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.

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 $\Delta Q \Delta Q'$, where $Q$ and $Q'$ are macroscopic quantities depending on a system of noninteracting 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

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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 expressions.

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 considered here can be written as

\[ Q_i = \sum_{i=1}^{s+1} \int q_i(x, p) \varphi_i(x, p) \, dx \, dp, \quad i = 1, 2, \ldots, \]

where \( q_i(x, p) \) is the density of particles of the \( j \)-th gas in the one-particle phase-space, we see that a quantity \( Q_i \) is open if and only if \( \varphi_{i+1} \neq 0 \), otherwise it will be closed. When the surroundings are much larger than the system itself the open quantities will be called canonical, this being a 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 \( p-q \) \( (i = q+1, q+2, \ldots p) \) being canonical. According to the results obtained in II the second-order fluctuation \( \Delta Q_i \Delta Q_j \) of two physical quantities of type (1) is given by

\[ \Delta Q_i \Delta Q_j = \frac{C^{(s+1), \ldots, p, q+r}}{C^{(1,2,\ldots p)}}, \]

where \( C^{(s+1), \ldots, p, q+r} \) is the minor determinant formed by the lines \( a, b, \ldots \) and columns \( a', b', \ldots \) of a certain matrix \( C \), the elements of which are given below:

\[ C_{ij} = \sum_{k=1}^{s+1} \int \frac{q_i q_j \varphi_k}{P_k} \, dx \, dp, \quad i, j = 1, 2, \ldots, p, p+r, p+t, \]