Fluctuations in the presence of fields

-Phenomenological Gaussian approximation and a new class of thermodynamic inequalities-

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Abstract

The work approaches the study of the fluctuations for the thermodynamic systems in the presence of the fields. The approach is of phenomenological nature and developed in a Gaussian approximation. The study is exemplified on the cases of a magnetizable continuum in a magnetoquasistatic field, as well as for the so called discrete systems. In the last case one finds that the fluctuations estimators depends both on the intrinsic properties of the system and on the characteristics of the environment. Following some earlier ideas of one of the authors we present a new class of thermodynamic inequalities for the systems investigated in this paper. In the case of two variables the mentioned inequalities are nothing but non-quantum analogues of the well known quantum Heisenberg ("uncertainty") relations. Also the obtained fluctuations estimators support the idea that the Boltzmann’s constant $k$ has the significance of a generic indicator of stochasticity for thermodynamic systems.

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I. INTRODUCTION

The literature from the last decades promoted some interesting attempts \([1-6]\) in order \([4]\) "to formulate a comprehensive and unified theory of thermodynamic in the presence of fields". As we know the respective attempts approached the description of the thermodynamic systems only in terms of macroscopic quantities regarded as deterministic variables, unendowed with fluctuations.

On the other hand it is a well established fact that, due to their inner microscopic structure, the thermodynamic systems must be characterized by means of variables endowed with fluctuations. The mean values of the respective variables coincide with the macroscopic quantities from the usual thermodynamics. The alluded fluctuations require a description in terms of some additional concepts of probabilistic nature (e.g. dispersions, correlations, higher order moments). Such a description can be done in a phenomenological or in a statistical-mechanics manner. In this paper we try to develop a description of fluctuations specific for thermodynamic systems in the presence of fields. Our description is done in a phenomenological manner. We will appeal to usual procedures of phenomenological theory \([2,4,7,8]\) as well as some ideas inspired by our earlier works on fluctuations \([9,10]\).

We start a search for a first approximation of the generalized distribution of fluctuation probabilities. For this we use the concept of adequate internal energy inspired by \([1]\). A first application is focused on the second order moments for the fluctuations in magnetizable continuum in a magnetoquasistatic field. Afterward we will investigate briefly the questions connected with the fluctuations in discrete systems in the presence of magnetic field. By using the results of the alluded investigations in a next section we will introduce a new class of thermodynamic inequalities, in a manner similar with the one developed in \([1]\).
II. GENERAL THEORETICAL CONSIDERATIONS

The phenomenological theory of fluctuations deals with real and continuous variables endowed with an 'ad hoc' stochasticity (without any reference to the microscopic structure of the thermodynamic systems). For small fluctuations in the proximity of equilibrium states the corresponding distribution of probabilities are given \[2,7,8\] by the formula

\[ w \sim \exp \left\{ \frac{\delta S'}{k} \right\} \]  

(1)

Here \( \delta S' = S'(x) - S'(\bar{x}) \) denote the variation of entropy due to the fluctuations, \( x \) signify the set of the macroscopic variables characterizing the system -with \( \bar{x} \) as equilibrium mean (or expected) value of \( x \) and \( k \) is the Boltzmann’s constant. The variation \( \delta S' \) refers to the ensemble of thermodynamic system and its environment. It is given by

\[ \delta S' = -\frac{\delta W_{\text{min}}}{T_{eq}} \]  

(2)

with \( T_{eq} \) =equilibrium temperature and \( \delta W_{\text{min}} \) =minimal work of fluctuations.

Observation: In (1) as well as in all the subsequent formulas for the probability distributions \( w \) we are omitting the constants which precedes the exponential functions. Evidently that, for all the cases, the respective constants can be determined by imposing the normalization condition for \( w \).

Let us focus our attention on the systems in the presence of fields (as they are viewed in \[4–6\]). Then we introduce the work \( \delta W_{\text{min}} \) through the relation

\[ \delta \hat{U} = \sum_r \hat{\xi}_r \delta Y_r + \sum_r \Psi_l \delta Z_l + \delta W_{\text{min}} \]  

(3)

Here we used the following notations: \( \delta A = \)the variation (due to the fluctuations) of the variable \( A \); \( \hat{U} = \)the internal energy in the presence of fields; \( \hat{\xi}_r \) are the field dependent intensive variables (e.g. \( \hat{\xi}_1 = T = \)temperature, while \( -\hat{\xi}_2 = \hat{p} \) and \( \hat{\xi}_3 = \hat{\zeta} \) denote the field dependent pressure and chemical potential); \( Y_r = \)the usual extensive thermodynamic variables (e.g. entropy \( S \), volume \( V \), number of particles \( N \)); \( \Psi_l \) and \( Z_l \) denote the additional
parameters due to the presence of fields (e.g. \( \Psi = VH, Z = B \) with \( H \) and \( B \) strength respectively the induction of the magnetic field).

**Observation:** As above regarded the quantities \( \Psi_l \) generally are not intensive parameters conjugated with \( Z_l \).

In (3) \( \hat{U} \) depends on \( X_r \) and \( Z_l \). Its total differential is given by:

\[
d\hat{U} = \sum_r \hat{\xi}_r \, dY_r + \sum_l \Psi_l \, dZ_l
\]  

For avoiding the irrelevant intricacy of the used formulas in the following we introduce the compacted notation \( \{Y_r\} \cup \{Z_l\} = \{\eta_i\} \) and \( \{\hat{\xi}_r\} \cup \{\Psi_l\} = \{\Phi_i\} \). So from (3) one obtains:

\[
\Phi_i = \left( \frac{\partial \hat{U}}{\partial \eta_i} \right)_{eq}
\]  

where the index eq. denote the equilibrium value of the indexed quantity.

For the variation \( \delta \hat{U} \) in the second order approximation in terms of the variations \( \delta \eta_i \) one can write

\[
\delta \hat{U} = \sum_i \left( \frac{\partial \hat{U}}{\partial \eta_i} \right)_{eq} \delta \eta_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 \hat{U}}{\partial \eta_i \partial \eta_j} \right)_{eq} \delta \eta_i \delta \eta_j + ...
\]  

By using the relations (2-6) from (3) one obtains:

\[
w \sim \exp \left\{ -\frac{1}{2kT} \sum_j \delta \Phi_j \delta \eta_j \right\}
\]  

For a given system, due to their physical nature, the variables from the sets \( \{\Phi_i\} \) and \( \{\eta_i\} \) are generally interdependent. But for such a system always one can select a restrictive set of physically independent variables \( \{X_a\}_{a=1}^n \). Then (7) transcribes as the following multivariable Gaussian distribution:

\[
w \sim \exp \left\{ -\frac{1}{2} \sum_{a=1}^n \sum_{b=1}^n \alpha_{ab} \, \delta X_a \, \delta X_b \right\}
\]  

where

\[
\alpha_{ab} = \frac{1}{kT} \sum_j \left( \frac{\partial \Phi_j}{\partial X_a} \right)_{eq} \left( \frac{\partial \eta_j}{\partial X_b} \right)_{eq}
\]
From the previous relations it directly results the fact that $\alpha_{ab}$ are field dependent elements of a matrix $\alpha$.

It is the place to be noted the fact that in the Gaussian distribution (8) the quantities $\{X_a\}$ are considered as continuous variables, each of them being defined in the range $(-\infty, \infty)$.

In the above mentioned Gaussian approximation the fluctuations of the independent variables $\{X_a\}$ are characterized by the correlations

$$C_{ab} = \overline{\delta X_a \delta X_b} = (\alpha^{-1})_{ab} \quad (10)$$

where $(\alpha^{-1})_{ab}$ are the elements of the inverse of the matrix $\alpha$ given by (9).

For any set of quantities $\{Q_m\}$ expressible in terms of independent variables $\{X_a\}$ [i.e. $Q_m = Q_m (X_a)$] the fluctuations are characterized by the correlations

$$C_{ms} = \sum_a \sum_b \left( \frac{\partial Q_m}{\partial X_a} \right)_{eq} \left( \frac{\partial Q_s}{\partial X_b} \right)_{eq} (\alpha^{-1})_{ab} \quad (11)$$

For $m = s$ the correlation $C_{mm} = \mathcal{D}_m$ denote just the dispersion of fluctuations for the quantity $Q_m$.

As in the case of fluctuations in the absence of fields [9] the correlations (11) constitute a real, symmetric and non-negative definite matrix. Then from (11) one obtains the relation:

$$\det \left[ \sum_a \sum_b \left( \frac{\partial Q_m}{\partial X_a} \right)_{eq} \left( \frac{\partial Q_s}{\partial X_b} \right)_{eq} (\alpha^{-1})_{ab} \right] \geq 0 \quad (12)$$

Any concrete application of the above description of the fluctuations in the presence of fields requires to consider the following steps:

- to establish the adequate expression (4) for the total differential $d\hat{U}$ of the internal energy (for such a goal the results from [4–6] are highly recommendable).

- to evaluate the minimal work $\delta W_{\text{min}}$ of fluctuations by using (3).

- to identify the set of the independent variables $\{X_a\}$. 

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• to take into account of the adequate equations of state and thermodynamic Maxwell relations (in this sense as guides can be used the works [2, 5–8]).

• to compute effectively the adequate correlations $C_{ms}$ through the relations (11) or (11).

• to find some relevant field dependent thermodynamic inequalities by using (12).

In the Sections III and IV we will present some detailed exemplifications in the above mentioned manner.

III. EVALUATION OF SOME CORRELATIONS

A. The case of a magnetizable continuum in the presence of magnetoquasistatic field

In the alluded case we suppose that the magnetic energy is stored within the frontiers of the system. The adequate expression of the internal energy differential, as in [4], has the form

$$d\hat{U} = TDs - \hat{p}dV + \hat{\zeta}dN + VHdB$$

(13)

In this relation, as well as in the subsequent ones, the implied symbols for physical variables signify the mean values regarding an equilibrium state. The quantities $\hat{p}$ and $\hat{\zeta}$ are intensive parameters which are dependent on field. These parameters have various expressions, depending on the approached situations.

The minimal work of the fluctuations is

$$\delta W_{\text{min}} = \delta \hat{U} - TD\delta S + \hat{p}\delta V - \hat{\zeta}\delta N - VH\delta B$$

(14)

As independent variables we take $T, V, N$ and $B$. Their independence must be regarded in a thermodynamic sense, because they can be interdependent from a statistical approach.

For the probability density (8) one obtains

$$6$$
\[ w \sim \exp \left\{ -\frac{1}{2kT} \left[ \left( \frac{\partial S}{\partial T} \right)_{V,N,B} (\delta T)^2 - \left( \frac{\partial \hat{p}}{\partial V} \right)_{T,N,B} (\delta V)^2 + \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,B} (\delta N)^2 + V \left( \frac{\partial H}{\partial B} \right)_{T,V,N} (\delta B)^2 \right] + 2 \left( \frac{\partial \hat{p}}{\partial V} \right)_{T,N,B} \delta V \delta N + 2 \left( \frac{\partial (V\hat{H})}{\partial V} \right)_{T,N,B} \delta V \delta B + 2V \left( \frac{\partial H}{\partial N} \right)_{T,V,B} \delta N \delta B \right\} \]

(15)

The matrix of the correlation coefficients is

\[
(\alpha) = \begin{pmatrix}
\alpha_{11} & 0 & 0 & 0 \\
0 & \alpha_{22} & \alpha_{23} & \alpha_{24} \\
0 & \alpha_{32} & \alpha_{33} & \alpha_{34} \\
0 & \alpha_{42} & \alpha_{43} & \alpha_{44}
\end{pmatrix}
\]

(16)

where

\[
\alpha_{11} = \frac{1}{kT} \left( \frac{\partial S}{\partial T} \right)_{V,N,B} ; \quad \alpha_{22} = -\frac{1}{kT} \left( \frac{\partial \hat{p}}{\partial V} \right)_{T,N,B} \\
\alpha_{33} = \frac{1}{kT} \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,B} ; \quad \alpha_{44} = \frac{V}{kT} \left( \frac{\partial H}{\partial B} \right)_{T,V,N} = \frac{V}{kT\mu} \\
\alpha_{12} = \alpha_{21} = 0; \quad \alpha_{13} = \alpha_{31} = 0; \quad \alpha_{14} = \alpha_{41} = 0 \\
\alpha_{23} = \alpha_{32} = \frac{1}{kT} \left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,B} \\
\alpha_{24} = \alpha_{42} = \frac{1}{kT} \left( \frac{\partial (V\hat{H})}{\partial V} \right)_{T,N,B} = \frac{H}{kT} \left[ 1 + \frac{\rho}{\mu} \left( \frac{\partial \mu}{\partial \rho} \right)_T \right] \\
\alpha_{34} = \alpha_{43} = \frac{V}{kT} \left( \frac{\partial H}{\partial N} \right)_{T,V,B} = -\frac{H}{kT\mu} \left( \frac{\partial \mu}{\partial \rho} \right)_T
\]

In the above relations \( \rho \) denotes the particle number in the unity volume \( \left( \rho = \frac{N}{V} \right) \) and \( \mu \) signifies the magnetic permeability of the system.

Then for the dispersions and correlations one finds:

\[
(\delta T)^2 = (\alpha^{-1})_{11} = \frac{1}{\alpha_{11}}
\]

\[
(\delta V)^2 = (\alpha^{-1})_{22} = \frac{1}{\det |\beta|}
\]

(17)
\[(\delta N)^2 = (\alpha^{-1})_{33} = \frac{\alpha_{22} \alpha_{24}}{\det |\beta|} \]  

\[(\delta B)^2 = (\alpha^{-1})_{44} = \frac{\alpha_{22} \alpha_{23}}{\det |\beta|} \]  

\[\delta T \delta V = \delta T \delta N = \delta T \delta B = 0 \]  

\[\delta V \delta N = (\alpha^{-1})_{23} = -\frac{\alpha_{23} \alpha_{34}}{\det |\beta|} \]  

\[\delta V \delta B = (\alpha^{-1})_{24} = -\frac{\alpha_{23} \alpha_{33}}{\det |\beta|} \]  

\[\delta N \delta B = (\alpha^{-1})_{34} = -\frac{\alpha_{22} \alpha_{23}}{\det |\beta|} \]  

where

\[\det |\beta| = \begin{vmatrix} \alpha_{22} & \alpha_{23} & \alpha_{24} \\ \alpha_{23} & \alpha_{33} & \alpha_{34} \\ \alpha_{24} & \alpha_{34} & \alpha_{44} \end{vmatrix} \]  

Let us focus on some particular cases:

1. \( V = \text{const}, N = \text{const}. \)

In this case the matrix \( \alpha \) is of the form
\[ (\alpha) = \begin{pmatrix} \alpha_{11} & 0 \\ 0 & \alpha_{22} \end{pmatrix} \]  

(26)

with

\[ \alpha_{11} = \frac{1}{kT} \left( \frac{\partial S}{\partial T} \right)_B ; \quad \alpha_{22} = \frac{V}{kT} \left( \frac{\partial H}{\partial B} \right)_T \]

The entropy of the system in the presence of the magnetic field is given by

\[ S = S_0 + \frac{1}{2} VH^2 \left( \frac{\partial \mu}{\partial T} \right)_\rho \]  

(27)

where \( S_0 \) denote the entropy in the absence of the field.

Then, for the regarded case, for the dispersions and correlations of various physical variables one obtains:

\[ \overline{(\delta T)^2} = \left( \alpha^{-1} \right)_{11} \frac{kT}{C_V + \frac{1}{2} TVH^2 \left( \frac{\partial^2 \mu}{\partial T^2} \right)_\rho - \frac{2}{\mu} \left( \frac{\partial \mu}{\partial T} \right)_\rho^2} \]  

(28)

\[ \overline{(\delta B)^2} = \left( \alpha^{-1} \right)_{22} \frac{kT}{V \left( \frac{\partial \mu}{\partial B} \right)_T} = \frac{kT \mu}{V} \]  

(29)

\[ \delta T \delta B = 0 \]  

(30)

\[ \delta T \delta S = \left( \frac{\partial S}{\partial T} \right)_B \overline{(\delta T)^2} = kT \]  

(31)

\[ \delta T \delta H = \left( \frac{\partial H}{\partial T} \right)_B \overline{(\delta T)^2} = \frac{kT^2}{C_V + \frac{1}{2} TVH^2 \left( \frac{\partial^2 \mu}{\partial T^2} \right)_\rho - \frac{2}{\mu} \left( \frac{\partial \mu}{\partial T} \right)_\rho^2} \]  

(32)

\[ = - \frac{H}{\mu} \left( \frac{\partial \mu}{\partial T} \right)_\rho C_V + \frac{1}{2} TVH^2 \left( \frac{\partial^2 \mu}{\partial T^2} \right)_\rho - \frac{2}{\mu} \left( \frac{\partial \mu}{\partial T} \right)_\rho^2 \]

\[ \delta B \delta H = \left( \frac{\partial H}{\partial B} \right)_T \overline{(\delta B)^2} = \frac{kT}{V} \]  

(33)

\[ \delta S \delta B = \left( \frac{\partial S}{\partial B} \right)_T \overline{(\delta B)^2} = kTH \left( \frac{\partial \mu}{\partial T} \right)_\rho \]  

(34)

In the above formulas \( C_V \) denotes the isochoric heat capacity: \( C_V = T \left( \frac{\partial S_0}{\partial T} \right)_{V,N} \). From (28) it directly results that in the absence of field \( \overline{(\delta T)^2} \) has the previously known expression [7–9].
2. \( B = \text{const.} \)

This case is associated with a constant magnetic flux. The quantities \( T, V \) and \( N \) will be regarded as random variables (i.e. endowed with fluctuations).

In the considered case, according to \([4]\), one can write

\[
d\hat{U} = TdS - \hat{p}dV + \hat{\zeta}dN \tag{35}
\]

where

\[
\hat{p} = p_{B,N} = p - \frac{1}{2}HB - \frac{1}{2}H^2\rho \left( \frac{\partial \mu}{\partial \rho} \right)_T \tag{36}
\]

\[
\hat{\zeta} = \zeta_{B,V} = \zeta - \frac{1}{2}H^2 \left( \frac{\partial \mu}{\partial \rho} \right)_T \tag{37}
\]

\( p \) and \( \zeta \) denote respectively the pressure and chemical potential in the absence of field.

The matrix of the correlation coefficients has the form

\[
(\alpha) = \begin{pmatrix}
\alpha_{11} & 0 & 0 \\
0 & \alpha_{22} & \alpha_{23} \\
0 & \alpha_{23} & \alpha_{33}
\end{pmatrix}
\tag{38}
\]

By using \([11]\) through of some uncomplicated algebraic operations one finds

\[
(\delta T)^2 = (\alpha^{-1})_{11} = \frac{kT}{(\partial S/\partial T)_{V,N,B}} \tag{39}
\]

\[
(\delta V)^2 = (\alpha^{-1})_{22} = \frac{\alpha_{33}}{\alpha_{22}\alpha_{33} - \alpha_{23}^2} = -kT \frac{\left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,V,B}}{\left( \frac{\partial \hat{\mu}}{\partial V} \right)_{T,N,B} \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,B} + \left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,B}^2} \tag{40}
\]

\[
(\delta N)^2 = (\alpha^{-1})_{33} = \frac{\alpha_{22}}{\alpha_{22}\alpha_{33} - \alpha_{23}^2} = kT \frac{\left( \frac{\partial \hat{\mu}}{\partial N} \right)_{T,N,B}}{\left( \frac{\partial \hat{\mu}}{\partial V} \right)_{T,N,B} \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,B} + \left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,B}^2} \tag{41}
\]
\[\delta V \delta N = (\alpha^{-1})_{23} = \frac{\alpha_{23}}{\alpha_{23}^2 - \alpha_{22}\alpha_{33}} = kT \frac{\left(\frac{\partial \zeta}{\partial V}\right)_{T,N,B}^2}{\left(\frac{\partial \zeta}{\partial V}\right)_{T,N,B} + \left(\frac{\partial \hat{\rho}}{\partial V}\right)_{T,N,B} \left(\frac{\partial \zeta}{\partial N}\right)_{T,V,B}} \] (42)

\[\delta T \delta V = 0; \delta T \delta N = 0 \] (43)

The formulas (39)-(42) imply the following relations:

\[
\left(\frac{\partial S}{\partial T}\right)_{V,N,B} = \frac{C_V}{T} + \frac{1}{2} V H^2 \left[\left(\frac{\partial^2 \mu}{\partial T^2}\right)_T - \frac{2}{\mu} \left(\frac{\partial \mu}{\partial T}\right)_T\right] \] (44)

\[
\left(\frac{\partial \hat{\zeta}}{\partial N}\right)_{T,V,B} = \left(\frac{\partial \zeta}{\partial N}\right)_{T,V} + \frac{H^2}{\mu V} \left(\frac{\partial \mu}{\partial \rho}\right)_T^2 - \frac{1}{2} \frac{H^2}{V} \left(\frac{\partial^2 \mu}{\partial \rho^2}\right)_T \] (45)

\[
\left(\frac{\partial \hat{\rho}}{\partial V}\right)_{T,N,B} = \left(\frac{\partial \rho}{\partial V}\right)_{T,N} - \frac{H^2 \rho^2}{\mu V} \left(\frac{\partial \mu}{\partial \rho}\right)_T^2 + \frac{1}{2} \frac{H^2 \rho^2}{V} \left(\frac{\partial^2 \mu}{\partial \rho^2}\right)_T \] (46)

\[
\left(\frac{\partial \hat{\zeta}}{\partial V}\right)_{T,N,B} = \left(\frac{\partial \zeta}{\partial V}\right)_{T,N} - \frac{H^2 \rho}{\mu V} \left(\frac{\partial \mu}{\partial \rho}\right)_T^2 + \frac{1}{2} \frac{H^2 \rho}{V} \left(\frac{\partial^2 \mu}{\partial \rho^2}\right)_T \] (47)

3. \(H = \text{const.}\)

In this case the courant densities (the sources of the magnetic field) are constant. We search the parameters of the fluctuations for the quantities \(T, V\) and \(N\).

The differential of the internal energy is given by (33) where according to [4]

\[
\hat{p} = p_{H,N} = p - \frac{1}{2} H B + \frac{1}{2} H^2 \rho \left(\frac{\partial \mu}{\partial \rho}\right)_T \] (48)

\[
\hat{\zeta} = \zeta_{H,V} = \zeta + \frac{1}{2} H^2 \left(\frac{\partial \mu}{\partial \rho}\right)_T \] (49)

In the approached case, as it was proved in [6], the entropy is

\[
S(H = \text{const.}) = S_0 - \frac{1}{2} V H^2 \left(\frac{\partial \mu}{\partial T}\right)_\rho \] (50)
With such an expression for entropy one obtains

\[
\frac{(\delta T)^2}{(\frac{\partial S}{\partial T})_{V,N,H}} = \frac{kT^2}{C_V - \frac{1}{2} TVH^2 \left( \frac{\partial^2 \mu}{\partial T^2} \right)_\rho} \tag{51}
\]

\[
\frac{(\delta V)^2}{(\frac{\partial \hat{\zeta}}{\partial N})_{T,V,H}} = -kT \frac{\left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,H} \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,H} + \left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,H}^2}{\left( \frac{\partial \hat{\gamma}}{\partial V} \right)_{T,N,H} \left( \frac{\partial \hat{\gamma}}{\partial N} \right)_{T,V,H} + \left( \frac{\partial \hat{\gamma}}{\partial V} \right)_{T,N,H}^2} \tag{52}
\]

\[
\frac{(\delta N)^2}{\delta V \delta N} = kT \frac{\left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,H}^2}{\left( \frac{\partial \hat{\gamma}}{\partial V} \right)_{T,N,H} + \left( \frac{\partial \hat{\gamma}}{\partial N} \right)_{T,N,H} \left( \frac{\partial \hat{\gamma}}{\partial V} \right)_{T,V,H}} \tag{53}
\]

where

\[
\left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V,H} = \left( \frac{\partial \hat{\zeta}}{\partial N} \right)_{T,V} + \frac{1}{2} \frac{H^2}{V} \left( \frac{\partial^2 \mu}{\partial \rho^2} \right)_T \tag{55}
\]

\[
\left( \frac{\partial \hat{p}}{\partial V} \right)_{T,N,H} = \left( \frac{\partial p}{\partial V} \right)_{T,N} - \frac{1}{2} \frac{H^2 \rho^2}{V} \left( \frac{\partial^2 \mu}{\partial \rho^2} \right)_T \tag{56}
\]

\[
\left( \frac{\partial \hat{\zeta}}{\partial V} \right)_{T,N,H} = \left( \frac{\partial \zeta}{\partial V} \right)_{T,N} - \frac{1}{2} \frac{H^2 \rho}{V} \left( \frac{\partial^2 \mu}{\partial \rho^2} \right)_T \tag{57}
\]

This subsection must be completed with the following important specifications:

- All the above relations refer to the case of linear magnetic materials, for which \( \mu \) is independent of \( H \) and depends only on the temperature \( T \) and particle density \( \rho \).

- For practical purposes it is more useful that the fluctuation to be evaluated for magnetization \( M \) but not for magnetic induction. Such a choice of evaluation can be done if
one subtract from the generalized internal energy the excitation energy corresponding to the magnetic field in vacuo, i.e. by introducing the function

\[ \hat{U}^* = \hat{U} - \frac{1}{2} V \mu_0 H^2 \]  

(58)

The alluded choice is possible only if it is neglected the change of \( H \) due to the presence of the magnetic system. Rigorously it must to be subtract from \( \hat{U} \) the quantity \( \frac{1}{2} V \mu_0 H^2 \), where \( H \) is the field strength generated in the vacuo by the sources, in absence of the system (for similar considerations see [1]). For most of the systems the magnetic susceptibility has a low value. Therefore one can be neglected the deformation of the field generated by the system presence. In such case one obtains:

\[ d\hat{U}^* = TdS - \hat{p}dV + \hat{\zeta}dN + VHd(\mu_0M) \]  

(59)

where

\[ M = \chi_m H \]  

(60)

\[ \hat{p} = p - \frac{1}{2} \mu_0 HM - \frac{1}{2} H^2 \rho \mu_0 \frac{\partial \chi_m}{\partial \rho} \]  

(61)

\[ \hat{\zeta} = \zeta - \frac{1}{2} H^2 \mu_0 \frac{\partial \chi_m}{\partial \rho} \]  

(62)

In the last three relations \( \mu_0 \) and \( \chi_m \) denote the magnetic permeability of vacuo and respectively the magnetic susceptibility.

When \( V \) and \( N \) have constant values one finds the restricted formula:

\[ (\delta M)^2 = kT \mu_0 \chi_m \frac{\rho}{V} \]  

(63)

known also from [2].
• In the case of a dielectric continuum the expressions of the fluctuations for various physical quantities can be obtained from the from the above presented formulas by means of the following substitutions: $B \rightarrow D; H \rightarrow E; \mu \rightarrow \varepsilon$, where $D$ is the electric induction, $E$ is the electric field strength and $\varepsilon$ the dielectric permittivity. Also it must to be replaced $\mu_0 M$ with $P$ (dielectric polarization) and $\chi_m$ with $\chi_e$ (dielectric susceptibility).

• It is easy to observe that the dispersions $(\delta A)^2$ and correlations $\delta A \delta B$ from the above established formulas appears as products of Boltzmann’s constant $k$ with expressions which contains exclusively mean values of the random variables. To be noted that the respective values identify themselves with the variables from the ordinary (non-stochastic) thermodynamics.

B. The case of discrete systems

The discrete systems are characterized by the fact that the field lines extend also in the outside of the system. Then the field energy is stored both in the inside and outside of the system. For such systems additionally to the deterministic- thermodynamic approach their study must be completed also with an investigation of the fluctuations (i.e. an evaluation of their stochastic characteristics). In the following we will approach the respective investigation for a particular case investigated determinist by Y. Zimmels [5]. The respective case regards a sphere of radius $R$ placed in an external uniform magnetic field of strength $H_0$.

For generalized internal energy of the sphere we have

$$dU_1 = TdS_1 - \hat{\rho}dV_1 + \hat{\zeta}dN_1 + \psi dB_1$$

This formula imply the following relations, taken by [3]:

$$\psi = V_1 \frac{B_1}{\mu_s} = V_1 H_1 \sqrt{\frac{\mu_s}{\mu_s}}$$

$$\mu_s = \frac{\mu_1}{9} \left( \frac{\mu_1}{\mu_2} - 2 \frac{\mu_2}{\mu_1} + 1 \right)$$

14
\[
\frac{1}{\mu'_s} = \frac{1}{9} \left( \frac{1}{\mu_2} + \frac{1}{\mu_1} - 2\frac{\mu_2}{\mu_1^2} \right) \quad (67)
\]

In the above relations as well as in the following ones the indexes 1 and 2 refer to the system (sphere) respectively to the environment.

Let us now discuss some particular situations:

1. \( V_1 = \text{const.}, N_1 = \text{const} \)

In this situation the entropy of the sphere, as in [5], is

\[
S_1 = S_{01} + \frac{1}{18} V_1 B_1^2 \left[ \alpha \frac{\partial \mu_2}{\partial T} - \beta \frac{\partial \mu_1}{\partial T} \right] \quad (68)
\]

where \( S_{01} \) denotes the entropy in the absence of the field and

\[
\alpha = \frac{1}{\mu_2^2} + \frac{2}{\mu_1^2} ; \quad \beta = 4\mu_2 \mu_3 - \frac{1}{\mu_1^2} \quad (69)
\]

The relation (65-69) refers to the discrete system in an equilibrium thermodynamic state.

If one takes as independent variables the quantities \( T \) and \( B_1 \), for their fluctuations one obtains:

\[
\frac{\langle \delta T \rangle^2}{\langle \delta S \rangle_{B_1}} = \frac{kT}{\alpha \frac{\partial \mu_2}{\partial T} - \beta \frac{\partial \mu_1}{\partial T}}
\]

\[
= kT^2 \left\{ C_V + \frac{1}{18} TV_1 B_1^2 \left[ \alpha \frac{\partial^2 \mu_2}{\partial T^2} - \beta \frac{\partial^2 \mu_1}{\partial T^2} + \frac{2}{\mu_1^3} \left( \frac{\partial \mu_1}{\partial T} \right)^2 \left( \frac{6\mu_2}{\mu_1} - 1 \right) - \frac{2}{\mu_2^3} \left( \frac{\partial \mu_2}{\partial T} \right)^2 - \frac{8}{\mu_1^3} \frac{\partial \mu_1}{\partial T} \frac{\partial \mu_2}{\partial T} \right] \right\}^{-1} \quad (70)
\]

\[
\frac{\langle \delta B_1 \rangle^2}{\langle \delta B_1 \rangle_{V_1}} = \frac{kT \mu'_s}{V_1} \left\{ \frac{1}{9} \left( \frac{1}{\mu_2} + \frac{1}{\mu_1} - 2\frac{\mu_2}{\mu_1^2} \right) \right\}^{-1} \quad (71)
\]

These relations show that for the discrete systems the fluctuations of the macroscopic parameters depend on the permeabilities of both the system and the environment.
2. $B_1 = \text{const.}$

In this situation as in [5] we take

$$dU_1 = TdS_1 - \hat{p}dV_1 + \hat{\zeta}dN_1 \tag{72}$$

with

$$\hat{p} = p_{B_1,N} = p - \frac{B_1^2}{2\mu'_s} + \frac{B_1^2}{18} \left[ \alpha \rho_2 \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} + \beta \rho_1 \frac{\partial \mu_1}{\partial \rho_1} \right] \tag{73}$$

and

$$\hat{\zeta} = \zeta_{B_1,N} = \zeta + \frac{B_1^2}{18} \left[ \frac{V_1}{V_2} \alpha \frac{\partial \mu_2}{\partial \rho_2} + \beta \frac{\partial \mu_1}{\partial \rho_1} \right] \tag{74}$$

It results that for $(\delta T)^2$ one obtains the same expression as in previous situation. This because the entropy is given also by (68).

The dispersions of $V_1$ and $N_1$ are:

$$\langle (\delta V_1)^2 \rangle = -kT \frac{\left( \frac{\partial \hat{\zeta}}{\partial N_1} \right)_{T,V_1,B_1}^2}{\left( \frac{\partial \hat{p}}{\partial V_1} \right)_{T,N_1,B_1} + \left( \frac{\partial \hat{\zeta}}{\partial V_1} \right)_{T,N_1,B_1}^2} \tag{75}$$

$$\langle (\delta N_1)^2 \rangle = kT \frac{\left( \frac{\partial \hat{\zeta}}{\partial V_1} \right)_{T,N_1,B_1}^2}{\left( \frac{\partial \hat{p}}{\partial N_1} \right)_{T,V_1,B_1} + \left( \frac{\partial \hat{\zeta}}{\partial N_1} \right)_{T,V_1,B_1}^2} \tag{76}$$

These expressions are only in a formal analogy with the corresponding ones for magnetizable continuum, because they imply specific particularities through the following partial derivatives.

$$\left( \frac{\partial \hat{p}}{\partial V_1} \right)_{T,N_1,B_1} = \left( \frac{\partial p}{\partial V_1} \right)_{T,N_1} + \frac{B_1^2}{18} \left[ \alpha \rho_2 \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} + \beta \rho_1 \frac{\partial \mu_1}{\partial \rho_1} \right] \tag{77}$$

$$\left( \frac{\partial \hat{\zeta}}{\partial N_1} \right)_{T,V_1,B_1} = \left( \frac{\partial \zeta}{\partial N_1} \right)_{T,V_1} + \frac{B_1^2}{18} \frac{\partial}{\partial N_1} \left( \frac{V_1}{V_2} \alpha \frac{\partial \mu_2}{\partial \rho_2} + \beta \frac{\partial \mu_1}{\partial \rho_1} \right) \tag{78}$$

$$\left( \frac{\partial \hat{\zeta}}{\partial V_1} \right)_{T,N_1,B_1} = \left( \frac{\partial \zeta}{\partial V_1} \right)_{T,N_1} + \frac{B_1^2}{18} \frac{\partial}{\partial V_1} \left( \frac{V_1}{V_2} \alpha \frac{\partial \mu_2}{\partial \rho_2} + \beta \frac{\partial \mu_1}{\partial \rho_1} \right) \tag{79}$$
3. \( H_1 = \text{const.} \)

Now for the used quantities as in [5] we have the expressions:

\[
\hat{p} = p_{H,N} = p - \frac{1}{2} H_1^2 \mu_s + \frac{H_1^2}{18} \left( \beta' \rho_1 \frac{\partial \mu_1}{\partial \rho_1} + \alpha' \rho_2 \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} \right) \tag{80}
\]

\[
\hat{\zeta} = \zeta_{H,V} = \zeta + \frac{H_1^2}{18} \left( \beta' \frac{\partial \mu_1}{\partial \rho_1} + \alpha' \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} \right) \tag{81}
\]

\[
\alpha' = \frac{\mu_1^2}{\mu_2^2} + 2 \quad ; \quad \beta' = \frac{2 \mu_1}{\mu_2} + 1 \tag{82}
\]

\[
S_1 (H_1 = \text{const.}) = S_{01} + \frac{1}{18} V_1 H_1^2 \left( -\beta' \frac{\partial \mu_1}{\partial T} + \alpha' \frac{\partial \mu_2}{\partial T} \right) \tag{83}
\]

Then for the fluctuation of the temperature one obtains:

\[
\overline{(\delta T)^2} = kT \frac{\partial S}{\partial T} \bigg|_{V_1, N_1, H_1} = kT \left\{ C_V + \frac{1}{18} TV_1 H_1^2 \left[ \beta' \frac{\partial^2 \mu_1}{\partial T^2} + \beta' \frac{\partial^2 \mu_1}{\partial T^2} - \frac{2}{\mu_2} \left( \frac{\partial \mu_1}{\partial T} \right)^2 - \frac{2 \mu_1^2}{\mu_2^2} \left( \frac{\partial \mu_2}{\partial T} \right)^2 + \frac{4 \mu_1 \mu_2}{\mu_2^2} \frac{\partial \mu_1}{\partial T} \frac{\partial \mu_2}{\partial T} \right] \right\}^{-1} \tag{84}
\]

Correspondingly for the fluctuation of \( V_1 \) and \( N_1 \) we find:

\[
\overline{(\delta V_1)^2} = -kT \frac{\partial \zeta}{\partial V_1} \bigg|_{T,V_1,H_1} \frac{\partial \zeta}{\partial N_1} \bigg|_{T,N_1,H_1} \left[ \frac{\partial \zeta}{\partial V_1} \bigg|_{T,V_1,H_1} \left( \frac{\partial \zeta}{\partial N_1} \bigg|_{T,N_1,H_1} + \left( \frac{\partial \zeta}{\partial V_1} \bigg|_{T,N_1,H_1} \right)^2 \right) \right] \tag{85}
\]

\[
\overline{(\delta N_1)^2} = kT \frac{\partial \zeta}{\partial N_1} \bigg|_{T,N_1,H_1} \left( \frac{\partial \zeta}{\partial V_1} \bigg|_{T,V_1,H_1} + \left( \frac{\partial \zeta}{\partial N_1} \bigg|_{T,V_1,H_1} \right)^2 \right) \tag{86}
\]

where

\[
\left( \frac{\partial \hat{p}}{\partial V_1} \right)_{T,N_1,H_1} = \left( \frac{\partial p}{\partial V_1} \right)_{T,N_1} + \frac{H_1^2}{18} \left[ \alpha' \rho_2 \frac{\partial \mu_2}{\partial \rho_2} + \beta' \rho_1 \frac{\partial \mu_1}{\partial \rho_1} + \frac{\partial}{\partial V_1} \left( \beta' \rho_1 \frac{\partial \mu_1}{\partial \rho_1} + \alpha' \rho_2 \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} \right) \right] \tag{87}
\]
\[
\left( \frac{\partial \tilde{p}}{\partial N_1} \right)_{T, V_1, H_1} = \left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} + \frac{H_1^2}{18} \frac{\partial}{\partial N_1} \left( \beta' \frac{\partial \mu_1}{\partial \rho_1} + \alpha' \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} \right) \quad (88)
\]

\[
\left( \frac{\partial \tilde{\zeta}}{\partial V_1} \right)_{T, N_1, H_1} = \left( \frac{\partial \zeta}{\partial V_1} \right)_{T, N_1} + \frac{H_1^2}{18} \frac{\partial}{\partial V_1} \left( \beta' \frac{\partial \mu_1}{\partial \rho_1} + \alpha' \frac{V_1}{V_2} \frac{\partial \mu_2}{\partial \rho_2} \right) \quad (89)
\]

It is interesting at this point to discuss the extreme case of infinite permeability for the sphere, when \( \frac{\mu_2}{\mu_1} \to 0 \). Then the field energy associated with the discrete system is stored exclusively in the outside of the system. In the alluded case

\[
\alpha = \frac{1}{\mu_2^2}; \quad \beta = 0; \quad H_1 = 0; \quad \lim_{\mu_1 \to \infty} B_1 = 3\mu_2 H_0; \quad \mu'_s = 9\mu_2 \quad (90)
\]

If \( V_1 \) and \( N_1 \) are constant for the temperature and the magnetic induction one obtains:

\[
\overline{(\delta T)^2} = kT^2 \left\{ C_V + \frac{1}{2} TV_1 H_0^2 \left[ \frac{\partial^2 \mu_2}{\partial T^2} - \frac{2}{\mu_2} \left( \frac{\partial \mu_2}{\partial T} \right)^2 \right] \right\}^{-1} \quad (91)
\]

\[
\overline{(\delta B_1)^2} = \frac{9kT \mu_2}{V_1} \quad (92)
\]

For \( B_1 = \text{const.} \), if one consider \( V_1 \ll V_2 \) the parameters \( \tilde{p} \) and \( \tilde{\zeta} \) have the following expressions

\[
\tilde{p} = p - \frac{\mu_2 H_0^2}{2} = p - \frac{1}{18} \frac{B_1^2}{\mu_2} \quad (93)
\]

\[
\tilde{\zeta} = \zeta \quad (94)
\]

given in \[5\].

The fluctuations of \( V_1 \) and \( N_1 \) are characterized by the dispersions:

\[
\overline{(\delta V_1)^2} = -kT \frac{\left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} + \left( \frac{\partial \mu_1}{\partial V_1} \right)_{T, N_1} + \frac{1}{2} H_1^2 \frac{\partial \mu_2}{\partial \rho_1} \frac{\partial \mu_2}{\partial \rho_2} \right)}{\left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} + \left( \frac{\partial \mu_1}{\partial V_1} \right)_{T, N_1} + \frac{1}{2} H_1^2 \frac{\partial \mu_2}{\partial \rho_1} \frac{\partial \mu_2}{\partial \rho_2} \right)^2} \quad (95)
\]

\[
\overline{(\delta N_1)^2} = kT \frac{\left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} + \left( \frac{\partial \mu_1}{\partial V_1} \right)_{T, N_1} + \frac{1}{2} H_1^2 \frac{\partial \mu_2}{\partial \rho_1} \frac{\partial \mu_2}{\partial \rho_2} \right)}{\left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} + \left( \frac{\partial \mu_1}{\partial V_1} \right)_{T, N_1} + \frac{1}{2} H_1^2 \frac{\partial \mu_2}{\partial \rho_1} \frac{\partial \mu_2}{\partial \rho_2} \right)^2} \quad (96)
\]
In the same extreme case for $H_1 = const.$ we obtain:

\[ \hat{p} = p - \frac{1}{2} \mu_2 H_0^2 \]  

(97)

\[ \hat{\zeta} = \zeta \]  

(98)

\[ (\delta V_1)^2 = -kT \left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} \left[ \left( \frac{\partial p}{\partial V_1} \right)_{T, N_1} - \frac{1}{2} H_0^2 \frac{\partial \mu_2}{\partial \rho_2} \right] + \left( \frac{\partial \zeta}{\partial V_1} \right)^2_{T, N_1} \]  

(99)

\[ (\delta N_1)^2 = kT \left( \frac{\partial \zeta}{\partial N_1} \right)_{T, V_1} \left[ \left( \frac{\partial p}{\partial V_1} \right)_{T, N_1} - \frac{1}{2} H_0^2 \frac{\partial \mu_2}{\partial \rho_2} \right] + \left( \frac{\partial \zeta}{\partial V_1} \right)^2_{T, N_1} \]  

(100)

It must be specified that in the alluded case ($\frac{\mu_2}{\mu_1} \rightarrow 0$) the fixed value of $H_1$ means $H_1 = 0$.

This subsection must be completed with the following specifications:

- The most important fact is that, in the case of discrete systems, the fluctuations of the intrinsic parameters of the systems depends on the magnetic permeability of the environment.

- For dielectric systems the evaluation of the fluctuations can be obtained by similar considerations, by means of the substitutions: $H \rightarrow E$, $B \rightarrow D$, $\mu \rightarrow \varepsilon$.

- As regard the here discussed dispersions $(\delta A)^2$ and the correlations $\delta A \delta B$ we have to note the same specification as the last one from the previous subsection.

IV. THERMODYNAMIC INEQUALITIES FOR SYSTEMS IN THE PRESENCE OF FIELDS

As it is known [9], the correlation coefficient constitute the elements of a non-negatively defined matrix. This fact is expressed by the inequalities

\[ \det |C_{ab}| > 0 \]  

(101)
\[
det \left| C_{ab}^{-1} \right| > 0 \quad (102)
\]

where \( C_{ab}^{-1} \) denote the inverse of the matrix \( C_{ab} \).

By using (101) and (102) it is possible to obtain a lot of thermodynamic inequalities. In order to exemplify the respective possibility, in the Table II we included some such inequalities which refer to a magnetizable continuum situated in a magnetoquasistatic field.

If one considers separately only two variables, \( X_1 \) and \( X_2 \), the formula (101) gives

\[
(\delta X_1)^2 (\delta X_2)^2 > (\delta X_1 \delta X_2)^2 \quad (103)
\]

This kind of relations, in our opinion [9-13], are completely similar with the well known Heisenberg’s (“uncertainty”) relations from quantum mechanics.

In the end of this section we illustrate the relation (103) for some concrete cases.

For a magnetizable continuum in a magnetoquasistatic field, when \( N \) and \( V \) are constant, from (103) we find the following inequalities:

\[
(\delta T)^2 (\delta B)^2 > 0 \quad (104)
\]

\[
(\delta T)^2 (\delta S)^2 > k^2 T^2 \quad (105)
\]

\[
(\delta B)^2 (\delta H)^2 > \frac{k^2 T^2}{V^2} \quad (106)
\]

\[
(\delta S)^2 (\delta B)^2 > k^2 T^2 H^2 \left( \frac{\partial \mu}{\partial T} \right)^2 \quad (107)
\]

For a sphere placed in an environment (the corresponding permeabilities being \( \mu_1 \) and \( \mu_2 \)), considering also \( N \) and \( V \) as constants, one obtains the relations:

\[
(\delta T)^2 (\delta B_1)^2 > 0 \quad (108)
\]

\[
(\delta T)^2 (\delta S_1)^2 > k^2 T^2 \quad (109)
\]

\[
(\delta B_1)^2 (\delta H_1)^2 > \frac{k^2 T^2 \mu_1^2}{V_1^2 \mu_s^2} \quad (110)
\]

\[
(\delta S_1)^2 (\delta B_1)^2 > \frac{1}{81} k^2 T^2 B_1^2 \mu_s^2 \left( \alpha \frac{\partial \mu_2}{\partial T} - \beta \frac{\partial \mu_1}{\partial T} \right)^2 \quad (111)
\]
V. SUMMARY, CONCLUSIONS AND CONNECTED REMARKS

The body of the present paper can be summarized and added with remarks as follows:

1. In the first section it was presented a phenomenological-theoretical approach of the fluctuations for the macroscopic parameters regarding the thermodynamic systems taken in the presence of the fields. We started with the expression of the differential of generalized internal energy. The respective start was complemented with the consideration that through the fluctuations the system passes in states which are in the neighbor of a thermodynamic equilibrium.

2. In the second section we particularized our approach to the case when the fields are of electromagnetic nature. We find that the estimators of fluctuations (i.e. dispersions and correlations) depend on the different field constraints.

3. The discrete systems are characterized by the fact that the fluctuations estimators are functions of both intrinsic quantities of the system and of the variables regarding the environment.

4. In the third section we presented a lot of thermodynamic inequalities which result from the fact that the correlations of the fluctuations constitute the elements of a non-negatively defined matrix. In their two-variable versions the respective inequalities are nothing but classical (non-quantum) analogues of the well known Heisenberg’s ("uncertainty") relations.

5. The last specifications from the subsection III.A and B reveal an interesting feature of the Boltzmann’s constant $k$ in the following sense:

   a) The quantities $\overline{(\delta A)^2}$ and $\delta A \delta B$ as fluctuation parameters are the estimators of the level of the stochasticity.
b) The formulas from the mentioned subsections shows the fact that the respective quantities appears as products of the Boltzmann’s constant $k$ with non-stochastic expressions.

c) Then it directly result the idea that $k$ can be regarded as a generic indicator of thermodynamic stochasticity.

6. At this point we wish to add the following connected remarks. The mentioned idea regarding $k$ was firstly promoted in the work [10] of one of us. In the same work was revealed the similarity of the Boltzmann’s constant $k$ with the Planck’s constant $\hbar$. The last one has the signification of generic indicator of quantum stochasticity. In the cases of classical (non-quantum) thermodynamical systems respectively of the quantum microparticles $k$ and $\hbar$ appear independently and singly. Then the respective systems can be regarded as endowed with an onefold stochasticity. In the case of the quantum statistical systems $k$ and $\hbar$ appear together in the expressions of the fluctuation parameters. This means that such systems are endowed with twofold stochasticity (for more details see [10]).

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1This preprint was deposited in CERN-Preprint Library and it can be accessed at the address [http://xxx.aps.org/quant-ph/0004013](http://xxx.aps.org/quant-ph/0004013)
### TABLES

| Independent variables | Inequalities |
|-----------------------|--------------|
| $S, V, N, B$          | $\frac{\partial (T, -\hat{p}, \hat{\zeta}, V H)}{\partial (S, V, N, B)} > 0$ |
| $T, V, N, B$          | $\frac{\partial (S, -\hat{p}, \hat{\zeta}, V H)}{\partial (T, V, N, B)} > 0$ |
| $T, V, N, H$          | $\det \begin{vmatrix} \frac{\partial S}{\partial X_a} \delta_{1a} & -\frac{\partial \hat{p}}{\partial X_a} \delta_{2b} & \frac{\partial \hat{\zeta}}{\partial X_a} \delta_{3b} & \frac{\partial (V H)}{\partial X_a} \delta_{4b} \end{vmatrix} > 0$ |
| $U, V, N, B$          | $\det \begin{vmatrix} \frac{\partial T}{\partial X_a} \frac{\partial S}{\partial X_b} - \frac{\partial \hat{p}}{\partial X_a} \delta_{2b} & \frac{\partial \hat{\zeta}}{\partial X_a} \delta_{3b} & \frac{\partial (V H)}{\partial X_a} \delta_{4b} \end{vmatrix} > 0$ |
| $\frac{1}{T}, V, N, B$ | $\det \begin{vmatrix} -T^2 \frac{\partial S}{\partial X_b} \delta_{1a} & -\frac{\partial \hat{p}}{\partial X_a} \delta_{2b} & \frac{\partial \hat{\zeta}}{\partial X_a} \delta_{3b} & \frac{\partial (V H)}{\partial X_a} \delta_{4b} \end{vmatrix} > 0$ |

**TABLE I.** New Thermodynamical Inequalities