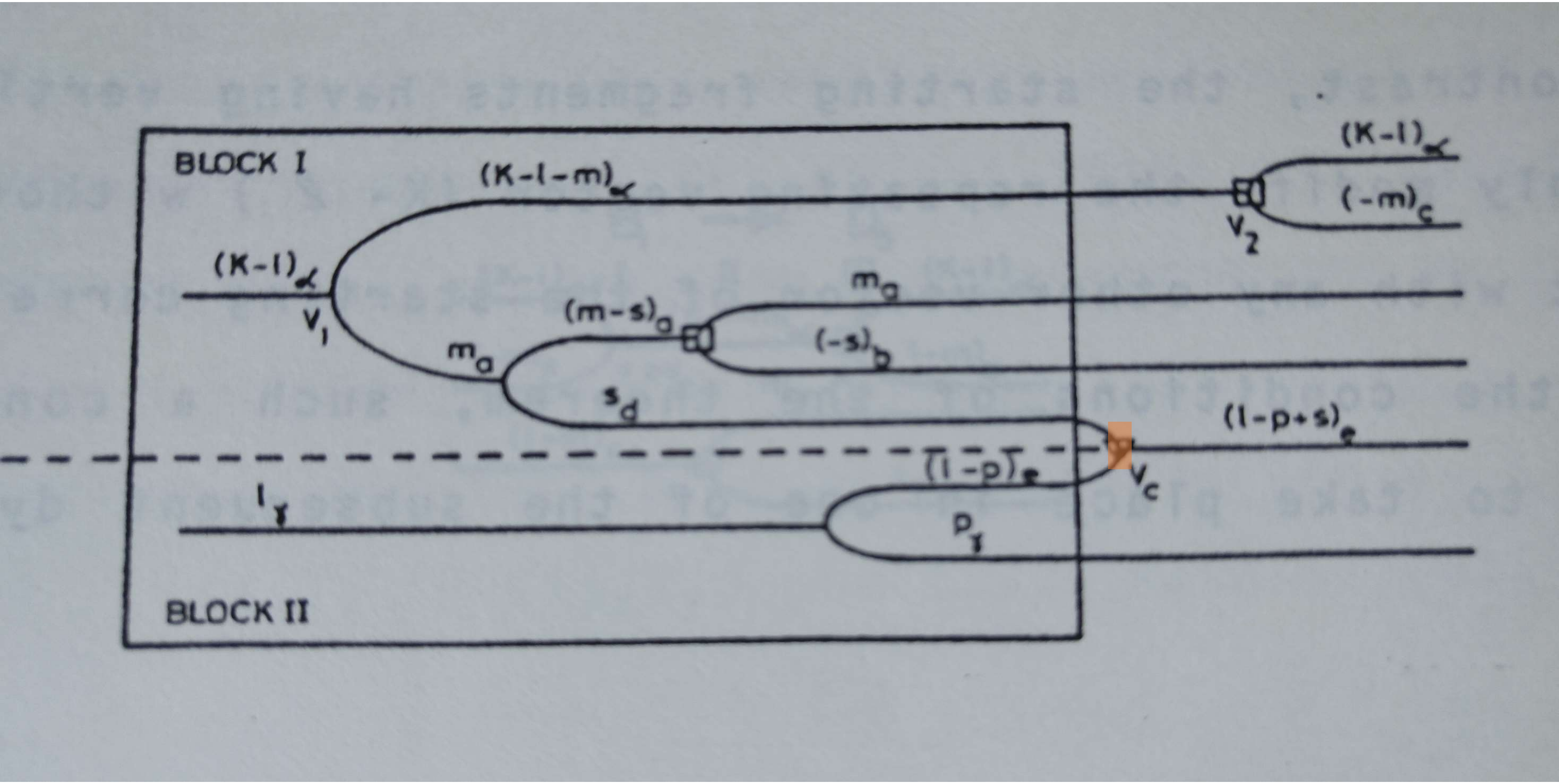
M_T = 1+7-4-3=1
M_I = 1+1-1-1=0
M_II = 0+1-1-0=0
M_III = 1+1-0-1=1
M_IV = -1+1-0-0=0
M_V = 0+1-1-0=0
M_VI = 1+1-1-1 = 0
M_VII = -1+1-0-0=
MENT
I
II
III
IV
V
VI
VII
(K-l-m)α
(K-l)α
V1
ma
Vc
lβ
(m-r)a
(l+r)β
ma
(-r)b
V2
(K-l)α
V3
(K-l-s)α
sd
(-r+p)b
lβ
(l-p+r)β

TOPOLOGIC THEOREM

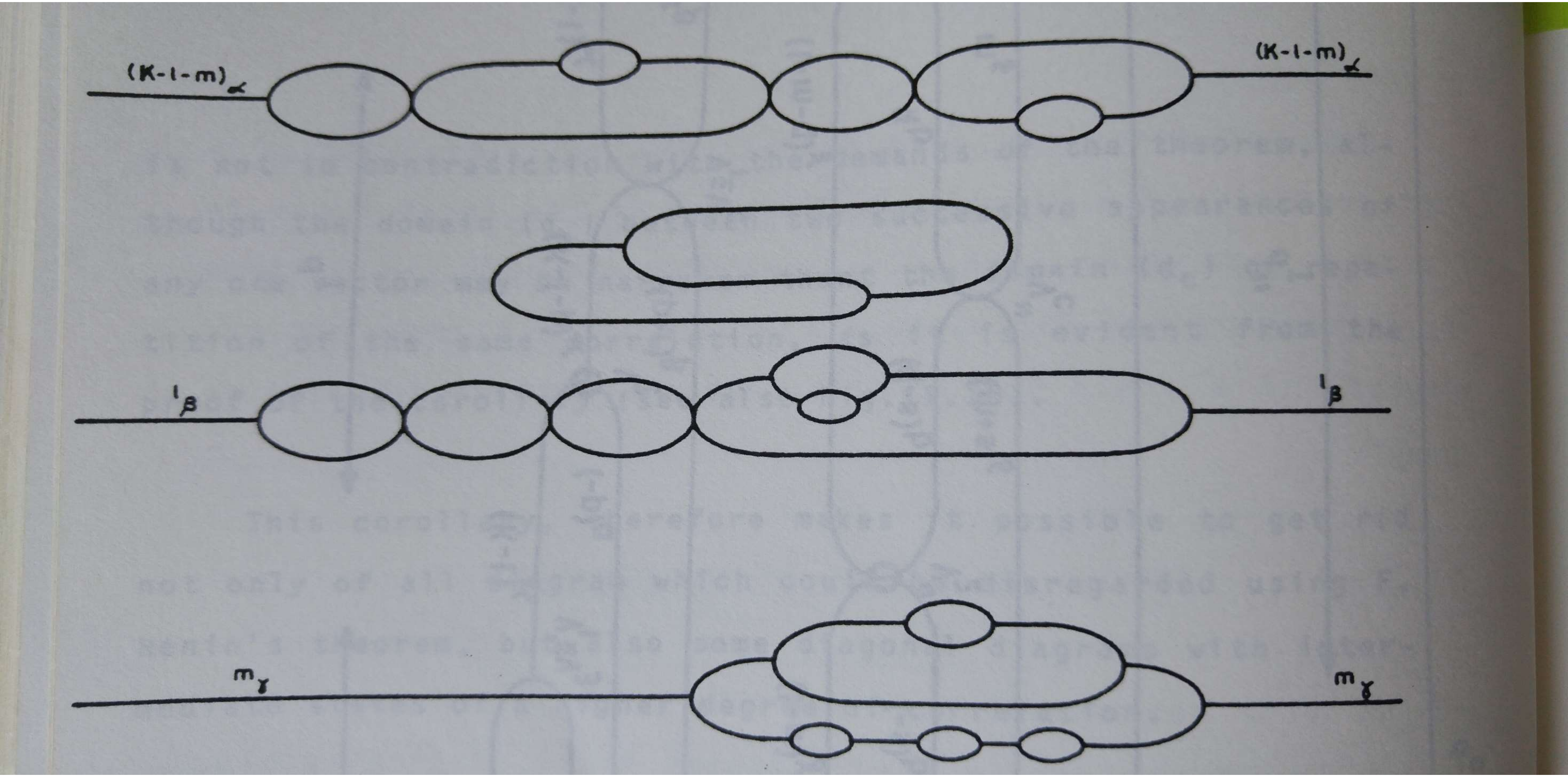
Wave vector (K-l) from Block I is connected with (-r) from Block II, increasing criterion M to 1 and making all diagram negligible in thermodynamic limit.

diagram with a repeating wave vector, is negligible in the thermodynamic limit, if this vector appears together with some other vector to the immediate left of the vertex V_1, and if these vectors are connected in the "domain" between the vertices V_1 and V_3. (By definition the vertex V_1 is included in the "domain", but V_3 is not)".

INTERCONNECTED BLOCKS ARE NEGLIGIBLE



FOUR INDEPENDENT DIAGONAL COLLISION BLOCKS



COLLISION SUPEROPERATOR

$$\overset{1}{\Theta}_{K_\alpha} = -\sum_m \sum_j F_m \left\{ \frac{\partial}{\partial v_{\alpha j}} \frac{1}{i\varepsilon + m v_{\alpha j}} \frac{\partial}{\partial v_{\alpha j}} - \frac{\partial}{\partial v_{\alpha j}} \frac{K}{[i\varepsilon + m v_{\alpha j}]^2} \right\} \quad (2.4)$$

thus contains, in addition to the usual homogeneous collisional term, ψ_{0_α}, a contribution due to the inhomogeneity K.

Using the property of the non-commutation between the differentiation cperators, $\frac{\partial}{\partial v}$ and the eigenvalues of the Liouvillian L_0, all contributions of the diagram can be expressed by means of the super-operator $\overset{1}{\Theta}_{K_\alpha}$ only :

FORMAL SOLUTION IN EXPONENTIAL FORM

The possibility of obtaining all time dependent terms by means of action of the superoperator $\overset{1}{\Theta}$ on L_0 eigenvalue, enables us to put the formal solution in the exponential form, up to the second order with respect to the coupling constant λ :

$$\rho^{(\kappa_\alpha)}_{\kappa_\alpha}(v_\alpha,\dots;t) \doteq e^{-it\{\kappa v_\alpha + \lambda^2 \overset{1}{\Theta}_{\kappa_\alpha}\}} \Big\{1 + \lambda^2 \sum_{m=1}^{3} (-1)^{m+1} \frac{1}{m!} \Big(D^m \Big(\overset{1}{\Theta}_{\kappa_\alpha} \{\kappa v_\alpha\}^{m-1}\Big)\Big)\Big\} \rho_{\kappa_\alpha}(v_\alpha,\dots;0)$$

[3 – 6]

GENERAL EQUATION in K - VACUUM SUBDINAMICS

$$\partial_t f_{K_\alpha}^{(K_\alpha)}(t) = -i \int dv_\beta \left\{ K v_\alpha + \Theta_{K_\alpha} \right\} \Psi_\beta^{(K_\alpha)}(t)\, f_{K_\alpha}^{(K_\alpha)}(t) \qquad \text{(IX.5)}$$

The superoperator Θ_{K_α} (of any order in λ) contains a homogeneous term corresponding to the homogeneous collision superoperator, Ψ_α and inhomogeneous terms, which depend of the wave vector K (see the explicit expressions (VII.87), (VII.93), and (IV.8), as well as the general formula (V.47)) :

[5] V. Skarka, Physica, **156A,** 651-678 (1989).
[6] V. Skarka and C. George Physica, **127A,** 473-489 (1984).

IRREVERSIBLE COLLISION SUPEROPERATOR

new representation is purely "diagonal", since the evolution superoperator connects the "privileged" components in the given (η)-subdynamics $\overset{(p)}{\rho}_\eta(0)$ and $\overset{(p)}{\rho}_\eta(t)$ (see (2.3) and (2.5)), which respectively correspond to the transformed post-initial and final distribution functions. The exponent in the evolution superoperator is also made more symmetric by this transformation Λ. It is called the kinetic superoperator, $\mathbb{K}$:

$$\sum_\omega \chi_\omega^{-1}\{wv_\omega + \Theta_\omega\}\chi_\omega = \sum_\omega \{wv_\omega + \overset{(e)}{\phi}_\omega + \overset{(o)}{\phi}_\omega\} = \sum_\omega \mathbb{K}_\omega \,. \tag{2.6}$$

The new collision superoperator ϕ_ω is split into parts $\overset{(e)}{\phi}_\omega$ and $\overset{(o)}{\phi}_\omega$ which are respectively even and odd with respect to the velocity inversion ($L \to -L$)[20,21].

The distribution function in the physical representation can be cluster-

expanded.

GENERAL EQUATION IN SUBDYNAMICS OF CORRELATIONS

In general, the subdynamics associated with the correlations of the n particles, is governed by the equations for the reduced distribution functions of x particles, where x = 1, 2, 3, ..., n :

$$\partial_t \varphi_\gamma^{(n)}(t) = -i \int \prod_j d\upsilon_j \, \mathbb{K}_\gamma \, \varphi_j^{(n)}(t) \, \varphi_\gamma^{(n)}(t)$$

[3 – 6]

ANALOG OF ENTROPY DUE TO COLLISION SUPEROPERATOR

$\overset{(e)}{\phi}$. Indeed, due to the dissipativity condition, $\overset{(e)}{\phi} \neq 0$, the causal and the anticausal evolutions are different [3-6]. The causality is thus incorporated into the differential equation like in the Boltzmann's and other irreversible equations. In the physical representation an analog to entropy can be obtained; it is given in terms of a quadratic functional of the complete distribution function, Ω which is a Lyapounov function [3-6]. The introduction of correlations into the definition of this new generalized $\mathcal{H}$ -quantity enables one to describe correctly the velocity inversion. Hence, Loschmidt's paradox is eliminated [3-6].

ANALOG OF NEGATIVE ENTROPY

$$(\partial_t \Omega) = \Big(\partial_t N \int dk_\alpha \int dv_\alpha \,|\overset{(p)}{f}_{k_\alpha}(t)|^2 \overbrace{\int \prod_n dv_n \overset{(p)}{\varphi}_n(t)}^{1}\Big) =$$

$$= -2\pi N \int dk_\alpha \int dv_\alpha \int dv_j \int dm \overbrace{\int \prod_n dv_n \overset{(p)}{\varphi}_n(t)}^{1} \Big(\frac{\lambda}{M} V_{(m)} m\Big)^2 \cdot$$

$$\cdot\, \delta(m v_{\alpha j}) \,|\partial_{v_j} \overset{(p)}{f}_{k_\alpha}(t)\, \varphi_j(t)|^2 \leq 0$$

[3-6]

Therefore, the Lyapounov functional Ω has, as the entropy, the property of additivity.

GENERAL EQUATION REDUCED TO BOLTZMANN EQUATION

$$\partial_t f_\alpha(x_\alpha, v_\alpha; t) + v_\alpha \nabla_\alpha f_\alpha(x_\alpha, v_\alpha; t) = \int dx_b \int dv_b \, \Psi \,.$$

$$\cdot \, \delta(x_\alpha - x_b) \, f_\alpha(x_\alpha, v_\alpha; t) \, f_b(x_b, v_b; t) \qquad \text{(IX.19)}$$

The non-linear homogeneous equation (VII.85a) reduces in the straightforward way, in the hydrodynamic and dilute gas approximations, to the homogeneous Boltzmann equation.

SUBDINAMICS SOLUTION OF BOLTZMANN EQUATION

$$f_{k\alpha}(t) = \sum_{n} f_{k\alpha}^{(n)}(t) = \sum_{n} \int dv_{\beta}\, e^{-it\{\kappa v_{\alpha} - \Psi_{\alpha}\}} \{1 - \Psi'_{\alpha}\} f_{n\alpha}(0)\, f_{n\beta}(0)$$

[3-7]

[7] V. Skarka, **RELATION BETWEEN THE KINETIC EQUATION IN THE SUBDYNAMICS APPROACH AND THE BOLTZMANN EQUATION FOR INHOMOHENEOUS GASES**, Physica, **129A,** 62-80 (1984).

IN ORDER TO SOLVE THE PARADOX THAT MACROSCOPIC EQUATIONS ARE IRREVERSIBLE, WHILE MICROSCOPIC EQUATIONS ARE REVERSIBLE, WHOLE DYNAMICS OF CORRELATIONS IS SPLIT INTO SUBDYNAMICS

PERTURBATION EXPANSION OF THE FORMAL SOLUTION OF LIOUVILLE EQUATION IS REPRESENTED BY DIAGRAMS. CONDITIONS FOR NEGLIGIBILITY OF DIAGRAMS IN THERMODYNAMIC LIMIT, ARE ESTABLISHED

STATISTICAL MECHANICS of IRREVERSIBLE PROCESSES in INHOMOGENEOUS GASES THROUGH the SUBDYNAMICS APPROACH is ESTABLISHED *AB INITIO*

VACUUM OF CORRELATIONS SUBDYNAMICS BECOMES IRREVERSIBLE, SINCE, COLLISIONS DESTROY INITIAL CONDITIONS, WHILE ALL OTHER SUBDYNAMICS REMAIN REVERSIBLE

GENERAL IRREVERSIBLE EQUATION AND ITS SOLUTION ARE REALIZED COMBINING ALL SUBDYNAMICS. ANALOG OF ENTROPY IS ESTABLISHED

GENERALIZED BOLTZMAN EQUATION AND ITS SOLUTION ARE OPTAINED