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HYDRODYNAMIC FLUCTUATIONS IN A RELAXING MEDIUM

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An analysis of the spectral intensities of fluctuations in an isotropic medium in the presence of internal relaxation processes is presented. It is shown that in this case only fluctuations of the generalized coordinates can be determined, whereas fluctuations of the generalized forces cannot be found. One consequence of this is that the Rytov results[3-5] for a dispersive medium are erroneous. Density and entropy fluctuations which affect light scattering are calculated for such media.

1. INTRODUCTION

A large number of problems, and primarily the calculation of the intensity and of the spectral composition of molecular scattering of light, call for the calculations of different thermodynamic variables in the medium. Although the correlation theory of fluctuations was developed only for extensive variables[1,2], it was in fact used widely and successfully in the calculation of the fluctuations of arbitrary quantities, and discrepancies between the results of different authors[8] have been revealed as a result of the application of this theory to the case of media in which the relaxation times of the internal variables are comparable with the characteristic times of the hydrodynamic processes[3-7]. This raises the need for analyzing in greater detail the conditions for the applicability of the theory and the need for reviewing certain previously obtained erroneous results.

It will be shown below that fluctuations of all variables (both extensive and intensive) can be calculated if a complete thermodynamic description of the system is available, i.e., if the set of independent variables (generalized coordinates x_j) used in the theory makes it possible to specify uniquely any instantaneous state of the system. This presupposes, of course, that there exist two distinctly separated time scales, namely the relatively large characteristic times of the processes of interest to us and the very short relaxation times of the rapid processes which we shall neglect. We are thus dealing with thermodynamic fluctuations, i.e., with that part of the fluctuation spectrum which is limited to sufficiently low frequencies of the macroscopic processes.

The situation is different if one uses the incomplete and abbreviated description, i.e., if certain variables such as the internal parameters ξ of Mandel'shtam and Leontovich[9] are not considered in explicit form, and their existence is taken into account implicitly via the frequency dispersion of the thermodynamic coefficients. It will be shown that for this case it is possible to find only the fluctuations of the generalized coordinates, but not the fluctuations of the generalized forces. It follows therefore, in particular, that the results obtained by Rytov[3-5], who calculated the fluctuations of the generalized coordinates (the density ρ, the entropy S, etc.) in terms of the fluctuations of the generalized forces, such as the pressure p and the temperature T, are fully applicable to the case of media without dispersion, but are in error for media with dispersion and call for revision. In this paper we calculate the fluctuations of the hydrodynamic variables ρ and S, which influence the scattering of light, and which can be determined in general form for any dispersion law. As to the fluctuations of p, T, ..., their calculation calls for the construction of a complete theory for concrete models with one, two, etc., parameters ξ.

2. COMPLETE AND INCOMPLETE THERMODYNAMIC DESCRIPTION

We postulate that a complete thermodynamic description of the system is possible in principle, i.e., we assume that any instantaneous state can be regarded as a state of incomplete thermodynamic equilibrium, defined by specifying a limited number of generalized coordinates x_j. In the thermodynamics of irreversible processes, such a state is set in correspondence[10] with the state of total equilibrium, in which the same values x_j are fixed with the aid of suitable external forces F_j. For the equilibrium change of x_j, we can write the system energy increment in the form $dU = F_j dx_j$.[1] The internal forces f_j are introduced, starting from the assumption that equilibrium is insured by compensation of F_j and f_j:

$$f_j = -F_j = -\partial U / \partial x_j. \tag{1}$$

The completeness of the description means, in particular, that the f_j are uniquely defined by specifying x_j, i.e., equations of state hold (they are called instantaneous or non-equilibrium). For small deviations from complete equilibrium we have[2]

$$\delta f_j = -B_{jk}\delta x_k, \quad \delta x_j = -b_{jk}\delta f_k. \tag{2}$$

The process of the change of the state is connected with the presence of uncompensated forces, and can be described by the "equations of motion"

$$M_{jk}x_k = F_j + f_j$$

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[1] We use the conventional summation over latin indices; there will be no summation over greek indices.

[2] In order to simplify the formulas, we shall henceforth omit the symbol δ where possible.

or

$$x_j = \int_{-\infty}^{t} \mu_{jk}(t-t')\,[F_k(t') + f_k(t')]\,dt' \equiv m_{jk}(F_k + f_k), \qquad (3)$$

where the operators M_{jk} are polynomials of d/dt without free terms. In this form, we can write both the Onsager equation and the hydrodynamic equations. Bearing this in mind, we shall not limit the order of the operators M_{jk}. In the most general case it is possible to define M_{jk} as m_{jk}^{-1}.

Actually, the equations describing the system are not always specified in the form (2) and (3); usually one knows the complete system of hydrodynamic equations without the external forces ($F_j = 0$), and the internal forces are not always defined in explicit form. However, if we introduce the forces f_j with the aid of the expression for the energy and the definition (1), then the system can be broken up by purely algebraic transformations into two groups, namely the equations of state (2), which do not contain the time, and equations of motion of the type (3). The possibility of such a transformation is a criterion of the completeness of the description. The external forces are introduced then by simply replacing f_j with $f_j + F_j$ in the equations of motion.

In the formulation of the equations we have assumed that the separation of the parameters into "coordinates" x_j and "forces" f_j can be carried out uniquely on the basis of their physical meaning, and also by starting from the non-linearized energy equation $\Delta U = -f_j \Delta x_j$. It is important, however, that in the case of the complete description, such a separation is not essential: the system (2)—(3) can be formally rewritten with the aid of a linear transformation in such a way that f_j are coordinates and x_j are forces[3]

$$\begin{aligned} b_{jm}M_{ml}b_{lk}f_k = x_j - b_{jn}F_n \equiv x_j + X_j;\\ x_j = -b_{jk}f_k. \end{aligned} \qquad (4)$$

The formal rule for introducing the "forces" X_j remains in force, although their physical meaning becomes unclear.

To change over to an incomplete description, we break up all the variables x_j into two groups, x_a, x_b, ..., x_h are the known variables, and x_p, x_q, ..., are the unknown internal parameters; the indices i, j, ..., n will be used, as before, to denote all the variables. Eliminating from (2) and (3) all the variables x_p, ..., f_p, ..., we obtain

$$f_a = -\tilde{B}_{ab}x_b, \qquad \tilde{B}_{ab} = B_{ab} + B_{ap}(B' + M')_{pq}{}^{-1}(B + M)_{qb}, \qquad (5)$$

$$\tilde{M}_{ab}x_b = f_a + F_a, \qquad \tilde{M}_{ab} = M_{ab} + M_{ap}(B' + M')_{pq}{}^{-1}(B + M)_{qb} \qquad (6)$$

(the prime denotes a submatrix with indices p, q, ...). Besides B_{ab}, we shall also use $\tilde{b}_{ab} = \tilde{B}_{ab}^{-1}$.

In the elimination of x_p and f_p we have assumed that $F_p = 0$. Usually this assumption is not stipulated especially, since a homogeneous system without external forces is cancelled out. Then, however, we lose the possibility of formally separating the system into the equations of state and the equations of motion, and both become differential. Fortunately, the internal variables x_p are frequently separated in the equations of motion, $M_{ap} = 0$ (at least in the case when x_p are relaxation variables, which can always be redefined in this manner[9]), and therefore Eqs. (6) and (3) coincide. Then the external forces F_p can be introduced on the basis of the physical meaning of the equations of motion.

The system (5)—(6) can also be rewritten in the form (4):

$$\tilde{b}_{ac}\tilde{M}_{cd}\tilde{b}_{db}f_b = x_a - \tilde{b}_{ae}F_e \equiv x_a + \tilde{X}_a, \;\; x_a = -\tilde{b}_{ab}f_b. \qquad (7)$$

A similar system can be obtained by eliminating x_p and f_p from (4) and assuming that $X_p = 0$, but this system will differ from (7), since $\tilde{X}_a \neq X_a$. This is natural, inasmuch as the conditions $F_p = 0$ and $X_p = 0$ are not equivalent. The condition $F_p = 0$ is a physical requirement denoting the impossibility of controlling the unknown parameters of the system, whereas $X_p = -b_{pa}F_a - b_{pq}F_q = 0$ specifies that the real external forces, are subject to a certain connection for whose existence of which there are no physical reasons whatever. The choice between the conditions $F_p = 0$ and $X_p = 0$ is determined by which of the variables x_j and f_j are actually coordinates and which are forces. Thus, the formal symmetry of the equations relative to the choice of the independent variables is lost when the incomplete description is used. We emphasize once more that this difficulty arises only for an inhomogeneous system of equations.

3. CALCULATION OF THE FLUCTUATIONS IN THE CASE OF THE COMPLETE AND INCOMPLETE DESCRIPTION

Complete description. The thermodynamic theory[11] yields the following formulas for the total intensities of the fluctuations:

$$\begin{aligned} \langle x_\alpha x_\beta\rangle = kTb_{\alpha\beta}, \qquad \langle f_\alpha f_\beta\rangle = kTB_{\alpha\beta},\\ \langle f_\alpha x_\beta\rangle = -kT\delta_{\alpha\beta}. \end{aligned} \qquad (8)$$

The time behavior of the fluctuations is described by the time correlation function

$$\varphi_{\alpha\beta}(t) = \langle x_\alpha(t')x_\beta(t'+t)\rangle, \qquad (9)$$

the calculation of which[12,1,2,13] is actually equivalent to a solution of the macroscopic problem of the free motion of a system with initial conditions

$$x_\alpha|_{t\leqslant 0} = x_\alpha{}^0 = \sqrt{\langle x_\alpha{}^2\rangle} = \sqrt{kTb_{\alpha\alpha}}, \qquad (10)$$

$$x_j|_{t\leqslant 0} = x_j{}^0 = \frac{\langle x_j x_\alpha\rangle}{\sqrt{\langle x_\alpha{}^2\rangle}} = x_\alpha{}^0\frac{b_{j\alpha}}{b_{\alpha\alpha}}, \qquad (11)$$

corresponding to external forces that are constant when $t \leq 0$

$$F_j{}^0 = -f_j{}^0 = \frac{x_\alpha{}^0}{b_{\alpha\alpha}}\delta_{j\alpha}. \qquad (12)$$

The solution, which is in the form $x_\beta(t) = x_j^0\psi_{\beta j}(t)$, is multiplied by x_α^0 and we obtain $\varphi_{\alpha\beta}(t)$ for $t > 0$. For $t < 0$ we have $\varphi_{\alpha\beta}(t) = \varphi_{\beta\alpha}(-t) = \pm\varphi_{\alpha\beta}(-t)$. The actual averaging is carried out, of course, after the calculation of $x_\alpha^0 x_\beta(t)$, but this does not change the final result.

After calculating $\varphi_{\alpha\beta}(t)$ we can find the spectral intensities of the fluctuations:

$$\langle x_\alpha x_\beta\rangle_\omega = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \varphi_{\alpha\beta}(t)\, e^{-i\omega t}\, dt. \tag{13}$$

Another equivalent method of calculating $\langle x_\alpha x_\beta\rangle_\omega$ is provided by the fluctuation-dissipation theorem (FDT), which expresses the spectral intensities of the fluctuations in terms of the susceptibilities $p_{\alpha\beta}(i\omega)$ relative to sinusoidal external forces. By specifying $F_k \sim e^{i\omega t}$, one obtains the solution of the system (2)–(3) in the form

$$x_j = p_{jk}(i\omega) F_k, \tag{14}$$

where $p_{jk} = (M + B)^{-1}_{jk}$, and then

$$\langle x_\alpha x_\beta\rangle_\omega = \frac{kT}{2\pi i\omega}\left(p_{\beta\alpha}{}^* - p_{\alpha\beta}\right). \tag{15}$$

Inasmuch as in the thermodynamic description of the system the instantaneous values of the internal forces are assumed to be unique functions of the coordinates, it is easy to get from (15)

$$\langle f_\alpha f_\beta\rangle_\omega = B_{\alpha j} B_{\beta k} \langle x_j x_k\rangle_\omega \equiv \frac{kT}{2\pi i\omega}\left(P_{\beta\alpha}{}^* - P_{\alpha\beta}\right). \tag{16}$$

It is clear that any of the described calculation methods is applicable to the system (4), and the same results (16) and (15) are obtained for $\langle f_\alpha f_\beta\rangle_\omega$ and $\langle x_\alpha x_\beta\rangle_\omega$, with $P_{\alpha\beta}$ defined as the "susceptibility" $f_j = P_{jk}(i\omega) X_k$.

The fluctuations are sometimes regarded as the result of the action of fictitious extraneous forces, the spectrum of which, in accordance with (15) and (14), is given by

$$\langle F_\alpha F_\beta\rangle_\omega = \frac{kT}{2\pi i\omega}\left[(M+B)_{\alpha\beta} - (M+B)_{\beta\alpha}{}^*\right] = \frac{kT}{2\pi i\omega}\left(M_{\alpha\beta} - M_{\beta\alpha}{}^*\right). \tag{17}$$

Incomplete description. The minimal work of the equilibrium transition $x_a^0 \to x_a$ at $F_p = 0$ is $R = -)1/2)f_a x_a$. By employing the usual procedure[11], we obtain for the fluctuations of the known variables formulas having the same form (8), but the coefficients B_{ab} and b_{ab} are replaced by

$$B_{ab}^0 = -\left(\frac{\partial f_a}{\partial x_b}\right)_{x_{c\neq b},\, f_p} = B_{ab} - \left(\frac{\partial f_a}{\partial x_r}\right)_{x_{j\neq r}} \left(\frac{\partial x_r}{\partial x_b}\right)_{x_{c\neq b},\, f_p};$$
$$b_{ab}^0 = -\left(\frac{\partial x_a}{\partial f_b}\right)_{f_{j\neq b}} = b_{ab}. \tag{18}$$

Thus, in the case of the incomplete description one obtains correct formulas for the fluctuations of the known coordinates, but the fluctuations of the forces are calculated incorrectly. The reason is simple: $b_{jk} = -(\partial x_j/\partial f_k)^i_{j\neq k}$ are coefficients that are at equilibrium with respect to changes of all the variables $x_{i\neq j,k}$, particularly with respect to changes of the unknown x_p. To the contrary, $B_{jk} = -(\partial f_j/\partial x_k)_{x_{i\neq k}}$ have the meaning of instantaneous moduli. In the case of the incomplete description, on the other hand, the usual thermodynamic methods make it possible to determine only the equilibrium moduli B^0_{ab}. Thus, for example, for fluctuations of the volume and of the pressure in a gas in which a chemical reaction is possible, formulas (8) yield

$$\langle \delta V^2\rangle = -kT\left(\frac{\partial V}{\partial p}\right)_\mu; \quad \langle \delta p^2\rangle = -kT\left(\frac{\partial p}{\partial V}\right)_n,$$

where n is the degree of completeness of the reaction, μ is the affinity (the difference between the chemical potentials of the reacting substances). To determine $(\partial p/\partial V)_n$, it is necessary to fix in with the aid of an external force F_n (of type μ), whereas $(\partial V/\partial p)_\mu$ is determined without an external action. If nothing is unknown concerning the reaction, then the usual theory yields $\langle \delta V^2\rangle = -kT(dV/\partial p)$; $\langle \delta p^2\rangle = -kT(dP/\partial V)$, and since it is impossible to introduce F_n, both the derivatives will be defined at a constant μ.

We have started here from the assumption that formulas (8), which are obtained in the case of the complete description, are true. Munster[14] raised objections to these formulas for $\langle f_\alpha f_\beta\rangle$ and $\langle f_\alpha x_\beta\rangle$, on the basis of the fact that simultaneous fluctuations of the conjugate variables x_α and f_α are impossible, since an ensemble in which neither x_α nor f_α is fixed is not defined. Obviously, however, a thermodynamic system in which x_α and f_α are specified only in the mean can exist (for example, p and V in a gas under a heavy piston). Munster considers it possible to calculate the fluctuations of f_α only at fixed x_α. Particular problems of this kind, of course, can also be solved with the aid of the general theory[11]. For the fluctuations of f_α and f_β at fixed x_α and x_β we have

$$\langle f_\alpha f_\beta\rangle = \langle x_j x_k\rangle \left(\frac{\partial f_\alpha}{\partial x_j}\right)_{x_{i\neq j}} \left(\frac{\partial f_\beta}{\partial x_k}\right)_{x_{i\neq k}} = -kT\left(\frac{\partial x_j}{\partial f_k}\right)_{x_\alpha,\, x_\beta,\, f_{i\neq\alpha,\,\beta,\,k}}$$
$$\times \left(\frac{\partial f_k}{\partial x_\beta}\right)_{x_{i\neq\beta}} \left(\frac{\partial f_\alpha}{\partial x_j}\right)_{x_{i\neq j}} = kT\left(\frac{\partial x_j}{\partial x_\beta}\right)_{f_{i\neq\alpha,\,\beta},\, x_\alpha} \left(\frac{\partial f_\alpha}{\partial x_j}\right)_{x_{i\neq j}}$$
$$= kT\left\{\left(\frac{\partial f_\alpha}{\partial x_\beta}\right)_{x_\alpha,\, f_{i\neq\alpha,\,\beta}} - \left(\frac{\partial f_\alpha}{\partial x_\beta}\right)_{x_{i\neq\beta}}\right\} = kT\left(B^\infty_{\alpha\beta} - B^0_{\alpha\beta}\right), \tag{19}$$

where j, k ≠ α, β. In (19) there is introduced the symbol B in place of the previous B, in order to emphasize that this is the instantaneous modulus, and B^0 is the equilibrium modulus with respect to changes of all the x_i.

Munster's result for fluctuations of the pressure in an ideal gas, or the more general result of Komarov and Fisher[15] for an arbitrary liquid, is obtained from this directly, since for a canonical ensemble we have

$$B_{VV}{}^\infty \equiv -\left(\frac{\partial p}{\partial V}\right)_S, \quad B_{VV}{}^0 \equiv -\left(\frac{\partial p}{\partial V}\right)_T.$$

It must be emphasized that in such a thermodynamic calculation of $\langle \delta p^2\rangle$ at V = const it is assumed that in the system there occur simultaneously fluctuations of other pairwise-conjugate variables (in this case S and T, with δS and $\delta T = (\partial T/\partial S)_V \delta S$ being functionally related). Thus, Munster's result is obtained from a calculation based on foregoing his initial assumption that such fluctuations are impossible.

Munster used the discrepancy between formulas (8) and (19) for a more extensive criticism of the thermodynamic theory of fluctuations[11], expressing doubts concerning the possibility in principle of rationally determining the fluctuations of intense variables. We see here that his example has no bearing at all on this problem. The thermodynamic theory is internally closed and admits of the calculation of fluctuations of all the variables, since they are uniquely connected by the equations of state. This is true, however, only in the case of a complete description of the system.

The spectral intensities of the fluctuations in the case of an incomplete description are calculated by starting from the system (5) and (6) by any of the two described methods. The results obtained for $\varphi_{ab}(t)$ and $\langle x_a x_b\rangle_\omega$ are the same as before. Indeed, the use on going from (2) and (3) to (5) and (6) the condition $F_p = 0$ alters neither the initial conditions (12) nor the calculations of the susceptibilities that relate x_a with F_b. Only the second equation in formula (17) is incorrect, since now $p_{ab}^{-1} \neq M_{ab} + \tilde{B}_{ab}$.

A certain difficulty may be raised by the calculation of $\varphi_{ab}(t)$ and $\langle x_\alpha x_\beta\rangle_\omega$ by solving the initial-condition problem. The latter are specified above in an inconvenient form, namely for the segment $-\infty < t \leq 0$ and not for the instant $t = 0$. In the case of the complete description, the continuity conditions require that the derivatives $\dot{x}_j$, $\ddot{x}_j$, etc., up to an order equal to the order of the operator M_{kj}, vanish at $t = 0$. In the incomplete description, the order of the system is increased, and it is necessary to specify initial values of the higher derivatives of x_a, x_b, ... It is possible to use instead the conditions (12) for f_a, f_b, ... as conditions supplementing (10) and (11). This procedure was used by Mountain[6,7]. It is easy to see, however, that this procedure, in spite of[8], is perfectly valid although not universally usable (the number of conditions (12) may not be sufficient).

Thus, not only the integral but also the spectral intensities of the fluctuations of the generalized coordinates x_a can be correctly calculated in the incomplete description of the system, when the moduli B_{ab} are replaced by the corresponding operators B_{ab}. This circumstance was apparently first pointed out by Rytov[3]. He, however, attempted to use the FDT for the calculation of the fluctuations of the generalized forces f_a. This problem, in the case of the incomplete description, cannot be solved. Indeed,

$$\begin{aligned}\langle f_a f_b\rangle_\omega &= B_{ac}B_{bd}\langle x_c x_d\rangle_\omega + (B_{ap}B_{bc}\\ &\pm B_{ac}B_{bp})\langle x_c x_p\rangle_\omega + B_{ap}B_{bq}\langle x_p x_q\rangle_\omega\\ &\neq B_{ac}B_{bd}\langle x_c x_d\rangle_\omega \neq B_{ac}{}^0 B_{bd}{}^0\langle x_c x_d\rangle_\omega \neq \tilde{B}_{ac}\tilde{B}_{bd}{}^*\langle x_c x_d\rangle_\omega.\end{aligned}$$

The first of the incorrect formulas does not take in general any account at all of the fluctuations of x_p, while the other two represent x_p as single-valued functions of x_a, whereas actually the fluctuations of x_p are partially independent of x_a and of course are unknown in the incomplete description.

Rytov started from the system (7) and employed the FDT in the form

$$\langle f_a f_b\rangle_\omega = \frac{kT}{2\pi i\omega}(\tilde{P}_{ba}{}^* - \tilde{P}_{ab}), \tag{20}$$

where $\tilde{P}_{ab}(i\omega)$ is the susceptibility matrix ($f_a = \tilde{P}_{ab}X_b$), and is the inverse of the matrix

$$P_{ab}{}^{-1} = (\tilde{b}_{ac}M_{cd}\tilde{b}_{db} + \tilde{b}_{ab}). \tag{21}$$

It is obvious that the result given by (20) does not coincide with (16), since $\tilde{P}_{ab} \neq P_{ab}$. The incorrectness of formula (20) can also be verified by integrating it with respect to the frequencies (the method of integration is indicated in Rytov's paper[3]; from now on it must be recognized that by virtue of the causality principle the functions $\tilde{b}_{ab}(i\omega)$, $\tilde{B}_{ab}(i\omega)$, $\tilde{P}_{ab}(i\omega)$, etc., cannot have poles at $\mathrm{Im}\,\omega < 0$[11], and in addition $M_{ab}(0) = 0$ and $M_{ab}(\infty) = \infty$). Integration yields

$$\langle f_a f_b\rangle = kT[\tilde{P}_{ab}(0) - \tilde{P}_{ab}(\infty)] = kTB_{ab}{}^0. \tag{22}$$

This should indeed be the case, since the FDT for $\langle f_\alpha f_\beta\rangle$ is equivalent, in this formulation, to the problem with initial conditions

$$f_\alpha|_{t\leqslant 0} = \sqrt{kTB_{\alpha\alpha}{}^0};\quad f_b|_{t\leqslant 0} = \frac{B_{b\alpha}{}^0}{B_{\alpha\alpha}{}^0} f_\alpha|_{t\leqslant 0}.$$

Rytov did not notice this error, since he considered the case of weak dispersion, when $B^0_{ab} \approx B_{ab}$.

One might hope that because of the cancellation of errors formula (20) will make it possible to obtain correct formulas for the fluctuations of the coordinates. This, however, is not true:

$$\begin{aligned}\frac{2\pi i\omega}{kT}\langle x_\alpha x_\beta\rangle_\omega &= \tilde{b}_{\alpha a}\tilde{b}_{\beta b}{}^*(\tilde{P}_{ba}{}^* - \tilde{P}_{ab})\\ &= \tilde{b}_{\alpha a}\tilde{b}_{\beta b}{}^*(\tilde{B}_{bc}{}^* p_{cd}{}^* \tilde{B}_{da}{}^* - \tilde{B}_{ac}p_{cd}\tilde{B}_{db})\\ &= \tilde{b}_{\alpha a}\tilde{B}_{ad}{}^* p_{\beta d}{}^* - \tilde{b}_{\beta a}{}^*\tilde{B}_{ad}p_{\alpha d} \neq p_{\beta\alpha}{}^* - p_{\alpha\beta},\end{aligned} \tag{23}$$

if the matrices $\tilde{B}_{ab}$ and $\tilde{b}_{ab}$ are not real. For simplicity we have confined ourselves here to the case of symmetrical matrices $\tilde{B}$ and $\tilde{b}$. Integration of (23) with respect to the frequencies leads to

$$\begin{aligned}\langle x_\alpha x_\beta\rangle = kT\Big\{ b_{\alpha\beta} + \sum_k \frac{\tilde{B}_{ad}(-s_k)}{s_k}\\ \times[p_{\beta d}(-s_k)\,\mathrm{Res}\,\tilde{b}_{\alpha a}(s_k) - p_{\alpha d}(-s_k)\,\mathrm{Res}\,\tilde{b}_{\beta a}(s_k)]\Big\}\end{aligned} \tag{24}$$

where $i\omega_k = s_k$ are the poles of the functions $\tilde{b}$. In a particular case when $b_{\alpha\beta} = 0$, the thermodynamic formulas predict independent fluctuations of x_α and x_β, whereas (24) yields $\langle x_\alpha x_\beta\rangle \neq 0$. This is precisely the result obtained by Rytov[3], who obtained in a relaxing medium a correlation between the fluctuations of the density at different points of the medium. A correct calculation, of course, cannot yield such a result for the complete (spectrally unresolved) fluctuations, if one does not assume from the very outset that the equations of state have a nonlocal character[16].

4. FLUCTUATIONS OF HYDRODYNAMIC VARIABLES

As the generalized coordinates x_i, which give the complete description of the single-component solid medium in the absence of relaxation, we can choose, for example, the values of the components of the displacement vector $\mathbf{u}$ for different volume elements dV and the increments of the entropy $\rho\delta S dV$ (S—entropy per unit mass). The conjugate internal forces will then be the quantities $\mathbf{f}dV$ and $-\delta T$, where $\mathbf{f}$ is the volume density of the elastic forces. The system of linearized hydrodynamic equations, separated into equations of state and equations of motion, takes the form

$$\rho\frac{\partial^2\mathbf{u}}{\partial t^2} - \left(\eta_\infty'' + \frac{1}{3}\eta_\infty'\right)\mathrm{grad}\,\mathrm{div}\frac{\partial\mathbf{u}}{\partial t} - \eta_\infty'\nabla^2\frac{\partial\mathbf{u}}{\partial t} = \mathbf{f}, \tag{25}$$

$$\rho T\frac{\partial S}{\partial t} = \varkappa\nabla^2 T, \tag{26}$$

$$\delta S = \frac{C_V}{T}\delta T + \frac{p_T}{\rho}\mathrm{div}\,\mathbf{u}, \tag{27}$$

$$\mathbf{f} = (K + {}^1\!/_3\mu)\,\mathrm{grad}\,\mathrm{div}\,\mathbf{u} + \mu\nabla^2\mathbf{u} - P_T\,\mathrm{grad}\,T. \tag{28}$$

Here K (the isothermal volume modulus), u (the shear modulus), C_V (the specific heat), and p_T (the thermal coefficient of pressure) can be replaced in a relaxing medium by the operators $\tilde{K}$, $\tilde{u}$, $\tilde{C}_V$, and $\tilde{p}_T$, which can be complex functions of the frequency in sinusoidal processes. The coefficients of the shear and bulk viscosities η'_∞ and η''_∞ pertain to rapid processes ($\omega \to \infty$); in slower processes, it is necessary to add to them the imaginary parts of the dynamic moduli $\tilde{K}(i\omega)$ and $\tilde{u}(i\omega)$. The form of the system (25)—(28) differs from the usual form in that it does not contain the additional coordinates and forces, such as the strain and elastic-stress tensors, the heat-flux vector, and the increment of the specific volume (density). Accordingly, the system does not contain the additional equations of state relating these variables with u, f, δS and δT; if these were to be retained, this would not influence in any manner the method of introducing external forces or the further calculations. Equations (27) and (28) have not been solved with respect to f and δT, as in the system (2), but this of course is of no significance.

By way of external forces, it is necessary to include in the system (25)—(28) the field of the volume forces with density F and the field of the fictitious extraneous "temperatures" ⊛, replacing f and −δT in (25) and (26) by f + F and ⊛ − δT. It is then necessary to expand all the variables into a spatial Fourier spectrum $u = \Sigma u_k \exp(ik \cdot r)$. After calculating the susceptibilities, it is then possible to find the spectral (ω, k)-intensities of the fluctuations of S and u. The latter make it possible to calculate the fluctuations of the quantities of greater physical interest, such as the strains $u_{ik} = (1/2)(\partial u_i/\partial x_k + \partial u_k/\partial x_i)$, and particularly the volume deformation $u_{jj} = -\delta\rho/\rho$. These calculations are analogous to those performed by Rytov[1]. They yield

$$\langle \delta\rho^2 \rangle_{\omega \mathbf{k}} = -\frac{\rho k T}{(2\pi)^4 i\omega} \left(\frac{k^2}{-\rho\omega^2 + k^2 \tilde{M}} - \text{c.c.} \right), \tag{29}$$

$$\rho^2 \langle \delta S^2 \rangle_{\omega \mathbf{k}} = -\frac{\rho k T}{(2\pi)^4 i\omega} \left[\frac{k^2 \varkappa \tilde{C}_V}{(i\omega\rho\tilde{C}_V + k^2\varkappa) T} + \frac{k^6 \varkappa^2 \tilde{p}_T{}^2}{\rho (i\omega\rho\tilde{C}_V + k^2\varkappa)(-\rho\omega^2 + k^2\tilde{M})} - \text{c.c.} \right], \tag{30}$$

$$\rho \langle \delta S \delta\rho \rangle_{\omega \mathbf{k}} = -\frac{\rho k T}{(2\pi)^4 i\omega} \left[\frac{k^4 \varkappa \tilde{p}_T}{(i\omega\rho\tilde{C}_V + k^2\varkappa)(-\rho\omega^2 + k^2\tilde{M})} - \text{c.c.} \right], \tag{31}$$

when

$$\tilde{M} = \tilde{K} + \frac{4}{3}\tilde{\mu} + i\omega \left(\frac{4}{3}\eta_\infty{}' + \eta_\infty{}'' \right) + \frac{i\omega T \tilde{p}_T{}^2}{i\omega\rho\tilde{C}_V + k^2\varkappa}. \tag{32}$$

Integration of these expressions with respect to ω and k yields for the spatial-correlation functions

$$\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle = \frac{kT\rho^2}{(\tilde{K} + {}^4/_3\tilde{\mu})_0} \delta(\mathbf{r} - \mathbf{r}');$$

$$\langle \delta S(\mathbf{r}) \delta S(\mathbf{r}') \rangle = \frac{k}{\rho} \left[\frac{{}^4/_3\tilde{\mu}\tilde{C}_V + \tilde{K}\tilde{C}_p}{\tilde{K} + {}^4/_3\tilde{\mu}} \right]_0 \delta(\mathbf{r} - \mathbf{r}') \tag{33}$$

etc. If we integrate (93) over an arbitrary volume V which is large compared with dV, then we obtain the well known expressions for the fluctuations of the thermodynamic quantities:

$$\langle \delta V^2 \rangle = \frac{VkT}{(\tilde{K} + {}^4/_3\tilde{\mu})_0}; \quad \langle \delta S^2 \rangle = Vk \left[\frac{{}^4/_3\tilde{\mu}\tilde{C}_V + \tilde{K}\tilde{C}_p}{\tilde{K} + {}^4/_3\tilde{\mu}} \right]_0;$$

$$\langle \delta V \delta S \rangle = VkT \left[\frac{\tilde{p}_T}{\tilde{K} + {}^4/_3\tilde{\mu}} \right]_0.$$

If there is no relaxation, when the system (25)—(28) yields the complete description, the same result is obtained also from Rytov's formulas. In the presence of relaxation, his formulas give incorrect results:

$$\langle \delta V^2 \rangle = VkT \left[\frac{1 - {}^4/_3\mu_0 (K_\infty - K_0)/K_\infty K_0}{K_0 + {}^4/_3\mu_0} \right];$$

$$\langle \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \rangle \neq 0 \quad \text{for} \quad \mathbf{r} \neq \mathbf{r}'.$$

The reasons for the error were discussed earlier.

The spectral intensities of the temperature, expressed in other generalized forces in a nonrelaxing medium, are given by Rytov's formulas, and in the relaxing medium cannot be calculated at all. This entails serious difficulties in the calculation of the intensity of the scattered light. Therefore, for example, in the case of an incomplete description it is impossible to take into account the contribution of the temperature fluctuations[17].

If the dielectric constant ε depends on the unknown internal variables x_p, then it is obviously impossible to replace the explicit allowance for these variables by introduction of dispersion in K, p_T, and C_V. It is in general meaningful to confine oneself to a calculation of the fluctuations of the hydrodynamic variables only if ε does not depend on x_p. As seen from the foregoing, this means actually that we must have $(\partial\epsilon/\partial x_p)_{S,\,\rho} = 0$, a condition hardly satisfied in experiments. On the other hand, if for example $(\partial\epsilon/\partial x_p)_{T,\,\rho} = 0$, then the theory described above does not suffice for the calculation of the reflection of light, and it is necessary to introduce the internal variables in explicit form.

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