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NOTE ON THE ROLE PLAYED BY CANONICAL QUANTITIES IN FLUCTUATION THEORY

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SUMMARY:

We look for a physical interpretation for the different terms appearing in the expressions of the second order fluctuations already developed in previous works. This is found to be possible by considering the system in question in close contact with appropriate surroundings of infinite extension. These surroundings must be such that some of the macroscopic constants of motion of the system remain unchanged, whereas the other ones (called canonical) are allowed to fluctuate freely around their former constant values. Other properties of the canonical quantities related to Fluctuation Theory are also considered.

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1. INTRODUCTION

In two previous papers [1,2] (hereafter quoted as I and II) we have developed an expression which can be used, under certain conditions, for calculating the second order fluctuation $\overline{\Delta Q \Delta Q'}$ where Q and Q' are macroscopic quantities depending on a system of non-interacting mixed gases. It has been proved in II that when one knows the values taken by p macroscopic constants of motion this expression can be written as a sum of $p+1$ terms, the first one depending only on the mean distribution of particles and the remaining p terms being related to the above-mentioned constants through an one-to-one physical correspondence. The particular case where the only constants of motion are the number of particles and the total energy was already discussed in I, where we have shown that the first term gives the fluctuation in the Grand Canonical Ensemble whereas the other two are respectively related to the interchange of particles and energy between the system and its surroundings. The aim of the present work will be to extend this interpretation to the more general case in which the initial conditions are given by any number of arbitrary physical quantities.

2. THE PHYSICAL MEANING OF THE FLUCTUATION EXPRESSION

Let us consider an assembly of s+1 weakly interacting gases, s of them composing the system and the remaining gas the surroundings; the union between system and surroundings being referred to as the total system. This separation in system and surroundings leads naturally to the classification of the physical quantities of the total system into two different groups; one containing the "closed" quantities which depend only on the distribution of particles in the system, and the other containing the "open" quantities which depend on the distribution of particles in the surroundings as well. Since all physical quantities Q_i considered here can be written as [2]

$$Q_i = \sum_{j=1}^{s+1} \int \phi_{ij}(x, p)\, \rho_j(x, p)\, dxdp \qquad i = 1, 2, \ldots \quad (1)$$

where $\rho_j(x, p)$ is the density of the particles of the j^{th} gas in the one-particle phase-space, we see that a quantity Q_i is closed if and only if $\phi_{i,s+1} = 0$, otherwise it will be open. When the surroundings are much larger than the system itself the open quantities will be called canonical, this being an natural extension of the idea of Canonical and Grand Canonical Ensembles. The Canonical Ensemble will be then described by a closed number of particles and a canonical energy, whereas in the Grand Canonical Ensemble both quantities will be canonical.

Let us now turn to the special case in which our knowledge about the total system in question is derived through the values taken by p macroscopic constants of motion of type (1), q of them being closed ($i = 1,2,\ldots, q$), and the remaining $p - q$ ($i = q + 1,\ldots p$) being canonical. According to II the second order fluctuation $\overline{\Delta Q_r\, \Delta Q_t}$ of two physical quantities of type (1) is given by:

$$\overline{\Delta Q_r\, \Delta Q_t} = \frac{C\begin{pmatrix}1,2,\ldots\, p, p+r\\ 1,2,\ldots\, p, p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots\, p\\ 1,2,\ldots\, p\end{pmatrix}}, \qquad (2)$$

where $C\begin{pmatrix}a, b, \ldots \\ a', b', \ldots\end{pmatrix}$ is the minor determinant formed by the lines a, b,... and columns a', b', ... of a certain matrix C, the elements of which are given below:

$$C_{ij} = \sum_{k=1}^{s+1} \int \frac{\phi_{ik}\,\phi_{jk}}{P_k}\, dxdp \qquad i,j = 1,2,\ldots p, p+r\ p+t, \qquad (3)$$

with $P_k^{-1} = \frac{\partial}{\partial u_k} \bar{\rho}_k(u_k(x,p)$ ($\bar{\rho}_k$ is the mean density) and the lines and columns relative to Q_r and Q_t being respectivelly labelled as $p+r$ and $p+t$.

Since the surroundings contain many more particles than the system, the function P_{s+1}^{-1} will have a large multiplicative factor which eventually goes to infinity as we increase the surroundings indefinitely. As the reader can easily verify from (1) and (3) some matrix elements will be affected in this process, others no, this depending on whether both subscripts i and j are or not related to canonical quantities. Those elements affected will increase indefinitely, the others remaining unchanged. Assuming Q_r and Q_t closed quantities, and calling respectively C and c the order of magnitude of the big and small matrix elements we get from (2):

$$\overline{\Delta Q_r\ \Delta Q_t} = \frac{C\begin{pmatrix}1,2,\ldots\ q, p+r \\ 1,2,\ldots\ q, p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots\ q \\ 1,2,\ldots\ q\end{pmatrix}} + O\ (c^2/C)\ , \qquad (4)$$

the last term on the right hand side going to zero as we increase the number of particles in the surroundings.

On the other hand, as we have already referred to in the Introduction, expression (2) can be written as a sum of p + 1 terms, this development being given by

$$\frac{C\begin{pmatrix}1,2,\dots p,p+r\\1,2,\dots p,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\dots p\\1,2,\dots p\end{pmatrix}} = C_{p+r,p+t} - \sum_{\ell=0}^{p-1} \frac{C\begin{pmatrix}1,2,\dots \ell,p+r\\1,2,\dots \ell,\ell+1\end{pmatrix} C\begin{pmatrix}1,2,\dots \ell,\ell+1\\1,2,\dots \ell,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\dots \ell\\1,2,\dots \ell\end{pmatrix} \quad C\begin{pmatrix}1,2,\dots \ell,\ell+1\\1,2,\dots \ell,\ell+1\end{pmatrix}} \qquad (5)$$

where we have adopted the convention $C\begin{pmatrix}1,2,\dots \ell\\1,2,\dots \ell\end{pmatrix}=1$ for $\ell = 0$. Since the last p terms of (5) can also be expressed as a condition of terms of type (3) in the form

$$\frac{\left[C\begin{pmatrix}1,2,\dots \ell,p+r\\1,2,\dots \ell,\ell+1\end{pmatrix}\Big/ C\begin{pmatrix}1,2,\dots \ell\\1,2,\dots \ell\end{pmatrix}\right]\left[C\begin{pmatrix}1,2,\dots \ell,\ell+1\\1,2,\dots \ell,p+t\end{pmatrix}\Big/ C\begin{pmatrix}1,2,\dots \ell\\1,2,\dots \ell\end{pmatrix}\right]}{\begin{pmatrix}1,2,\dots \ell,\ell+1\\1,2,\dots \ell,\ell+1\end{pmatrix}\Big/ C\begin{pmatrix}1,2,\dots \ell\\1,2,\dots \ell\end{pmatrix}},$$

we are naturally led to the following question: "Given a system composed by s gases with p closed constants of motion, will it be possible to find an appropriate surrounding for each term appearing in the development (5) of (1) (Q_r and Q_t closed quantities) such that the interpretation contained in (4) can be applied to all them ?" The answer to this question depends evidently on proving whether the matrix elements C_{ij} will or not be the same in both cases. In order to discuss this point we shall start from the set of equations which determine the mean densities $\overline{\rho}_j$. These equations are [2]

$$G'_j(\overline{\rho}_j) + \sum_{i=1}^{p} \gamma_i \, \phi_{ij} = 0 \qquad j = 1,2,\dots \qquad (6)$$

where G_j is a function depending on the Statistic obeyed by the particles in the j^{th} gas and the γ_i's are constant, the values of which can be obtained through the substitution into (1) of the functions $\bar{\rho}_j$ obtained from (6). Considering firstly the system composed by s gases with p closed constants of motion we get:

$$\sum_{j=1}^{s} \int \phi_{ij} \bar{\rho}_j \, dxdp = Q_i \qquad i = 1,2,\ldots p. \tag{7}$$

When we wish to consider the same system in contact with adequate surroundings such that the first q quantities are still closed and the last p-q are no longer constants (open), we must of course know how to extend these p-q quantities to the surround<u>d</u>ings; i.e.: how they will depend on the distribution of particles in the surroundings. For sake of generality we shall complete the initial conditions by introducing p-q arbitrary functions $\phi_{q+1,s+1}$, $\phi_{q+2,s+1}, \ldots \phi_{p,s+1}$. The new particle densities $\bar{\rho}_j'$ j = = 1,2,...s,s + 1 will now be obtained through s + 1 equations of type (6):

$$G_j'(\bar{\rho}_j') + \sum_{i=1}^{p} \gamma_i' \phi_{i,j} = 0 \qquad j = 1,2,\ldots s+1, \tag{8}$$

where the coefficients γ_i' must now satisfy

$$\sum_{j=1}^{s} \int \phi_{ij} \bar{\rho}_j' \, dxdp = Q_i \qquad i = 1,2,\ldots q,$$

$$\sum_{j=1}^{s+1} \int \phi_{ij} \bar{\rho}_j' \, dxdp = Q_i' \qquad i = q+1,\ldots p . \tag{9}$$

Since the first s equations in (8) are unchanged, $\bar{\rho}_j'$ and $\bar{\rho}_j$

for $j = 1,2,\ldots s$ will have the same structure, the only possible difference between them being those eventually sxisting between the γ_i and the γ_i'. However, by taking $Q_i' = Q_i + \int\phi_{is+1}\bar{\rho}_{s+1}'dxdp$, $i = q+1,\ldots p$ (i.e.: by taking the mean value of $\sum_{j=1}^{s}\int\phi_{ij}\rho_j'\,dxdp$ equal to its former constant value Q_i) we see that γ_i' and γ_i will be equal, hence $\bar{\rho}_j' = \bar{\rho}_j$ $j = 1,2,\ldots s$, and the matrix elements appearing in (3) will be equal to the corresponding ones in (4). Expression (5) can be then written as:

$$\overline{(\Delta Q_r \Delta Q_t)}_{c\ell} = \overline{(\Delta Q_r \Delta Q_t)}_{1,2,\ldots p} - \sum_{\ell=1}^{p} \frac{\overline{(\Delta Q_r \Delta Q_\ell)}_{\ell,\ell+1\ldots p}\overline{(\Delta Q_t \Delta Q_\ell)}_{\ell,\ell+1\ldots p}}{\overline{(\Delta Q_\ell^2)}_{\ell,\ell+1\ldots p}}, \tag{10}$$

where $c\ell$ means "closed" and the subscripts were employed to indicate the canonical quantities (with mean values equal to the constant values they had in the closed system). A point which deserves attention is the independence of (10) with the way in which the p-q quantities were extended to the surroundings. This means that the second order fluctuation appearing in (10) do not depend on the physical properties of the surrounding (e.g. type of statistics involved, mass of the particles, presence of external fields) so far as they are much larger than the system and the mean values of the "extended" quantities are unchanged. Another interesting point, already stressed in I, is the physical interpretation of the matrix elements C_{ij}. If we substitute the arbitrary quantities Q_r and Q_t by $\sum_{j=1}^{s}\int\phi_{ij}\rho_j dxdp$, i taking any value between 1 and p, we shall obtain from (5) and (10) that C_{ij} gives the value of $\overline{\Delta Q_i \Delta Q_j}$ when all quantities are canonical, a result which agrees with our previous discussions .

The recurrence relation

$$\frac{C\begin{pmatrix}1,2,\ldots p,p+r\\1,2,\ldots p,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots p\\1,2,\ldots p\end{pmatrix}} = \frac{C\begin{pmatrix}1,2,\ldots p-1,p+r\\1,2,\ldots p-1,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots p-1\\1,2,\ldots p-1\end{pmatrix}} - \frac{C\begin{pmatrix}1,2,\ldots p-1,p+r\\1,2,\ldots p-1,p\end{pmatrix}C\begin{pmatrix}1,2,\ldots p-1,p\\1,2,\ldots p-1,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots p-1\\1,2,\ldots p-1\end{pmatrix}C\begin{pmatrix}1,2,\ldots p-1,p\\1,2,\ldots p-1,p\end{pmatrix}}, \quad (11)$$

from which expression (5) was derived (see II) can also be interpreted with the help of our previous results. Defining the correlation between Q_r and Q_t by the usual expression $r(Q_r, Q_t) = \frac{\overline{\Delta Q_r\ \Delta Q_t}}{\left(\overline{\Delta Q_r^2}\ \overline{\Delta Q_t^2}\right)^{\frac{1}{2}}}$, we see that (11) can be written as:

$$(\overline{\Delta Q_r \Delta Q_t})_{c\ell} = (\overline{\Delta Q_r \Delta Q_t})_p - \sqrt{(\overline{\Delta Q_r^2})_p (\overline{\Delta Q_t^2})_p}\ r_p(Q_r, Q_p)\ r_p(Q_t, Q_p), \quad (12)$$

where the subscript p is again employed to indicate that the p^{th} quantity is canonical in the conditions already discussed. Expression (12) is also a generalization of particular results obtained in I.

An alternative from for expression may be obtained with the help of (2), (4) and (11). In fact, from (11) we get

$$\frac{C\begin{pmatrix}1,2,\ldots p,p+r\\1,2,\ldots p,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots p\\1,2,\ldots p\end{pmatrix}} =$$

$$= C_{p+r,p+t} \prod_{\ell=0}^{p-1} \left[1 - \frac{C\begin{pmatrix}1,2,\ldots \ell,p+r\\1,2,\ldots \ell,\ell+1\end{pmatrix}C\begin{pmatrix}1,2,\ldots \ell,\ell+1\\1,2,\ldots \ell,p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots \ell,p+r\\1,2,\ldots \ell,p+t\end{pmatrix}C\begin{pmatrix}1,2,\ldots \ell,\ell+1\\1,2,\ldots \ell,\ell+1\end{pmatrix}}\right], \quad (13)$$

which, with the help of (2) and (4) yields:

$$\overline{(\Delta Q_r \Delta Q_t)}_{cl} = \overline{(\Delta Q_r \Delta Q_t)}_{1,2,\ldots p} \prod_{\ell=1}^{p} \left[1 - \frac{r_{\ell\ldots p}(Q_r, Q_\ell)\, r_{\ell\ldots p}(Q_t, Q_\ell)}{r_{\ell\ldots p}(Q_r, Q_t)} \right]. \tag{14}$$

3. THE GEOMETRICAL MEANING OF THE CANONICAL QUANTITIES

It has been shown in II that the fluctuation expressions (5) have a definite geometrical meaning if we associate to each quantity Q_i a vector ψ_i in an infinite dimension vector space. These vectors are:

$$\psi_i = \left(\psi_{i1}\ \psi_{12}, \ldots\ \psi_{is}\right) = \left(\frac{\phi_{i1}}{P_1}, \frac{\phi_{i2}}{P_2}, \ldots \frac{\phi_{is}}{P_s}\right) \quad i = 1,2\ldots p, p+r, p+t, \tag{15}$$

with the usual definitions for the vector sum and scalar multiplication; the scalar product being given by

$$(\psi_i, \psi_j) = \sum_{k=1}^{s} \int P_k\ \psi_{ik}\ \psi_{jk}\ dxdp = C_{ij}\ . \tag{16}$$

Calling respectively $\psi'_\alpha(1,2,\ldots p)$ and $\psi''_\alpha(1,2,\ldots p)$ ($\alpha = p+r$ or $p+t$) the parallel and orthogonal component of ψ_α with respect to the subspace spanned by the vectors $\psi_1, \psi_2, \ldots \psi_p$, the following relation then holds:

$$\overline{\Delta Q_r\ \Delta Q_t} = \frac{C\begin{pmatrix}1,2,\ldots p, p+r\\1,2,\ldots p, p+t\end{pmatrix}}{C\begin{pmatrix}1,2,\ldots p\\1,2,\ldots p\end{pmatrix}} = \left(\psi''_{p+r}(1,2,\ldots p)\ \psi''_{p+t}(1,2,\ldots p)\right) \tag{17}$$

However, we have already shown that when all quantities are canonical the fluctuation expressions reduce to their first term only, according to (16) is equal to $\left(\psi_{p+r}, \psi_{p+t}\right)$. We then have

$$(\Delta Q_r\, \Delta Q_t)_{1,2,\ldots p} = (\psi_{p+r},\, \psi_{p+t}) \quad . \qquad (18)$$

Since $\left(\psi_{p+r},\, \psi_{p+t}\right) = \left(\psi'_{p+r}(1\ldots p)\ \psi'_{p+t}(1\ldots p)\right) + \left(\psi''_{p+r}(1\ldots p)\, \psi''_{p+t}(1\ldots)\right)$, by taking $Q_r = Q_t$ we see from (17) and (18) that the square of the component parallel to the subspace spanned by the canonical constants of motion must be zero for vectors representing closed quantities. That is, the closed quantities tend to be orthogonal to the open ones in the canonical limit. This can also be seen by direct inspec tion as the reader will easily verify.

Expression (17) can also be employed to interpret geometrically the different terms of (5). Using the symbol $\wedge$ to denote unitary vectors we may write:

$$\overline{\Delta Q_r^2} = \left(\psi''_{p+r}(1,2,\ldots p)\right)^2 = \left(\psi_{p+r}\right)^2 - \sum_{\ell=0}^{p-1}\left(\psi''_{p+r}(1,2,\ldots \ell),\, \hat{\psi}''_{\ell+1}(1,2\ldots \ell)\right)^2 \qquad (19)$$

which can be readily identified as a geometrical recurrence procedure to find the square of the component of a vector orthogonal to a given subspace.

Another interesting expression is obtained by setting $Q_r = Q_t$ in (17) and (18). Comparing the results obtained we get

$$\left(\overline{\Delta Q_r^2}\right)_{c\ell} = \left(\overline{\Delta Q_r^2}\right)_{1,2\ldots p} \quad \cos^2\left(\psi_{p+r}\ \ \hat{n}(1,2,\ldots p)\right) ,$$

where $\hat{n}(1,2,\ldots p)$ is the unit vector normal to the subspace of the constants of motion. From (20) and (14) we finally get:

$$\cos^2\left(\psi_{p+r}\ \ \hat{n}(1,2,\ldots p)\right) = \prod_{\ell=1}^{p}\left[1 - r^2_{\ell\ldots p}(Q_r,\, Q_\ell)\right] .$$

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