SOVIET PHYSICS JETP VOLUME 34, NUMBER 5 MAY, 1972

CALCULATION OF THERMODYNAMIC FORCE FLUCTUATIONS IN A RELAXING MEDIUM

V. P. ROMANOV, V. A. SOLOV'EV and L. S. FILATOVA

Leningrad State University

Submitted May 25, 1971

Zh. Eksp. Teor. Fiz. **61**, 2103–2109 (November, 1971)

The problem of calculation of generalized-thermodynamic-coordinate and generalized-force fluctuations in systems in which the presence of intrinsic relaxation processes which cannot be observed directly leads to dispersion of the thermodynamic coefficients is considered in a general form. It was previously shown that the spectral intensities of coordinate fluctuations can be calculated by means of the thermodynamic and hydrodynamic equations by the same methods as those in the case of systems with frequency-independent coefficients. Closed formulas are obtained for spectral correlators of the force-force and force-coordinate type and are valid for an arbitrary discrete set of relaxation processes. The problem of using dispersive coefficients for calculating fluctuations of quantities which are arbitrary functions of the generalized coordinates is also considered.

1. There is a large group of problems, such as the calculation of thermal noise, theory of molecular scattering of light, etc., in which it becomes necessary to calculate the spectral intensities of fluctuations of different thermodynamic quantities, starting from the thermodynamic and hydrodynamic equations of the medium. Particular interest attaches in this case to media in which there are internal, latent parameters, usually of the relaxation type, which are inaccessible to direct observation and become manifest in experiment only through the dispersion of the thermodynamic coefficients (see, for example,[1,2]). As shown in[3], for such media it is possible to calculate by the usual methods the fluctuations of the generalized coordinates, i.e., the extensive variables or their kinematic combinations, such as density or concentration. As to the generalized forces, such as pressure, temperature, etc., it has been impossible to construct a general method for the calculation of their fluctuations that would be applicable to a system with dispersive coefficients; the only possible way was to return to the complete thermodynamic description of the system, which considers in explicit form all the internal parameters responsible for the dispersion in the frequency range of interest to us. Such calculations were carried out for certain particular cases in[4-7]. We shall consider this problem here in general form.

2. As in[3], we start from a complete thermodynamic description of the system, given in the form of a set of generalized coordinates x_i and their conjugate generalized forces f_i. The coordinates and forces are connected by the equations of state $f_i = -B_{ik}x_k$ and by the equations of motion $M_{ik}x_k = f_i$. Here M_{ik} are differential operators (polynomials of d/dt or of $i\omega$ without free terms), and the thermodynamic coefficients B_{ik} (quantities such as the elastic moduli) are assumed to be independent of the frequency. The possibility of writing down the system of thermodynamic and hydrodynamic equations in this form, with constant B_{ik}, is a criterion of the completeness of the description.

Let the variables $x_a = x_1, x_2, \ldots, x_m$ be the "usual" quantities accessible to measurement, and let $x_p = x_{m+1}, x_{m+2}, \ldots, x_n$ be the internal parameters. We can then rewrite the system of equations of state and motion in the expanded form

$$f_a = -B_{ab}x_b - B_{ap}x_p, \quad f_q = -B_{qb}x_b - B_{qp}x_p; \tag{1}$$

$$M_{ab}x_b = f_a, \quad M_{qp}x_p = f_q. \tag{2}$$

Here and from now on the indices a, b, ..., h run through values from unity to m, and the indices p, q, ..., v from m + 1 to n; the indices i, j, k and l pertain to the entire set of variables $x_1, \ldots, x_n$. We assume, as usual[1-3], that the internal parameters are separated in the equations of motion, $M_{ap} = M_{pa} = 0$. Of fundamental practical interest are cases when x_p are the relaxation variables, $M_{qp} = L_{qp}d/dt$ (L_{qp} are the Onsager coefficients), and x_p can always be chosen to be normal coordinates diagonalizing the matrices B_{qp} and M_{qp}, but there is no need to introduce such limitations here.

To change over to the incomplete description it is necessary to eliminate the quantities x_p and f_p from (1) and (2), which yields[1)]

$$f_a = -\tilde{B}_{ab}x_b, \quad M_{ab}x_b = f_a \tag{3}$$

$$\tilde{B}_{ab} = B_{ab} - B_{ap}(M' + B')_{pq}^{-1}B_{qb}, \tag{4}$$

where B_{ab} is the instantaneous modulus and $B_{ab} - B_{ap}B_{pq}^{-1}B_{qb}$ the equilibrium modulus; only the second term in this formula depends on the frequency. From now on M' and B' stand for submatrices with indices m + 1, ..., n, while M'' and B'' are submatrices with indices 1, ..., m; these symbols will be omitted where there is no fear of misunderstanding.

The complete-description equations (1) and (2) do not, as a rule, follow from direct experiment. They are constructed on the basis of the experimentally obtained dynamic coefficients $\tilde{B}_{ab}$ by introducing assumptions concerning the nature of the excluded parameters with the aid of a theoretical model (see, for example,[2]). In

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[1)] This formula was incorrectly given earlier in [3].

the absence of a sufficiently well justified model, the choice of the parameters $x_{m+1}, \ldots, x_n$ remains ambiguous—they are defined accurate to an arbitrary linear transformation.

3. To calculate the spectral intensities of the fluctuations it is convenient to use the fluctuation-dissipation theorem (FDT):

$$\langle x_i x_j^* \rangle_\omega = -\frac{kT}{2\pi i\omega}(p_{ij} - p_{ji}^*), \qquad (5)$$

$$\langle f_i f_j^* \rangle_\omega = -\frac{kT}{2\pi i\omega}(P_{ij} - P_{ji}^*), \qquad (6)$$

where k is Boltzmann's constant, T the temperature, and $p_{ij}(i\omega)$ and $P_{ij}(i\omega)$ are the generalized susceptibilities. To calculate p_{ij} it is necessary to replace in the right-hand sides of the equations of motion (2) f_j by $f_j + F_j$, where F_j are harmonic extraneous forces ($F_j \sim e^{i\omega t}$); then, solving the system (1) and (2) with respect to x_i, we obtain $x_i = (M + B)_{ij}^{-1} F_j = p_{ij} F_j$. Analogously, the P_{ij} are determined from the solution of the same equation with respect to f_i, which can be written in the form $f_i = P_{ij} X_j$, where the "forces" are given by $X_j \equiv -B_{ji}^{-1} F_i$. Thus, the problem of calculating the fluctuations reduces to solving the purely macroscopic problem of calculating the susceptibilities p_{ij} and P_{ij}.

If the system is specified by the incomplete-description equations (3), then the susceptibilities p_{ab} pertaining to the usual variables are calculated in exactly the same manner as for the complete system, namely, by applying extraneous forces (the complete set $F_j = F_1, \ldots, F_n$ in the case of the complete description or the abbreviated set $F_a = F_1, \ldots, F_m$ in the incomplete description) to the system, we obtain from (1), (2) and (3) the identical results:

$$p_{ab} = (M + \tilde{B})_{ab}^{-1} = (M'' + \tilde{B})_{ab}^{-1}. \qquad (7)$$

4. To calculate the susceptibilities P_{ab} it is necessary to start from the complete-description equations (1) and (2). Expressing the forces F_a and F_p in terms of X_b and X_q we obtain

$$(M_{ab} + B_{ab}) x_b = -B_{aq} x_q - B_{ab} X_b - B_{aq} X_q, \qquad (8)$$

$$(M_{pq} + B_{pq}) x_q = -B_{pb} x_b - B_{pb} X_b - B_{pq} X_q. \qquad (9)$$

From (9) we obtain

$$x_q = -(M' + B')_{qp}^{-1} [B_{pb}(x_b + X_b) + B_{ps} X_s] \qquad (10)$$

and, substituting in (8), we obtain, using (4),

$$\begin{aligned} x_c = &-(M'' + \tilde{B})_{cd}^{-1} \tilde{B}_{db} X_b \\ &+ (M'' + \tilde{B})_{cd}^{-1} [B_{dr}(M' + B')_{rp}^{-1} B_{ps} - B_{ds}] X_s. \end{aligned} \qquad (11)$$

Substituting (11) in (10), we also obtain an expression for x_q in terms of X_b and X_s. Now

$$\begin{aligned} f_a = -B_{ac} x_c - B_{aq} x_q = [&\tilde{B}_{ac}(M'' + \tilde{B})_{cd}^{-1} \tilde{B}_{db} \\ &+ B_{ar}(M' + B')_{rp}^{-1} B_{pb}] X_b + \{\tilde{B}_{ac}(M'' + \tilde{B})_{cd}^{-1} \cdot \\ &\cdot [B_{ds} - B_{dr}(M' + B')_{rp}^{-1} B_{ps}] + B_{ar}(M' + B')_{rp}^{-1} B_{ps}\} X_s. \end{aligned}$$

Taking (7) and (4) into account, we see that the susceptibility P_{ab} of interest to us (the coefficient of X_b) is equal to

$$P_{ab} = \tilde{B}_{ac} p_{cd} \tilde{B}_{db} - (\tilde{B}_{ab} - B_{ab}). \qquad (12)$$

Substitution of (12) in (6) gives a formula for calculating the spectral intensities of the fluctuations of the generalized forces $\langle f_a f_b^* \rangle_\omega$.

We see that P_{ab} and $\langle f_a f_b^* \rangle_\omega$ are expressed only in terms of the coefficients p_{cd}, which are calculated from the incomplete system (3), and also in terms of the complex moduli $\tilde{B}_{ab}(i\omega)$ and their dispersive parts $B_{ab} - \tilde{B}_{ab}$. We note that the real constants B_{ab} (the instantaneous moduli) could be discarded, since they cancel out in (6), but it is more convenient to retain them, for this fcailitates the calculation of the total fluctuations by the Rytov method[8]

$$\langle f_a f_b \rangle = \int_{-\infty}^{+\infty} \langle f_a f_b^* \rangle_\omega \, d\omega = kT[P(0) - P(\infty)] = kTP(0),$$

inasmuch as

$$M_{cd}(\infty) = \infty, \qquad P_{ab}(\infty) = B_{ac}[M''(\infty) + \tilde{B}(\infty)]_{cd}^{-1} B_{db} = 0.$$

Then

$$\langle f_a f_b \rangle = kT[\tilde{B}_{ac}(0) \tilde{B}_{cd}^{-1}(0) \tilde{B}_{db}(0) - \tilde{B}_{ab}(0) + B_{ab}] = kTB_{ab},$$

as should be the case in accordance with the usual thermodynamic theory.

5. We can calculate in similar fashion the spectral intensities of the crossing fluctuations of the type $\langle f_a x_b^* \rangle_\omega$. We have

$$\begin{aligned} \langle f_a x_b^* \rangle_\omega &= -B_{ac} \langle x_c x_b^* \rangle_\omega - B_{ap} \langle x_p x_b^* \rangle_\omega \\ &= \frac{kT}{2\pi i\omega}(B_{ac} p_{cb} + B_{ap} p_{pb} - B_{ac} p_{bc}^* - B_{ap} p_{bp}^*). \end{aligned} \qquad (13)$$

To calculate the susceptibilities P_{pb} we replace f_a by $f_a + F_a$ in (2), and then

$$x_p = -(M' + B')_{pq}^{-1} B_{qc} x_c = -(M' + B')_{pq}^{-1} B_{qc} p_{cb} F_b \equiv p_{pb} F_b. \qquad (14)$$

In exactly the same manner, to calculate p_{bq} we replace f_q by $f_q + F_q$ in (2), and obtain

$$x_q = (M' + B')_{qp}^{-1} (-B_{pd} x_d + F_p).$$

Substituting this expression in the first equation of (1), we get

$$f_a = -\tilde{B}_{ab} x_b - B_{aq}(M' + B')_{qp}^{-1} F_p,$$

which yields, after substituting in the first equation of (2) and solving:

$$x_b = -p_{bc} B_{cq} (M' + B')_{qp}^{-1} F_p \equiv p_{bp} F_p. \qquad (15)$$

Substituting (14) and (15) in (13), we obtain ultimately

$$\langle f_a x_b^* \rangle_\omega = \frac{kT}{2\pi i\omega}(\tilde{B}_{ac} p_{cb} - p_{bc}^* \tilde{B}_{ca}^*). \qquad (16)$$

Analogously

$$\langle x_b f_a^* \rangle_\omega = \frac{kT}{2\pi i\omega}(p_{bc} \tilde{B}_{ca} - \tilde{B}_{ac}^* p_{cb}^*) = \pm \langle f_a x_b^* \rangle_\omega.$$

It is thus possible to calculate the spectral intensities of the fluctuations of all the quantities used in the incomplete description of the system without returning to the complete description, i.e., without introducing the internal parameters in explicit form. Of course, this leaves open the question of the possibility of generalizing formulas (16), (6), and (12) to the case of a medium having a continuous relaxation spectrum, or generally to the case of a system with an arbitrary aftereffect law, for which it is impossible to construct a complete description with a finite number of internal parameters[2)].

6. Formulas (5)–(7), (12), and (16) give the entire necessary information, if there are grounds for assuming that the fluctuations of the experimentally observed quantities y_α, such as the dielectric constant ϵ in the light-scattering problem, depend only on $x_a = x_1, \ldots, x_m$ and (or) on $f_a = f_1, \ldots, f_m$, but do not depend directly on $x_p = x_{m+1}, \ldots, x_n$. Thus, if the internal variable x_p is the energy of the intramolecular vibrations, then we can assume with good approximation that ϵ depends only on the density ρ and on the temperature, and that $(\partial\epsilon/\partial x_p)_{\rho,T} = 0$. On the other hand, if the internal variables are, for example, the ordering parameters in structural relaxation, then ϵ can depend on x_p at least as strongly as on the temperature. In the case of anisotropy fluctuations, the dependence of the tensor ϵ on the internal parameters is probably decisive. In such cases, of course, introduction of the internal parameters in explicit form is obligatory.

It is natural, however, to ask whether here, too, the explicit account of the internal parameters can be replaced by introducing frequency-dependent dynamic coefficients[9]. Let $y_\alpha = D_{\alpha a}x_a + D_{\alpha p}x_p$. Then, eliminating x_p with the aid of (2), we obtain $y_\alpha = [D_{\alpha a} - D_{\alpha p}(M' + B')^{-1}_{pq}B_{qa}]x_\alpha \equiv \tilde{D}_{\alpha a}x_\alpha$. The coefficients $\tilde{D}_{\alpha a}$ can be determined from experiment if the quantities y_α admit of sufficiently rapid measurements to be able to trace the "instantaneous" values of y_α when x_a is varied.

In the complete description we have $\langle y_\alpha y_\beta^*\rangle_\omega = D_{\alpha i}D_{\beta j}\langle x_i x_j^*\rangle_\omega$ and by virtue of (5) the problem reduces to the calculation of the susceptibilities p_{ij}. The quantities p_{ab}, p_{pb}, and p_{bp} were obtained above. To calculate p_{pq} it is necessary to replace f_q in the second equation of (2) by $f_q + F_q = -B_{qb}x_b - B_{qp}x_p + F_q$ and to solve this equation with respect to x_p. Using (15), we obtain

$$p_{pq} = (M' + B')_{pr}{}^{-1}B_{rc}p_{cd}B_{ds}(M' + B')_{sq}{}^{-1} + (M' + B')_{pq}{}^{-1}.$$

Substitution of the obtained values of the susceptibilities yields

$$\langle y_\alpha y_\beta^*\rangle_\omega = -\frac{kT}{2\pi i\omega}[\tilde{D}_{\alpha a}p_{ab}\tilde{D}_{\beta b} + D_{\alpha p}(M' + B')_{pq}{}^{-1}D_{\beta q} - \text{c.c.}] \quad (17)$$

(it was assumed here that x_p and x_q have the same parity with respect to sign reversal, so that $M_{pq} = M_{qp}$). The second term in (17) is not expressed in terms of the parameters of the dynamic coefficients $\tilde{D}_{\alpha\beta}(\omega)$, so that exact calculation of $\langle y_\alpha y_\beta^*\rangle_\omega$ is impossible in the incomplete description. However, if y_α and y_β depend weakly on the internal variables, then the terms that are quadratic in $D_{\alpha p}$ and $D_{\beta q}$ can be discarded (see[5]). In this case it is possible, using only the first term in (17), to calculate fluctuations of the type $\langle y_\alpha y_\beta^*\rangle_\omega$ somewhat more accurately than when the influence of the internal parameters on y_α and y_β is completely neglected.

The results obtained above for $\langle f_a f_b^*\rangle_\omega$ could also be obtained as a particular case of formula (17), but the method used in Sec. 4 is more convenient, since the susceptibilities P_{ab} may be of interest in themselves. It is useful to note that neither the exact nor the approximate formula (17) coincides with the seemingly natural expression

$$\langle y_\alpha y_\beta^*\rangle_\omega = \tilde{D}_{\alpha a}\tilde{D}_{\beta b}{}^*\langle x_a x_b^*\rangle_\omega.$$

7. As an example of the application of the derived formulas, let us calculate the temperature fluctuations in a homogeneous isotropic medium in which there are internal relaxation processes. The system of hydrodynamic equations of such a system in the ω, **k** representation is

$$\begin{gathered}\sigma_{11} = \left(\tilde{K}_T + \frac{4}{3}\tilde{\mu}\right)u_{11} - \tilde{p}_T\delta T,\\ \delta T = \frac{T}{\tilde{C}_V}\delta S - \frac{T\tilde{p}_T}{\tilde{C}_V}u_{11},\end{gathered} \quad (18)$$

$$-\rho\omega^2 u_{11} + i\omega k^2({}^4/_3\eta + \zeta)u_{11} = -k^2(\sigma_{11} - \Sigma_{11}),\ i\omega T\delta S = -k^2\varkappa(T - \mathcal{T}),$$

where the x_1 axis is chosen along the direction of the wave vector **k**. We use here the standard hydrodynamic notation[10]; Σ_{11} and $\mathcal{T}$ are the extraneous stresses and the temperature (the external forces conjugate to u_{11} and δS); S and C_V are given per unit volume.

Solving the system (18), we obtain $u_{11} = p_{uu}\Sigma_{11} + p_{uS}\mathcal{T}$, and $\delta S = p_{uS}\Sigma_{11} + p_{SS}\mathcal{T}$, where the susceptibilities are

$$p_{uu} = k^2\left(i\omega + \frac{k^2\varkappa}{\tilde{C}_V}\right)\frac{1}{D}, \quad (19)$$

$$p_{uS} = k^2\varkappa\frac{\tilde{p}_T}{\tilde{C}_V}\frac{1}{D}, \quad (20)$$

$$p_{SS} = \frac{k^2\varkappa}{T}\left[-\rho\omega^2 + i\omega k^2\left(\frac{4}{3}\eta + \zeta\right) + k^2\left(\tilde{K}_T + \frac{4}{3}\tilde{\mu} + \frac{T\tilde{p}_T{}^2}{\tilde{C}_V}\right)\right]\frac{1}{D}. \quad (21)$$

Here

$$\begin{aligned}D = \Big[-\rho\omega^2 + i\omega k^2\left(\frac{4}{3}\eta + \zeta\right)\\ + k^2\left(\tilde{K}_T + \frac{4}{3}\tilde{\mu}\right)\Big]\left(i\omega + \frac{k^2\varkappa}{\tilde{C}_V}\right) + \frac{i\omega k^2 T\tilde{p}_T{}^2}{\tilde{C}_V}.\end{aligned} \quad (22)$$

The dynamic coefficients of the equations of state $\sigma_{11} = \tilde{B}_{uu}u_{11} + \tilde{B}_{uS}\delta S$, and $\delta T = \tilde{B}_{uS}u_{11} + \tilde{B}_{SS}\delta S$ are equal to

$$\tilde{B}_{uu} = \tilde{K}_T + \frac{4}{3}\tilde{\mu} + \frac{T\tilde{p}_T{}^2}{\tilde{C}_V},\qquad \tilde{B}_{uS} = -\frac{T\tilde{p}_T}{\tilde{C}_V},\qquad \tilde{B}_{SS} = \frac{T}{\tilde{C}_V}. \quad (23)$$

Substitution in formulas (6), (12), and (16) yields

$$\langle\delta T^2\rangle_{\omega\mathbf{k}} = -\frac{kT}{(2\pi)^4 i\omega}(P_{TT} - P_{TT}{}^*), \quad (24)$$

where

$$\begin{gathered}P_{TT} = \frac{T}{C_{V\infty}} - \frac{i\omega}{D}\frac{T}{\tilde{C}_V}\left[-\rho\omega^2 + i\omega k^2\left(\frac{4}{3}\eta + \zeta\right) + k^2\left(\tilde{K}_T + \frac{4}{3}\tilde{\mu}\right)\right],\\ \langle\delta T u_{11}{}^*\rangle_{\omega\mathbf{k}} = -\left\langle\delta T\frac{\delta\rho^*}{\rho}\right\rangle_{\omega\mathbf{k}} = \frac{kT}{(2\pi)^4 i\omega}\left(\frac{i\omega}{D}\frac{k^2T\tilde{p}_T}{\tilde{C}_V} - \text{c.c.}\right)\end{gathered} \quad (25)$$

It can be verified by direct calculation that these formulas coincide in the case of one relaxation process with those obtainable by using the results of[5], where a complete description of the system was employed. Formulas

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[2)] We are grateful to S. M. Rytov for this remark.

(24) and (25) make it possible to introduce a correction for the temperature fluctuations[11] into the formulas for light scattering in a medium with arbitrary dispersion law. If the dielectric constant of the medium depends directly on the internal parameters, then such a correction may not be sufficient and it becomes necessary to use formulas such as (17) or to change over to the complete description.

The authors consider it their pleasant duty to thank S. M. Rytov for a discussion and valuable advice.

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Translated by J. G. Adashko
220