Theory of rapid and steep-gradient low-amplitude processes

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(Submitted July 11, 1974)
Zh. Eksp. Teor. Fiz. **68**, 956–973 (March 1975)

A semiphenomenological theory of rapid and steep-gradient processes in media with a microstructure is considered. The equations of motion for the major macroscopic quantities can be obtained on the basis of a general kinetic description of the *n*-particle structural elements of the medium by means of the projection method. The transfer kernels or nonequilibrium kinetic coefficients (NKC), which determine the relations between the fluxes and forces are specified by using certain general principles, exact relationships (dissipation-fluctuation and moment), model considerations, and also experimental and numerical data. The theory with a single quantity (rapid diffusion) is considered. It yields the asymptotic form of the relaxation NKC for the case of an appreciable time dispersion, as well as the diffusion NKC. Diffusion waves are discussed and neutron transfer in small assemblies is analyzed. The hydrodynamics of rapid process is considered and relations are given for hydrodynamic NKC in the case of longitudinal motion. They are specified in a more concrete form for a simple fluid (gas) by employing data on radiation scattering and numerical data. Shear waves in a simple fluid (argon) are studied.

1. INTRODUCTION

In recent years, appreciable deviations from the results prescribed by the thermodynamics of irreversible processes ("disequilibrium effects") are observed in increasing numbers in studies of nonequilibrium processes in various media. In addition to those noted in[1], these include zero sound, the non-exponential decrease of a neutron pulse in small assemblies, the Scott effect, damping of the type $\exp(-t^{\alpha})$ with $\alpha < 1$, spin echo in polymers, and others. Deviations occur for processes whose space-time scales are comparable with the internal characteristic times and lifetimes of the structure elements of the medium (molecules or clusters of various types).

At the present time, it is possible to derive general relations for a large class of rapid and steep-gradient (RS) processes of low amplitude, microscopic equations of motion of general form have been formulated, and the main quantities contained in them, namely the transport kernels or the nonequilibrium kinetic coefficients (NKC) that are contained in these quantities, have been considered. Such a program was realized for general Boltzmann systems[1,2]. Generalized hydrodynamics of simple liquids was proposed by Richards (1960) and Mori[3], and was developed most completely in an article by Akcasu and Daniels[4]. The theory of rapid thermal conductivity was formulated by Guyer and Krumhansl[5]. The macroscopic description of highly non-equilibrium processes in an electron gas was discussed by a number of authors. A great influence on the formation of the theory of rapid processes was exerted by the phenomenological theory of Leontovich and Mandel'shtam[6].

In this paper, on the basis of a general kinetic description, we consider the macroscopic theory of RS processes that are linear in the deviation from a stationary, translationally invariant state. In the main part of the paper we give equations for the major macroscopic quantities (MMQ) of general form, and study the main problem of the RS processes, namely the determination of the form of the NKC. In comparison with the Mori formalism[3], the equations of Sec. 2 take into account the disequilibrium of the stationary state under the influence of external forces, take a form characteristic of nonequilibrium thermodynamics, and contain, in particular, diagonal relaxation terms that do not vanish in homogeneous systems. The absence of the latter from Mori's equations is due to the reversible character of the Liouville operator.

The main (macroscopic) problem of the theory of RS processes, namely the determination of the form of the NKC, has still not been satisfactorily solved, although definite progress was made in this direction. In this paper we present a general method of obtaining relations for the NKC—the functions of the Laplace parameter, the wave vector, and the field. The method is based on exact moment expressions for the NKC, which are derived in analogy with the Leontovich-Mandel'shtam method[6]. We use also the asymptotic forms of the NKC for small and large gradients and velocities, the general principles of nonequilibrium thermodynamics, model considerations, and experimental data obtained in the intermediate range of the arguments of the NKC.

In Sec. 3 we consider a theory of rapid diffusion, which contains one major macroscopic quantity. We obtain here an asymptotic expression for the relaxation NKC in homogeneous systems "with vanishing frequency." A semiphenomenological relation is also given for the diffusion NKC; the values of its parameters are indicated for the case of neutron diffusion (in graphite and in water). The simple variant of the diffusion NKC is analogous in form to the thermal-conductivity NKC used in the analysis of second sound[5], and also the shear-viscosity NKC given in[7]. With the aid of the expression obtained for the diffusion NKC we discussed "diffusion" waves (density, thermal, shear). The theory points to their existence; the question of their observability depends on the character of the system.

Section 4 is devoted to the hydrodynamics of fast processes (HFP) in a molecular fluid (gas). For a simple gas it was proposed by the present author in[2], but here it is presented in constructive form. In the case of longitudinal motion of a simple liquid, relations are given for the hydrodynamic NKC, both diagonal and crossing; the results of a number of studies[1,4,8] are made much more precise. The choice is discussed of the values of the parameters from experiments on light scattering and neutron scattering and on the propagation of hypersound. Also investigated is rapid shear in a simple fluid, and the limit of appearance of shear waves, which indicates the possibility of their observation, is obtained with the aid of the assumed dependence of the shear-viscosity NKC.

2. GENERAL THEORY

Let the dynamics of a many-particle system be described by a kinetic equation of general form (or by a system of such equations) for the distribution function (vector) of n particles: $f = \{f_l^n(\mathrm{pmtx})\}$; here the momentum p, the internal angular momentum m, the index l of the internal state, and x are all n-dimensional vectors. For a small perturbation $\Phi = \{\varphi_l\}$ of the stationary distribution $f_S = \{f_{Sl}\}$, $f = f_S(1 + \Phi)$, the general kinetic equation (system) takes the form

$$\partial_t\Phi=\mathscr{E}\Phi+q, \quad \mathscr{E}\equiv\mathscr{E}^d+J, \tag{1}$$

where

$$\mathscr{E}^d=-\nabla\cdot\mathbf{V}-(\mathbf{F}_p\cdot\partial_{\mathbf{p}}+\mathbf{F}_m\cdot\partial_{\mathbf{m}})\equiv\mathscr{E}^\nabla+\mathscr{F} \tag{2}$$

is the flux (matrix) operator and J is the collision (matrix) operator, $\mathbf{F}_{\mathrm{pm}}(\mathrm{pmHE})$ are force operators, and q is a term corresponding to the source. The operator $\mathscr{E}^d$ describes the fluxes in phase space Γ_n and has a reversible character, i.e., $\mathscr{E}^d \to -\mathscr{E}^d$ under time reversal. The operator J determines the irreversible interaction of the group of n particles with the remaining N − n particles. Owing to the homogeneity and stationarity of the unperturbed system, the evolution operator $\mathscr{E}$ is translationally-invariant in x and in t.

Inasmuch as the entropy perturbation is given in the first nonvanishing approximation by

$$\delta S(t)=-\frac{k_B}{\Omega_\Gamma}\sum_l\int d\Gamma_n\varphi_l^*\varphi_l f_{sl}\equiv-k_B\langle\Phi,\Phi\rangle_{\mathrm{H}}, \tag{3}$$

it is natural to use the Hilbert spaces of the vectors Φ in Γ_n and the "densities" $\Phi(x_1)$ in $\Gamma_n(x_1)$ with respective scalar products $\langle\Psi, \Phi\rangle_{\mathrm{H}}$ and $\langle\Psi, \Phi\rangle$, where

$$\langle\Psi,\Phi\rangle_{\mathrm{H}}=\frac{1}{V}\int dx_1\langle\Psi,\Phi\rangle.$$

We note that the mean values and their densities are expressed by these scalar products.

We assume that the collision operator also has the following general properties:

1) it is dissipative:

$$\mathrm{Re}\,J\leqslant0, \quad \langle\Phi, (J+J^+)\Phi\rangle_{\mathrm{H}}\leqslant0, \tag{4}$$

2) it has a finite number of collision invariants Ψ_m ($m \geq 0$):

$$J\Psi_m=0, \quad J^+\Psi_m^+=0. \tag{5}$$

Obviously, outside the subspace $\{\Psi_m\}$ the operator J is negative, i.e., Re J < 0. The first property denotes that stable systems are considered, and the second reflects the presence of conservation laws.

The flux operator, owing to the reversible character, is generally speaking anti-Hermitian and has a zero trace

$$\langle\Phi,\mathscr{E}^d\Phi\rangle_{\mathrm{H}}=0. \tag{6}$$

The properties (4)–(6) can hold also for a density space, i.e.,

$$\langle\Phi, (J+J^+)\Phi\rangle\leqslant0, \quad \langle\Phi,\mathscr{E}^d\Phi\rangle=0, \tag{6'}$$

as, for example, in the case of Boltzmann systems.

We are next interested in the linear deviations of the major macroscopic quantities (MMQ) from the stationary value

$$c_\alpha(tx_1)=\langle\Psi_\alpha, \Phi(tx_1)\rangle \tag{7}$$

(we assume henceforth $x_1 = r$). The microscopic attributes of the MMQ $\Psi_\alpha(\mathrm{pm}, x_i - x_j)$ can be regarded as orthogonal; in addition, it is convenient ot use in the general analysis the normalized quantities

$$c_\alpha'=\langle\Psi_\alpha', \Phi\rangle, \quad \Psi_\alpha'=\Psi_\alpha/n_\alpha, \quad \langle\Psi_\alpha', \Psi_\beta'\rangle=\delta_{\alpha\beta}$$

(we shall henceforth omit the primes).

Using the Zwanzig-Mori projection scheme, we represent Φ in the form $\Phi = P\Phi + \Phi$, $P\Phi = \Psi_\alpha\langle\Psi_\alpha, \Phi\rangle$ and obtain in analogy with[1], under the condition $\Phi_{t=0} = 0$, closed equations for the MMQ:

$$\partial_t c_\alpha+\nabla\cdot\mathbf{V}_{\alpha\beta}*c_\beta+\mathscr{F}_{\alpha\beta}\cdot c_\beta=-\dot{c}_\alpha+q_\alpha. \tag{8}$$

Here

$$\mathbf{V}_{\alpha\beta}\equiv\langle\Psi_\alpha, \mathbf{V}\Psi_\beta\rangle, \quad \mathscr{F}_{\alpha\beta}\equiv\langle\alpha, (\mathbf{F}_p\cdot\partial_{\mathbf{p}}+\mathbf{F}_m\cdot\partial_{\mathbf{m}})\beta\rangle$$

are tensor operators; the asterisk denotes a tensor-argument (t, r) contraction, and a dot denotes a tensor contraction. According to (6′), the diagonal matrix elements $V_{\alpha\alpha}$ and $\mathscr{F}_{\alpha\alpha}$ are equal to zero.

The "dissipation" MMQ $\dot{c}_\alpha$ is singled out in the right-hand sides of (8). It is expressed in terms of the thermodynamic forces $X_\alpha^g = \nabla C_\alpha$, $X_\alpha = C_\alpha$ and the external forces $X_q = \delta\mathbf{F}_e(t)$ (in analogy with (I.10)[1)]):

$$-\bar{c}_\alpha(t\mathbf{r})=\nabla\cdot\mathbf{K}_{\alpha\beta}{}^g*X_\beta{}^g-\mathbf{K}_{\alpha\beta}{}^{gr}*X_\beta{}^g-\mathbf{K}_{\alpha\beta}{}^r*X_\beta+\mathbf{K}_\alpha{}^F*\delta\mathbf{F}_e; \tag{9}$$

$K_{\alpha\beta}^r \equiv -J_{\alpha\beta} - K_{\alpha\beta}^h$. We have separated here the gradient, the gradient-relaxation, the relaxation, and the force terms. These relations establish the operator connection between the fluxes and the forces, and are generalizations of the well-known relations of nonequilibrium thermodynamics to include the case of linear RS processes. The dissipation obviously can be expressed in terms of the MMQ in the form (Mori)

$$-\dot{c}_\alpha=-d_{\alpha\beta}*c_\beta+\mathbf{K}_\alpha{}^F*\delta F_e, \quad d_{\alpha\beta}\equiv\langle\alpha, \mathscr{E}\hat{\mathscr{R}}\hat{\mathscr{E}}\beta\rangle-J_{\alpha\beta}. \tag{10}$$

The operator $\mathscr{D} = [d_{\alpha\beta}]$ determines the rate of dissipation of the MMQ Re $\mathscr{D}$ and the dispersion Im $\mathscr{D}$, $\hat{\mathscr{R}} \equiv [\partial t - (1 - P)\mathscr{E}]^{-1}$.

The Fourier-Laplace transforms of the transfer kernels in (9)—the nonequilibrium kinetic (NK) tensors $K_{AB}(\mathrm{skF})$—are expressed in terms of the correlation functions $\langle\Psi, R\Phi\rangle \equiv R_{\Psi\Phi}(\mathrm{skF})$ by general dissipation-fluctuation relations similar to (I.13). They are obtained from the solution of the system of equations for the quantities $\dot{c}_{\alpha I} = \dot{c}_\alpha + J_{\alpha\beta}c_\beta$

$$-s\mathscr{R}_{\alpha\beta}\dot{c}_{\beta I}=\langle\alpha, \mathscr{E}\hat{\bar{\mathscr{R}}}\hat{\mathscr{E}}\beta\rangle c_\beta+s\langle\alpha, \mathscr{R}\hat{q}\rangle \tag{11}$$

(α takes on values at which $\dot{c}_{\alpha I} \neq 0$). These relations take the following form[2)]: for gradient NKC

$$K_{i\alpha,j\beta}(s\mathbf{kF})=\frac{\Delta^{\gamma\alpha}}{\Delta}\langle\gamma, \mathscr{R}_F V_i\mathscr{R}G_{j\beta}\rangle, \tag{12}$$

for relaxation and force NKC

$$K_{\alpha\beta}{}^h=\frac{\Delta^{\gamma\alpha}}{\Delta}\langle\gamma, \mathscr{R}_F H_\beta\rangle, \quad K_{i\alpha}{}^F=\frac{\Delta^{\gamma\alpha}}{\Delta}\langle\gamma, \mathscr{R}q_{ei}\rangle, \tag{13}$$

for gradient-relaxation NKC

$$K_{\alpha i\beta}=\frac{\Delta^{\gamma\alpha}}{\Delta}[\langle\gamma, \mathscr{R}_F G_{\beta i}\rangle+\langle\gamma, \mathscr{R}_F V_i\mathscr{R}H_\beta\rangle]. \tag{14}$$

Here $\Delta = \|\mathscr{R}_{\gamma\delta}\|$ and $\Delta^{\gamma\delta}$ is the cofactor of the element $R_{\gamma\delta}$,

$$\mathscr{R}_F \equiv (s-\mathscr{E}^F)^{-1}, \quad \mathscr{E}^F \equiv J-\mathscr{F}, \quad \mathscr{R} \equiv (s-\mathscr{E})^{-1},$$
$$G_{i\gamma} \equiv \hat{V}_i \Psi_\gamma, \quad H_\gamma \equiv \hat{\mathscr{E}}^F \Psi_\gamma. \tag{15}$$

Relations (12)—(14), unlike the similar formulas of[1], are suitable for the case when the MMQ include nonconserved quantities, i.e., such that $\mathscr{E}^F \Psi_\alpha \neq 0$. (It is easily seen that expressions (I.13) for these MMQ become infinite as $k \to 0$ and $s \to 0$). If Ψ_α are the zeros of the operator $\mathscr{E}^F$, $\mathscr{R}_F \Psi_\alpha = \Psi_\alpha / s$, then formulas (12)—(14) coincide with (I.13). By virtue of (15), we are left here only with gradient and force NKC. We note that the dissipation-fluctuation relations (12)—(14), together with the possibility of experimentally determining the NKC, enable us to establish their properties and to obtain approximate expressions for the NKC on the basis of expressions for the correlation functions. According to (11), the $\mathscr{D}$ matrix is represented in terms of the correlation functions in the form

$$d_{\alpha\beta}(s\mathbf{kF}) = \nu_{\alpha\beta} - \frac{\Delta^{\gamma\alpha}}{s\Delta} \langle \gamma, \mathscr{E}\hat{\mathscr{R}}\mathscr{E}\beta \rangle, \quad \nu_{\alpha\beta} \equiv -J_{\alpha\beta} \tag{16}$$

(the second term does not appear if $\dot{c}_{\alpha I} = 0$).

The spectrum of Eqs. (8) and (9) is determined by a dispersion function whose zeros are the eigenvalues $s(\mathbf{kF})$ or $k(s\mathbf{F})$:

$$D(s\mathbf{kF}) = \| s\delta_{\alpha\beta} + i\mathbf{k} \cdot V_{\alpha\beta} + \mathscr{F}_{\alpha\beta} + d_{\alpha\beta} \| = 0. \tag{17}$$

The expression of D in terms of the correlation function is given by formula (I.14). As is well known[1], in addition to the discrete (collective) spectrum, the discussed theory admits, as a rule, also of a continuous part of the spectrum.

The general causes of the (r, t) nonlocality of the fundamental relations (9), as is well known (see I), are the abbreviated description and the comparability of the scales of the processes with the internal ones. The internal scales are determined by the times and lengths τ_I and l_I of the structural elements of the medium[3] (the latter have internal degrees of freedom (energy, orientational, structural, and there is a set of similar characteristics). For example, in associated liquids, the structural elements of the medium are complexes combining about 10^3 molecules, and the (t, r) dispersion comes into play at frequencies $\omega \sim 10^{11}$ sec^{-1} and wave numbers $k \sim 10^7$ cm^{-1}; near the liquid-vapor transition, l_I is of the order of the average dimension of the density fluctuation, namely 10^{-5} cm; in the case of a turbulent medium, the internal scale is connected with the range and with the lifetime of the vortex, etc.

On the basis of Eqs. (8), together with the closed relations (9) and (10), we proceed to construct a semiphenomenological theory of RS processes. Let us discuss the production of entropy. In the lowest order in the amplitude, for the investigated dissipative systems, according to (3) and (4), we have (q = 0)

$$\delta S(t) = k_B n_0 \int d\mathbf{r}\, [c_\alpha^* \dot{c}_\alpha - \langle \hat{\Phi}, J\hat{\Phi} \rangle] \geqslant 0. \tag{18}$$

The production of entropy is expressed in terms of the MMQ via formulas (9) and (I.7). However, only the first term (in the parentheses) is expressed in terms of operators with transfer kernels and in terms of the relaxation frequencies that are contained in (9). (It is precisely this term which is considered in nonequlibrium thermodynamics.) Since, in addition, the second term is absent if the MMQ are conserved and is small if the number of MMQ is large[4], we confine ourselves to the first term. We assume the entropy principle in the form

$$\delta S(t) \sim \int d\mathbf{r} c_\alpha^* \dot{c}_\alpha = \frac{1}{2} \int d\mathbf{k}' X_A(\mathbf{k}-\mathbf{k}', t) \cdot K_{AB}(\mathbf{k}'t) * X_B(\mathbf{k}') + \text{c.c.} \geqslant 0. \tag{19}$$

For the investigated systems, it is expedient to formulate a dissipation principle as applied to Eqs. (8) and (9). It consists of the condition that the real part of the operator of the evolution of the medium (given by the system (8) and (9) be negative. Recognizing that the flux operator of the equations for the MMQ (a) is anti-Hermitian, the dissipation principle in the s and k representation takes the form

$$c_\alpha^* (d_{\alpha\beta} + d_{\beta\alpha}^*) c_\beta \geqslant 0. \tag{20}$$

This means that the real part of the $\dot{\mathscr{D}}$ matrix is positive. In an actual analysis it is useful to use the principle in the form of the condition that the spectrum of (8) and (9) be located in the left half-plane. In the case of small gradients and velocities, the criteria (19) and (20) coincide.

Let us dwell on the NKC symmetry properties. We use their representation in the Mori form[1]

$$K_{AB}(s\mathbf{kF}) = \langle \Phi_A^+, \hat{\mathscr{R}} \Phi_B \rangle, \quad \Phi_C = G_{i\gamma}, H_\gamma, \tag{21}$$

The known (index) symmetry of the kinetic Onsager coefficients and the (tensor) Curie symmetry in the case of RS processes take a more complicated form. The NK tensors will have the Onsager symmetry $K_{AB} = K_{BA}$ under the condition

$$\hat{\mathscr{R}}^+(s\mathbf{kF}) = \hat{\mathscr{R}}^*(s\mathbf{kF}), \tag{22}$$

which is quite restrictive. For Boltzmann systems without a field, Eq. (22) is satisfied and $K_{AB} = K_{BA}$[1]. It should be indicated that this result differs from the general Mori result[2] $K_{AB}(i\omega, k) = \epsilon_A \epsilon_B K_{BA}(i\omega, k)$, if $\epsilon_A \epsilon_B = -1$. The NKC tensor symmetry is determined by the symmetry of the system and of the external forces. Thus, for example, for isotropic systems the fourth-rank NK tensor has 12 nonzero components and 5 independent ones. It is useful to regard the symmetry of the complex conjugation of the NKC. For Boltzmann systems without forces, it takes the form $(I.37)_2$. This symmetry, jointly with the Onsager symmetry, is connected with the invariance of the complete description with respect to time reversal.

The discussion of the properties of the NKC and the derivation of approximate relations for them in a wide range of arguments is conveniently carried out by using the "exact moment form" of the NKC. It is obtained in the following manner. We supplement the MMQ set c_α with the quantities c_γ, the attributes of which Ψ_γ are formed, in accordance with the equation, with the aid of the formulas (15),

$$\Psi_\gamma = G_{i\alpha} / \langle G_{i\alpha}, G_{i\alpha} \rangle^{1/2}, \ H_\alpha / \langle H_\alpha, H_\alpha \rangle^{1/2}.$$

(We assume that the Ψ_γ are orthogonalized.) Equations (8) and (10) for the quantities c_α and c_γ take the form

$$sc_\alpha - \mathscr{E}_{\alpha\beta} c_\beta - c_\alpha(\mathbf{k}) = (\mathscr{E}_{\alpha\gamma}{}^F - i\mathbf{k} \cdot \mathbf{V}_{\alpha\gamma}) c_\gamma, \tag*{$(23)_1$}$$
$$sc_\gamma + [i\mathbf{k} \cdot \mathbf{V}_{\gamma\delta} + \mathscr{F}_{\gamma\delta} + d_{\gamma\delta}] c_\delta = (\mathscr{E}_{\gamma\beta}{}^F - i\mathbf{k} \cdot \mathbf{V}_{\gamma\beta}) c_\beta; \tag*{$(23)_2$}$$

β and δ run respectively through the same values as α and γ. We have assumed here q = 0 and have taken for c homogeneous initial conditions. Determining the quantities c_γ from (23) in terms of c_α and substituting them in $(23)_1$, we obtain exact moment expressions for the NK tensors, namely for the gradient tensors

$$K_{i\alpha,\,j\beta}(s\mathbf{k}\mathbf{F})=V_{\alpha i\delta}(\mathbf{k})\,V_{\gamma j\beta}(\mathbf{k})\,\Delta^{\gamma\delta}/\Delta, \tag{24}$$

for the relaxation-gradient tensors

$$K_{\alpha i\beta}=[V_{\alpha i\delta}\mathscr{E}_{\gamma\beta}{}^{F}+\mathscr{E}_{\alpha\delta}{}^{F}V_{\gamma i\beta}]\Delta^{\gamma\delta}/\Delta \tag{25}$$

and for the relaxation tensors

$$K_{\alpha\beta}{}^{h}=\mathscr{E}_{\alpha\delta}{}^{F}\mathscr{E}_{\gamma\beta}{}^{F}\Delta^{\gamma\delta}/\Delta, \tag{26}$$

where

$$\Delta(s\mathbf{k}\mathbf{F})=\|s\delta_{\gamma\delta}+i\mathbf{k}\mathbf{V}_{\gamma\delta}+\mathscr{F}_{\gamma\delta}+d_{\gamma\delta}\|, \tag{27}$$

and $\Delta^{\gamma\delta}$ is the cofactor5). The obtained expressions make it possible to establish in a manner simpler, than (12)—(14) a number of properties of NKC, for example, to reveal symmetries. They are quite convenient for the construction of a semiphenomenological theory. The factors $V_{\alpha i\delta}(\mathbf{k})\,V_{\gamma j\beta}(\mathbf{k})$, which can be called "structure factors" of the gradient NKC, do not depend on k in the case of a simple gas, and can be easily calculated; for a simple liquid they are obtained from Schofield's calculations[9] (their values coincide with the "gas" values as $k\to\infty$). It must be assumed that the anomalous behavior of the NKC near the phase-transition points is due to the singularities of the structure factors6).

In the derivation of suitable relations for the NKC in a wide range of the arguments, it is expedient to use the basic principles of non-equilibrium thermodynamics, modified with allowance for the high rates and the gradients, as well as relations that follow from the exact expressions. Let us make their content more precise.

1. Dissipativeness. This principle is closely connected with the stability criterion, and it is conveniently used in the form of a condition that the real part of the eigenvalues of Eqs. (8) and (9), which are the roots of the dispersion equation (17) be negative. These criteria can be applied also to the denominator of the NKC—to the function $\Delta(s\mathbf{k}\cdot\mathbf{F})$ (27), which is more convenient in applications.

2. Symmetry. We discuss symmetry using as an example an isotropic system such as a simple liquid. The kinetic theory specifies the symmetries (crossing and complex-conjugation) in the form

$$K_{AB}(s\mathbf{k})=K_{BA}(s\mathbf{k}),\quad \mathbf{k}_{AB}{}^{*}(s\mathbf{k})=\varepsilon_{A}\varepsilon_{B}K_{AB}(s^{*}\mathbf{k}), \tag{28}$$

which is analogous to the Boltzmann case[1]. From the second formula, recognizing that $K^{*}_{AB}(s\mathbf{k})=K_{AB}(s^{*},-\mathbf{k})$, it follows that the diagonal NKC are even functions of k, while the NKC which connects quantities of different parity are odd functions of k. For isotropic systems, the NK tensors have high tensor symmetry (see, e.g.,[10]). In particular, the NK tensor of second order has a structure

$$K_{ij}(s\mathbf{k})=\frac{k_ik_j}{k^2}K_L(s,|k|)+\left(\delta_{ij}-\frac{k_ik_j}{k^2}\right)K_{\perp}(s,|k|). \tag{29}$$

3. Asymptotic form. Weakly non-equilibrium case:

$$s'=s\tau_I,\quad k'=kl_I,\quad F'=F\tau_I/p_I\ll 1.$$

At zero values of the arguments, the NK tensors take on a well-known form[11]. Perturbation theory for small values of the arguments with ordering in powers of the gradients, is analogous to the well-known Chapman-Enskog method[1]; ordering in powers of ∂_t leads to a "temporal" variant of perturbation theory, which is intended for the study of the stationary regime (for example, problems in sound).

Weak-gradient rapid regimes: $k'\ll 1$, $s'\sim 1$. These regimes are described by a relaxation theory obtained by confining oneself in the fundamental relations (9) to terms of second order in the gradients. Perturbation theory for this case was discussed in[1]. The relaxation approximation is satisfactory when the transport time is much smaller than the "maximal" lifetime of the structure elements of the medium. For simple liquids (and gases), these times are of the same order, but this approximation can be used to describe the "tail" of the light-scattering spectrum. In the relaxation approximation, no account is taken of the structure of the media, since values of NKC at k = 0 and $K_{AB}(s0F)$ are used.

Ultrafast processes with large gradients: $s'\gg 1$, $k'\sim 1$. The principal term of the asymptotic form, $s\to\infty$, is calculated directly from formulas (12)—(14) and (16). We then obtain

$$K_{AB}(s\mathbf{k}\mathbf{F})\approx\langle\Phi_A{}^{+},\ \Phi_B\rangle/s, \tag{30}$$

$$d_{\nu\mu}s\mathbf{k}\mathbf{F})\approx\nu_{\nu\mu}-\frac{1}{s}[i\mathbf{k}\cdot\langle\mathbf{G}_{\nu}{}^{+},\mathbf{G}_{\mu}\rangle\cdot i\mathbf{k}-i\mathbf{k}\cdot(\langle\mathbf{G}_{\nu}{}^{+},H_{\mu}\rangle+\langle H_{\nu}{}^{+},\mathbf{G}_{\mu}\rangle)+\langle H_{\nu}{}^{+},H_{\mu}\rangle] \tag{31}$$

(ν and μ can take on the values of α from (11)—(16), and values of γ from $(23)_2$). Formula (30) indicates the principal term of the asymptotic form; it vanishes for the off-diagonal gradient NKC, while the next term $\sim s^2$ can be obtained by using (31) in the exact moment expressions for the NKC.

Steep-gradient regime: $k''\gg 1$. The correlation functions in terms of which the NKC are expressed are calculated with the aid of the expansions

$$\mathscr{R}_{\Psi\Phi}(s\mathbf{k}\mathbf{F})=\left\langle\Psi,\frac{1}{s+i\mathbf{k}\cdot\mathbf{v}+\nu}\sum_{n=0}\left[(\mathscr{E}+i\mathbf{k}\cdot\mathbf{V})\frac{1}{s+i\mathbf{k}\cdot\mathbf{v}+\nu}\right]^{n}\Phi\right\rangle, \tag{32}$$

$$\mathscr{R}^{(1)}_{\Psi\Phi}=\langle\Psi,[s+i\mathbf{k}\cdot\mathbf{v}+\nu]^{-1}\Phi\rangle,\ldots; \tag*{$(32)_1$}$$

the positive quantity ν has been introduced for convenience in the analysis of the cases s = −1, 0. It is assumed here that as $k\to\infty$ the system becomes "gas-like."7) Let us discuss the form of the NKC in the approximation $(32)_1$, for which the correlation function takes the form

$$\mathscr{R}^{(1)}_{\Psi\Phi}=\frac{1}{ikv_T}\int\frac{\langle\Psi,\Phi\delta_u\rangle}{u-z}du,\quad z=i\frac{s+\nu}{kv_T}, \tag{33}$$

where $\delta_u=\delta(u-v_3')$ and $u=u_3/v_T$. Using (33) with $s=-i\omega$ and with real k, and assuming the well-known regularization, we obtain in accordance with (12) for gradient NKC, in the case of longitudinal motion, the expressions

$$K^{as}_{\alpha\alpha}(-i\omega,k)\approx a_{\alpha}v_T/|k|,\quad K^{as}_{\alpha\beta}\approx ia_{\alpha\beta}v_T/|k|, \tag{34}$$

where $a_{\alpha,\alpha\beta}$ are constants that can be calculated.

4. Structure and connections between the NKC. The exact expressions (12)—(14) and (24)—(26) given above for the NKC reveal their structure. It is obvious that the NKC take the form of ratios with a common denominator. The algebraic form of the denominator (27) shows that its lowest degree in s should be not less than the number of "internal" relaxation processes in the system. Thus, in the case of the hydrodynamics of a simple liquid there are two internal relaxation processes for longitudinal motion—thermal flux and longitudinal viscous stress, and the lowest degree of the denominator is 2. Using expressions (24)—(27), we can indicate the connections between the NKC.

5. Sum rules. These rules and the relations for the

temporal moments were used in the discussion of the form of the correlation function in a number of papers[12-14]. The results can be used to determine the form of the NKC directly with the aid of formulas (12)—(14).

The principles and considerations indicated above, as well as the use of the exact moment form for the NKC, make it possible to choose for these coefficients suitable relations with experimentally-determined parameters. Direct measurement of the NKC is difficult, and information concerning these coefficients must be extracted from various tasks. The most convenient are data on sound propagation and the scattering of radiation or neutrons (in a maximal range of frequencies and scattering angles). These data compliment each other and are sufficient for the determination of the hydrodynamic NKC in the one-dimensional case. In an acoustic experiment, one usually measures the propagation constant $k(\omega) = k_r + ik_i$, with which the acoustic root of Eq. (17) is connected. The thermal branch is determined from the Rayleigh part of the density-density correlation function $\overline{n(-k)n(\omega, k)}$, where ω and k are proportional to the change of the energy and momentum upon scattering.

3. CONCERNING THE THEORY OF RAPID DIFFUSION

Let us consider a theory in which one MMQ is investigated, namely the theory of rapid diffusion (TRD). Such an MMQ can be the density, the energy, the transverse component of the velocity, or the angular (spin) momentum. Separation of one MMQ presupposes that its relaxation time is largest or that it is precisely this quantity which is observed in the experiment.

Various problems that fit naturally within the framework of the TRD have been discussed earlier (generalized Ohms law, diffusion of resonant radiation[15], low-temperature thermal conductivity[5], diffusion of neutrons in small assemblies[1,2], etc). Here we present a general formulation of the TRD, discuss the relations for the NKC, and also indicate the characteristic physical consequences of this theory.

The general equation of the TRD, according to (8) and (9), takes the form

$$\partial_t c - q_\Psi = -\nabla \cdot \delta \mathbf{j}_c - K_r * c + \mathbf{K}_F * \delta \mathbf{F}_e, \qquad (35)_1$$

$$\delta \mathbf{j}_c = -K_d^{(2)} * \nabla c + \mathbf{K}_{dr} * c + K_F^{(2)} * \delta \mathbf{F}_e. \qquad (35)_2$$

These equations contain the operators8) $K_d^{(2)}$, K_r, $K_F^{(2)}$, K_{dr}, and K_F, which represent diffusion, relaxation, "conductivity," diffusion-relaxation, and force, respectively. (The operators K_{dr} and K_F are apparently small as a rule; they vanish if Ψ is an eigenfunction of $\mathscr{E}^F$.) In the case of a conserved MMQ, only the first, current-dependent term remains in the right-hand side of $(35)_1$, and only the diffusion and force contributions remain in the current of $(35)_2$. In this case the dissipation-fluctuation relation (12) for the NK diffusion tensor takes the form

$$K_d^{(2)}(s\mathbf{k}\mathbf{F}) = \frac{\langle \mathbf{j}_\Psi^+, \mathscr{R}\mathbf{j}_\Psi \rangle}{s\langle \Psi, \mathscr{R}\Psi \rangle}, \quad \mathbf{j}_\Psi \equiv \hat{\mathbf{V}}(\mathbf{k})\Psi. \qquad (36)$$

The correlation functions of the quantity Ψ and of its current j_Ψ can be determined from experiment or from a numerical analysis.

There are a number of known effects in which the transport coefficients $K_{ij}^{\alpha}(skF)$ and K_{ij}^{F} are not at equilibrium for large values of the arguments. These manifest themselves most clearly in anomalous situations, when the disequilibrium is essential at small arguments. For small k, such an effect was observed in the case of diffusion of resonant radiation (Biberman (1947)[15]), for small s this situation was indicated by the author[2,16] in the case of systems with vanishing frequency, and the disequilibrium of the conductivity in weak fields was observed for these systems in[17]9).

The TRD spectrum is determined by the dispersion equation

$$D_{\mathrm{RD}}(s\mathbf{k}\mathbf{F}) = s - i\mathbf{k} \cdot K_d^{(2)} \cdot i\mathbf{k} + i\mathbf{k} \cdot \mathbf{K}_{dr} + K_r = 0. \qquad (37)$$

According to (37), at small k the diffusion mode (in the regular case) takes the form

$$s_1(\mathbf{k}F) = -\nu(F) - i\mathbf{k} \cdot K_{dr}(-\nu 0\mathbf{F}) - \mathbf{k} \cdot K_d^{(2)}(-\nu 0\mathbf{F}) \cdot \mathbf{k} + \ldots, \qquad (38)$$

$\nu(\mathbf{F}) \equiv K_r(-\nu 0\mathbf{F})$, (In the case of diffusion of resonant radiation[15] we have $s_1(k) \approx -\gamma |k|^m$, $0 < m < 1$.)

We consider next isotropic systems without a field. Formulas (24)—(26) then simplify and the diffusion and relaxation NKC take the form

$$K_{ij}{}^d(s\mathbf{k}) = V_{\Psi ii} V_{jj\Psi} \frac{\Delta^{ij}}{\Delta}, \quad K^r(s\mathbf{k}) = \nu_\Psi - \nu_{\Psi 4}\nu_{4\Psi} \frac{\Delta^{44}}{\Delta}, \qquad (39)$$

where $\Delta = \| \Delta_{\gamma\delta} \|$ is given by (27), and $\gamma, \delta = 1, \ldots, 4$;

$$V_{\Psi ij} = \delta_{ij} \langle \Psi, V_i \Psi_j \rangle; \quad \Psi_j = V_j \Psi / n_j, \quad \Psi_4 = \hat{J}\Psi / n_4.$$

In the regular case, the quantities $\nu_{4\Psi}$ are small; the terms containing them can be neglected and only the diffusion NKC need be used.

Let us dwell on the case of systems with a collision frequency that vanishes at certain energies (the gradients are small). From the results and formulas of[16,2] it is obvious that $k_{11}^d(s0)$ and $K^r(s0)$ are analytic functions if $\mathrm{Im}\, s \neq 0$; at $s = -\lambda \pm i0$ (λ real) they are equal to $K^{d,r}(-\lambda \pm i0) = K_r^{d,r}(-\lambda) \mp iK_i^{d,r}(-\lambda)$. The quantities $K^{d,r}(-\lambda)$ in the case $\nu(p) \approx \nu_*(p_T/p)^\gamma$ at $p/p_T \gg 1$ behave as $\lambda \to 0$ the following manner: $K_r(0) \neq 0$ and

$$K_i(-\lambda) \approx K_r{}^2(0)\varphi(\lambda)\gamma^{-1} \exp[-(\nu_0/\lambda)^{2/\gamma}]; \qquad (40)$$

$\varphi(\lambda)$ is a slowly varying factor. In cases when the collision frequency vanishes at finite energies10) $(p_0^2/2m)$, for example $\nu(p) \approx \nu_* |(p - p_0)/p_0|^\nu$ near p_0, where $\gamma < 1$, the quantities K_i take the form

$$K_i(-\lambda) \approx \frac{\pi}{\gamma} K_r{}^2(0) \exp\left(-\frac{p_0{}^2}{p_T{}^2}\right) \left(\frac{\nu_0}{\lambda}\right)^{1-1/\gamma}. \qquad (41)$$

Relations (40) and (41) determine the distribution (spectrum) of the long relaxation times. Expression (41) at $k = 0$ yields a damping law11) in the form $t^{-1/\gamma}$.

Let us consider the steep-gradient regime. The main contribution is made in this case by the diffusion term. According to (39), the diffusion NKC for one-dimensional motion is of the form

$$K_d(sk) = \frac{\chi(k)}{s + d_1(sk)} \qquad (42)$$

(it is assumed that Ψ is an almost intrinsic attribute, i.e., $\Psi_4 \sim 0$). The structure factor $\chi(k)$ depends noticeably on k only at $k \sim a^{-1}$ (a is the interaction radius) also in the vicinity of the phase transition; as $k \to \infty$ it becomes equal to the gas value $\chi_G = \langle \Psi\nu_1^2\Psi\rangle^2/n_1^2$.

The most interesting is the dynamic part $d_1(sk)$ of the NKC. Within the framework of the semiphenomenological theory, on the basis of the result of Sec. 2, we can assume for this quantity the following interpolation expression:

$$d_1(sk)=\nu_1\left[(1+a)+a\frac{-1+l_1^2k^2}{s\tau_2+(1+l_2^2k^2)^{1/2}}\right] \tag{43}$$

with five positive parameters, where $a < 1$. Obviously, the model (43) corresponds to two internal space-time scales $l_{1,2}$ and $\tau_{1,2}$. The frequency ν_1 is connected with the equilibrium value of the diffusion NKC: $K_d(-\nu 0) = \chi_0/(\nu_1 - \nu)$. The value of the complex $\nu_1 l_1^2 a/l_2$ is obtained from the steep-gradient limit of the NKC (34):

$$\nu_1 l_1^2 a/l_2=\chi_G/a_d v_T. \tag{44}$$

The remaining parameters are determined from the experimental data in the intermediate region. We shall assume henceforth for the sake of simplicity that $a = 1/2$ and, as a rule, will use the simple model $\tau_2 = 0$ and $l_1 = l_2$. We note that formula (43) ensures satisfaction of the dissipation condition (without limitations on the parameters).

Let us discuss the roots of the dispersion equation

$$s+\nu+k^2K_d(sk)=0. \tag{45}$$

In the approximation $d_1 \approx d_1(0k) \equiv \nu_1(k)$12) we obtain two trajectories:

$$s_{1,2}(k)=-\frac{\nu+\nu_1(k)}{2}\pm\left[\left(\frac{\nu+\nu_1(k)}{2}\right)^2-(k^2\chi+\nu\nu_1(k))\right]^{1/2}. \tag{46}$$

Obviously, $s_1(k)$ shifts to the left with increasing k. Starting with a certain value of k, it is possible to satisfy the inequality

$$(\nu+\nu_1(k))^2<4[k^2\chi(k)+\nu\nu_1(k)], \tag{47}$$

which denotes the presence of three "diffusion" waves13). The criterion (47) is verified simply as $k \to \infty$, when the gas model can be used, and takes the form

$$\chi_G<(2a_dv_T)^2. \tag{47'}$$

The use of (43) reduces (45) to a cubic equation in s with real coefficients at $\operatorname{Im} k = 0$. Criteria similar to (47) and (47′) are quite difficult to formulate for it. As $k \to \infty$, it takes the form

$$\Lambda^3\chi_G l_2+\Lambda^2(\chi_G\tau_2+\nu_1 l_1^2 a)+\Lambda l_2+\tau_2=0, \quad \Lambda\equiv k/s. \tag{48}$$

Obviously, its roots, $s(k)$ or $k(s)$, have an acoustic character, i.e., $s_n = k/\Lambda_n$.

Thus, if Eq. (45) has complex roots $s(k)$ (k is real) for "moderate" k, then free "diffusion" waves of the density, thermal, shear, and spin type can be observed. Their presence is revealed by the form of the correlation function: $\operatorname{Re} R_{\Psi\Psi}(sk) = \operatorname{Re} c(sk)/c_0(k)$. Thus, according to the TRD equation, in the approximation $d_1 \approx \nu_1(k)$, the correlation function has the pole form

$$\operatorname{Re} R_{\Psi\Psi}\equiv S_\Psi(\omega k)=\operatorname{Re}\frac{\nu_1(k)-i\omega}{s_2-s_1}\left[\frac{1}{s_1+i\omega}-\frac{1}{s_2+i\omega}\right]; \tag{49}$$

$s_{1,2}(k)$ are given by formula (46), which reveals the presence of $\operatorname{Im} s_{1,2}$. Diffusion waves other than density waves were discussed earlier, but an analysis of these essentially non-equilibrium phenomena calls for more perfect models, similar to those used in the present paper.

More amenable to observation are generated waves of frequency ω. They are described by a propagation constant, by the root $k(\omega)$ of Eq. (45) with the smallest value of $|\operatorname{Im} k|$; this constant can be used also to determine whether free waves are present. Within the framework of a simple model with $\chi = \text{const}$, this constant is given by

$$\begin{gathered} k^2(\omega)\approx-A(1+(1-B/A^2)^{1/2}], \\ A=\frac{s+\nu}{2\chi}[2s+\nu_1-\nu_1^2l^2(s+\nu)/4\chi], \quad B=\frac{s}{\nu^2}(s+\nu_1)(s+\nu)^2, \end{gathered} \tag{50}$$

$s = -i\omega$. From this we obtain at $\omega \gg \nu_1$

$$k^2(\omega)\approx\frac{\omega^2}{2\chi}[1-v_1^2+v_1(v_1^2-4)^{1/2}], \quad v_1\equiv\frac{\nu_1^2l^2}{4\chi} \tag{50'}$$

which is a relation of the acoustic type. The damping is obviously determined by the quantity $\operatorname{Im}(\nu_1^2 l^2 - 16\chi)^{1/2}$ (see (47′)).

Let us apply the TRD to the analysis of the (density) diffusion of neutrons. Experiment on the damping of the neutron momentum in assemblies of thickness h is usually described by the fall-off coefficient $\alpha = -s_1(k)$, $k \equiv B(h)$. The evolution of the momentum follows an $e^{-\alpha t}$ law. The mode with the smallest damping at small k is expressed in terms of the parameters of the theory that uses the model (43) in the following manner:

$$s_1(k)=-\nu-k^2\chi_0/(\nu_1-\nu)+\ldots \tag{51}$$

The coefficients of absorption, diffusion, and diffusion cooling (the coefficient of k^4) were determined for various media[20,21]; these coefficients yield the three parameters of the theory. For density diffusion we have $a_d = 1/\sqrt{\pi}$ and $\chi_G = v_T^2/2$, while relation (44) yields the value of the fourth parameter.

The parameters are best determined by using for $s_1(k)$ an expression that is suitable in a wide range. Within the framework of the simple model, we obtain from the experimental $\alpha(k)$ relation and from (44) for water[22] the following parameter values: $\nu = 4770\ \text{sec}^{-1}$, $\chi = \chi_G = v_T^2/2$, $v_T(27^\circ\text{C}) = 2.24 \cdot 10^5$ cm/sec, $\nu_1 = 6.8 \times 10^5\ \text{sec}^{-1}$, and $l = \sqrt{\pi}\, v_T/\nu_1$. The value of k ($= k_c$) starting with which (47) holds true is $k_c = 2.5\ \text{cm}^{-1}$. Thus, for assemblies of thickness $h_c < 0.7$ cm, the evolution of the momentum will follow the nonexponential law $\exp(-\alpha_r t)\cos\alpha_i t$. It is clear that such a law with $\alpha_i \neq 0$ points to the presence of free neutron waves. A similar analysis for graphite using the experimental data[23] makes it possible to represent satisfactorily the function $\alpha(k)$ by assuming $v_T = v_T(k)$. However, the resultant value $k_c \approx 0.3\ \text{cm}^{-1}$ is larger than the experimental $k_c \approx 0.09\ \text{cm}^{-1}$.

4. HYDRODYNAMICS OF FAST PROCESSES

Let us discuss the theory of fast processes of small amplitudes in molecular liquids and gases; in this theory, the MMQ are the density $\rho \sim c_0$, the velocity $u_i \sim c_i$, the internal energy per unit mass $\vartheta \sim c_4$, and the internal angular momentum $M_i \sim c_{i+4}$. These quantities are "conserved," with the exception of the last one, which is part of the total (conserved) angular momentum. In addition to the rotational (quasiclassical) degrees of freedom of the molecules, there can be excited in these systems also vibrational and other degrees of freedom. A constructive theory of the hydrodynamic type, which covers also steep-gradient regimes, had its initial development in[2,4,7,1]. Its original formalism was presented by Richardson (1960) and by Mori[3].

The equations of the hydrodynamics of fast processes (HFP), according to (8) and the tensor concepts, are the following:

$$\partial_t\rho_\alpha+i\mathbf{k}\cdot\mathbf{V}_{\alpha\beta}\rho_\beta-q_\alpha=-\dot{\rho}_\alpha,\quad \alpha=0,\ i,\ 4, \tag{52$_1$}$$

$$\partial_t M_i+\mathscr{F}_{ij}M_j-q_{i+4}=-\dot{M}_i, \tag{52$_2$}$$

where

$$\rho=(\rho,\ \mathbf{u},\ \vartheta),\quad \mathbf{V}_{\alpha\beta}=\langle\alpha',\ \mathbf{V}\beta'\rangle n_\alpha/n_\beta,\quad \mathscr{F}_{ij}=\langle i',\ \mathscr{F}j'\rangle n_i/n_j.$$

The closing relations (9) in the case of homogeneous fields take the form

$$-\dot{\mathbf{u}}=i\mathbf{k}\cdot\{\overset{(4)}{K}_{uu}\cdot\overset{(2)}{X}_1+\overset{(3)}{K}_{u\vartheta}\cdot\mathbf{X}_2+\overset{(4)}{K}_{uM}\cdot\overset{(2)}{X}_3-\overset{(3)}{K}_{uM}\cdot\mathbf{M}\}, \tag{53$_1$}$$

$$-\dot{\vartheta}=i\mathbf{k}\cdot\{\overset{(3)}{K}_{\vartheta u}\cdot\overset{(2)}{X}_1+\overset{(2)}{K}_{\vartheta\vartheta}\cdot\mathbf{X}_2+\overset{(3)}{K}_{\vartheta M}\cdot\overset{(2)}{X}_3-\overset{(2)}{K}_{\vartheta M}\cdot\mathbf{M}\}, \tag{53$_2$}$$

$$-\dot{\mathbf{M}}=i\mathbf{k}\cdot\{\overset{(4)}{K}_{Mu}\cdot\overset{(2)}{X}_1+\ldots\}-\sum_{L=u,\vartheta}\overset{(n_L+1)}{K}_{ML}\cdot\overset{(n_L)}{X}_L-\overset{(2)}{K}_{Mr}\cdot\mathbf{M}+\overset{(2)}{K}_{MF}\cdot\delta\mathbf{F}_e, \tag{53$_3$}$$

where $X_1^{(2)}\equiv\{ik_iu_j\}$, $\mathbf{X}_2=ik\vartheta$, $X_3^{(2)}=\{ik_iM_j\}$, and M are the forces. The following nonequilibrium-coefficient tensors are involved here: the viscosity; the "thermal conductivity" $K^{(2)}_{\vartheta\vartheta}$; the gyroviscosity $K^{(4)}_{MM}$; the viscous thermal conductivity $K^{(3)}_{\vartheta u}$; the gyro-shear viscosity $K^{(4)}_{uM}$; the gyrorelaxation viscosity $K^{(3)}_{uM}$; and the relaxation coefficient $K^{(2)}_{Mr}$; the thermal viscosity $K^{(3)}_{u\vartheta}$; the viscous thermal conductivity $K^{(3)}_{\vartheta u}$; the gyroshear viscosity $K^{(4)}_{uM}$; the gyrorelaxation viscosity $K^{(3)}_{uM}$; and the relaxation shear gyroviscosity $K^{(3)}_{Mu}$; the gyro-

The relations (53) greatly modify the known phenomenological laws[24,25] and point to many hitherto not considered contributions. In the viscous-stress tensor $\sigma^{(2)}$ defined by $-\dot{u}=\nabla\cdot\sigma^{(2)}$, and in the heat flux q defined by $\dot{\vartheta}=\nabla q$, the contributions from the thermal viscosity and viscous thermal conductivity were previously regarded on a par with the Barnett coefficients. The description of Scott's gyrothermal effect, which manifests itself in a sufficiently rarefied gas, calls for allowance for the thermal viscosity and for a discussion of its dependence on k and on the field. At large gradients, the off-diagonal terms are just as significant as the diagonal ones. The last terms in $(53)_{1,2}$ lead to the appearance of stresses and of a heat flow even if u and ϑ are homogeneous, since the angular momentum is inhomogeneous. In the phenomenological-theory[24,25] expression $(53)_3$ for M, use was made of equilibrium values of the third, fifth, and seventh terms; it was assumed there that

$$K^{jik}_{uM}(0)=K^{ijk}_{Mu}(0)/I=\nu_M\epsilon_{jik}/2,\quad K^{ij}_{Mr}(0)=\nu_M\delta_{ij},\quad \nu_M=4\zeta/\rho_0 I,$$

where ϵ_{ijk} is the Levi-Civita symbol. The nonequilibrium character of relation $(53)_3$ is significant if the angular momentum relaxation time greatly exceeds the relaxation time of the stress tensor. We note that when $(53)_3$ is used, it is necessary to take into account the conservation of the total angular momentum (in the absence of the field)

$$\partial_t\int d\mathbf{r}(\mathbf{M}+[\mathbf{r},\times\mathbf{u}])=0. \tag{54}$$

The latter imposes a limitation on the form of the corresponding tensors in the semiphenomenological approach.

Let us refine the behavior of the off-diagonal NKC as functions of k. Using the representation of the NK tensors in the form (21) and the resolvent identity (see footnote 2), we obtain

$$\begin{gathered}K^{(a+b)}_{AB}(s\mathbf{k}\mathbf{F})=-i\mathbf{k}K^{(a+b+1)}_{ABV}+K^{(a+b)}_{AB}(s0\mathbf{F}),\\ K^{(a+b+1)}_{ABV}=\langle\Phi_A{}'^{+},\hat{\mathscr{R}}_F\hat{\mathrm{V}}\hat{\mathscr{R}}\Phi_B{}'\rangle n_\alpha/n_\beta.\end{gathered} \tag{55}$$

Inasmuch (at least in the case of weak fields) by virtue of the tensor symmetry we have $\langle\Phi^+_A,\hat{\mathscr{R}}_F\Phi_B\rangle=0$, if $A\neq B$, the off-diagonal NKC vanish as $k\to 0$ and it is expedient to deal with the NK tensors K_{ABV} (of higher rank), which differ from zero at $k=0$. (It is precisely for these that we should use the names given above.)

Let us consider in greater detail the HFP of an isotropic liquid (gas) in which the vibrational degrees of freedom are excited but the rotational ones are immaterial. In this case, what is stationary is the equilibrium distribution $f_0=\{n_0\exp(-E_l/\vartheta_0)/\Omega\}$, and the attributes of the MMQ are as follows:

$$\Psi_0=\{\rho_0\},\quad \Psi_i=\left\{\sum_s^n p_{is}/m\right\},$$

$$\Psi_4=\left\{\sum_s E_{ls}-\langle E\rangle_0\right\}\Big/m,\quad n_i\equiv u_T,\quad n_4\equiv\vartheta_T.$$

The momentum and energy transport equations (52) (without sources) take the form

$$\rho_0\partial_t u_i+ik_iu_T\left(u_L(k)\rho+\frac{\rho_0}{\vartheta_T}u_{L\vartheta}(k)\vartheta\right)=-ik_j\pi_{ij}, \tag{56$_1$}$$

$$\rho_0\partial_t\vartheta+\frac{\rho_0}{u_T}u_{L\vartheta}(k)\vartheta_Tik_iu_i=-ik_iq_i, \tag{56$_2$}$$

where $u_L(k)=V_{330}(k)$ and $u_{L\vartheta}(k)=V_{334}(k)$ are the isothermal and thermal longitudinal velocities, respectively. The viscous-pressure tensor and the heat flux are expressed in terms of the MMQ in the following manner:

$$\pi_{ij}(t\mathbf{k})=-\eta_{ijlk}*ik_lu_k+ik_l\frac{u_T}{\vartheta_T}\chi_{kijl}*ik_l\vartheta, \tag{57$_1$}$$

$$q_i(t\mathbf{k})=ik_l\frac{\vartheta_T}{u_T}\chi_{lijk}*ik_ju_k-\lambda_{ij}*ik_j\vartheta. \tag{57$_2$}$$

We have used here the symmetry of the crossing NK tensors (28). The tensor symmetry of the NKC is perfectly analogous to that for a simple liquid[4]. The identification of $V_{\alpha\beta}(k)$ with the generalized thermodynamic quantities is realized in the same manner as in[4].

We start the derivation of suitable relations for the NK tensors by using the exact moment expressions that follow from the minimally expanded (according to the equation) macroscopic description. It reduces to supplementation of Eqs. (56) with equations similar to $(23)_2$ for π_{ij} and q_i. Inasmuch as (56) contains only the divergences of the fluxes $ik_j\pi_{ij}$ and ik_iq_i, the number of additional equations decreases to four. Solving them relative to the divergences, we arrive at relations analogous to (24). In the one-dimensional case of longitudinal motion (along z) the expanded system of attributes includes $\Psi_5=G_{33}$ and $\Psi_6=G_{34}$. For this case the NKC $\eta_{3333}\equiv\eta_L$ (longitudinal viscosity), $\lambda_{33}\equiv\lambda$, and $\chi_{3333}\equiv\chi$ take the form

$$\eta_L(sk)=\rho_0\chi_3(k)[s+d_6]/\Delta, \tag{58}$$

$$\lambda(sk)=\rho_0\chi_4(k)[s+d_5]/\Delta, \tag{59}$$

$$\chi(sk)=\rho_0\chi_{34}(k)W/\Delta, \tag{60}$$

where

$$\Delta(sk)=[s+d_5][s+d_6]+k^2W^2, \quad W(sk)\equiv V_{56}(k)+d_{56}/ik,$$

$$d_\gamma\equiv d_{\gamma\gamma}(sk), \quad \chi_\alpha\equiv V_{\alpha,\,\alpha+2}V_{\alpha+2,\alpha}, \quad \chi_{34}(k)=(\chi_3\chi_4)^{1/2}.$$

The quantities $V_{\alpha\beta}$ and the structure factors do not depend on k in the case of a gas; they were discussed in[4] for a simple liquid.

At small k and s, the NKC (58)–(60) reduce to their equilibrium values, and whereas the quantities $\eta_{10} = \chi_{30}/d_{50}$ and $\chi_0 = \chi_{40}/d_{60}$ are well known for many liquids, the thermal viscosity χ_0 was calculated only for a simple gas and will serve as an additional weak-gradient parameter. Its value can be obtained from data on ultrasound or on the scattering of radiation.

In the case of steep gradients $kv_T \gg \omega$, in accord with (34) and with allowance for expressions (58)–(60), we obtain the relations

$$\begin{aligned}\eta_L^{as}(k)/\rho_0&=\chi_3^G d_6^{as}/\Delta^{as}=a_3v_T/|k|,\\ \lambda^{as}(k)/\rho_0&=\chi_4^G d_5^{as}/\Delta^{as}=a_4v_T/|k|,\\ \chi^{as}(k)/\rho_0&=\chi_{34}^G W^{as}/\Delta^{as}=-a_{34}v_T/|k|.\end{aligned} \tag{61}$$

Here $a_3 = \sqrt{\pi}\,(0.2/\sqrt{6} + 1/3)$, $a_4 \doteq 1.2/\sqrt{\pi}$, and $a_{34} \doteq 0.2\sqrt{3}$; the quantities χ^G are calculated in accordance with the gas model. From (61) it follows that $d^{as}_{5,6}(k) = d_{5,6}|k|$ and $W^{as} = \text{const}$. The obvious relations

$$\chi^G_{3,4}\,d_{5,6}/(d_5d_6+W_{as}{}^2)=a_{3,4}v_T, \quad -\chi_{34}^G W_{as}/(\ldots)=a_{34}v_T \tag{62}$$

enable us to determine the three parameters.

Let us determine more concretely the form of the NKC by using model relations that connect their asymptotic values. First, we can take for $d_{5,6}(sk)$ an expression of the form (43). However, to decrease the number of parameters, it is expedient to choose $d_{5,6}(sk) \approx \nu_{3,4}(k)$; $\nu_{3,4}(k)$ can be interpolated by the very simple relation $\nu_{3,4}(k) = \nu_{3,4}(1 + l^2_{3,4}k^2)^{1/2}$, where $\nu_{3,4}$ are the relaxation frequencies of the viscous stresses and of the heat flux. The quantity $W^2(sk)$ can be interpolated by a rational-fraction function of the type

$$W^2(sk)=w_0^2(1+w_1s+w_2k^2+w_3s^2)/(1+w_4k^2+w_5s+w_6s^2), \tag{63}$$

where the parameters w_0, w_2/w_4, and w_3/w_6 are determined in accordance with the asymptotic relation in terms of the quantities χ_0, V^G_{56}, and $W(\infty, k)$. If we assume the structure factors to be known, we obtain a theory with 11 parameters; six of them are determined by the limiting values (three are calculated at $k \to \infty$). As a simple model we can assume $w_{1,3,5,6} = 0$ and $l_3 = l_4$; the use of this model does not require any experimental data in the intermediate region.

To determine the parameters in the expressions for the NKC, it is convenient to use experiments on the propagation of ultrasound and on the scattering of radiation or neutrons. In the latter, one customarily investigates the spectral density-density correlation function, which can be obtained by solving the one-dimensional equations (56) and (57):

$$S(\omega k)=2S(k)u_2u_T\,\mathrm{Re}\frac{(ik)^2}{s^2D(sk)}\left[s+\frac{k^2}{\rho_0}\chi(sk)\right], \quad s=-i\omega, \tag{64}$$

$$D(sk)=\left[s+\frac{k^2}{s}u_L+\frac{k^2}{\rho_0}\eta_L\right]\left[s+\frac{k^2}{\rho_0}\lambda\right]+k^2\left[u_{L\theta}-\frac{k^2}{\rho_0}\chi\right]^2; \tag{65}$$

S(k) is a structure factor. The function $S(\omega k)$ was measured and calculated for various media. For a simple gas it was determined from the scattering of light[26] and was calculated from the Boltzmann equation[27]; the values considered there were $\omega' \sim 1$ and $k' \sim 1$, for which ordinary hydrodynamics is not suitable. For liquids, the function $S(\omega k)$ was calculated by the molecular-dynamics method[28] and was determined from coherent neutron scattering[29] up to values $\omega \sim \nu_0$, $k \sim v_T\nu_0$, $\nu_0 \sim 10^{13}\ \text{sec}^{-1}$ (ν_0 is the "collision frequency" in the liquid). Data on hypersound, suitable for the determination of the parameters, are available only for gases[30]; frequencies $\omega' \sim 10$ were attained in them. Similar regimes, $k' \lesssim 10$ and $\omega' \lesssim 10$, can be described within the framework of the HFP. We note that the HFP based on radiation-scattering data makes it possible, in the case of liquid, to analyze hypersound in a region that is not accessible to modern experiment.

When choosing the values of the parameters, account must be taken of the restrictions imposed on them by the dissipation condition. In the assumed model (63), this condition as applied to the denominator of the NKC (60) is equivalent to the Routh-Hurwitz criterion for the polynomial

$$w_6s^4+b_1s^3+b_2s^2+b_3s+b_4, \quad b_1=w_5+(\nu_1(k)+\nu_2(k))w_6,\ldots$$

and leads to the system of inequalities

$$w_6>0, \quad w_5>0, \quad w_3>-l_3l_4/w_0^2, \quad w_2<w_4w_3/w_6,\ldots \tag{66}$$

Let us specify more concretely the values of the NKC parameters (58)–(60) for a monatomic gas within the framework of the simple model. The equilibrium values of the NKC are known[31]:

$$\eta_{L0}=\frac{\chi_3}{\nu_3}\rho_0=\frac{4}{3}\eta, \quad \lambda_0=\frac{\rho_0\chi_4}{\nu_4}=\frac{\lambda_T}{c_v}, \quad \chi_0=\frac{\rho_0\chi_{34}W_0}{\nu_3\nu_4}=\frac{\bar{\omega}_3\eta_0^2}{\rho_0}. \tag{67}$$

Here η is the shear viscosity, λ_T is the thermal conductivity, $\nu_4 \doteq 2\nu_3/3$, $\bar{\omega}_3 \approx 2.7$, $W_0 = -2v_T/\sqrt{15} + (d_{56}/ik)_0 = 2\bar{\omega}_3v_T/3\sqrt{15}$. The steep-gradient asymptotic expression (62) yields the values of the parameters $l_{3,4}$ and w_2/w_4. To choose the latter parameter w_2 we need one experimental point from the region of the mean values of k. To this end we can use the calculated values of $S(\omega k)$[27]; for example, we can take the point $\omega = 0$ and $k' = 1$. The value of w_2' obtained thereby will be suitable for all monatomic gases in a wide range of temperatures and pressures. It must be recognized that at rather high frequencies, $\omega' > 1$, it becomes apparently necessary to use expression (63) for W(sk); the additional parameters are best determined from an acoustic experiment[30].

In conclusion, let us consider the shear flow of a simple liquid (gas). The velocity $u_1(tz)$ is determined by the expression

$$\partial_t u_1(tz)=\partial_z\int dz'\int_0^t dt'\,\eta_\perp(t-t',z-z')\,\partial_{z'}u_1(t'z') \tag{68}$$

and by the corresponding boundary conditions. (In the simplest case $u_1(t0) = \varphi(t)$, where $\varphi(t)$ is determined by the law of motion of an infinite plane; for a pulsed regime $\varphi(t) = \delta(t)$ and for a stationary regime $\varphi(t) \sim \cos\omega t$.) Just as in the problem of free shear, it is convenient here to use the (semi-spatial) Laplace-Fourier representation

$$su_1(sk)=-k^2\eta_\perp(sk)u_1-ik(\eta_\perp * u_1)_{z=0}(s)-(\eta_\perp * u_1)'_{z=0}(s)+u_1(t=0,k). \tag{69}$$

The shear-viscosity NKC assumes in accordance with (42) the form

$$\eta_\perp(sk)=\rho_0\chi_\perp(k)\,/\,[s+d_1(sk)], \tag{70}$$

with $\rho_0\chi_\perp(k) = C_{44}(k)$[9,4]; $d_1(sk)$ can be taken in the form (43).

We confine ourselves to the first stage of the discussed problem—the determination of the zeroes of the dispersion equation (the solution of the stationary problem consists of finding the roots $k = k(\omega)$). Using the approximation $d_1 \approx \nu_1(k)$ and assuming for $\nu_1(k)$ the interpolation dependence (3.20) of[4], we obtain the zeroes of $s_{1,2}(k)$ in accordance with formula (46) at $\nu = 0$. Let us discuss the question of the shear waves with the aid of this relation. According to the condition (47), the criterion for the appearance of free waves takes at $\nu = 0$ the form

$$\nu_1{}^2(k)=2k^2\chi_\perp(k)+[\nu_{10}{}^2-2k^2(\chi_\perp(k)-v_0{}^2)](1+k^2/k_0{}^2)^{-1}=4k^2\chi_\perp(k). \tag{71}$$

From the character of the behavior of $\chi_\perp(k)$[4] it is clear that this equation has a unique root; for liquid argon, its value, according to the data of[4], is $k_c \approx 1.9 \times 10^7\ \text{cm}^{-1}$. Thus, the shear waves in liquid argon can be regarded as observable.

In concluding the discussion of the theory of RS processes, which was proposed in this paper, it should be noted that it can be used as a basis for the construction of a general phenomenological theory of linear processes in very complicated media, whose structure elements are conglomerates of more than 10^6 molecules.

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[1] We use this notation for the formulas of [1].

[2] In the derivation of these formulas and in other places we used the operator identity $(A - B)^{-1} - A^{-1} = A^{-1}B(A - B)^{-1} = (A - B)^{-1}BA^{-1}$. From this identity follows the formula $\hat{\mathscr{R}}=[I+\mathscr{R}P\mathscr{E}]^{-1}\mathscr{R}$, which is indicated in [1] in distorted form.

[3] They can be particles and quasiparticles, clusters, domains, turbons, and other formations.

[4] This, of course, does not mean that it is small in the general case.

[5] The employed scheme can be regarded as a generalization and verification of the Leontovich-Mandel'shtam construction of the relaxation theory [6]; the c_γ play the role of the internal parameters.

[6] The anomalous behavior of the NKC as a result of the singularity of the quantities $d_{\alpha\beta}$ is usually connected with the "kinetic" singularities of the systems.

[7] This hypothesis was used earlier in the study of liquids [12,7,4].

[8] Of course, their meanings and designations are determined by the considered MMQ.

[9] An appreciable time dispersion of the relaxation coefficient was demonstrated by a recent experiment on spin-echo damping [18].

[10] For example, in the case of Ramsauer transport of electrons in a gas.

[11] This damping can be slower than the spatial damping $t^{-n/2}$ [16].

[12] This means that the relaxation time of the first internal process is much larger than that of the second one.

[13] In the kinetic diffusion picture in a gas they correspond to a continuous spectrum of s off the real axis; the appearance of the imaginary part is connected with the fact that the trajectory reaches the continuum at $k = k_{\lim}$ [2,16,19].

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Translated by J. G. Adashko
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