HYDRODYNAMICAL FIELD FLUCTUATIONS IN A NON-EQUILIBRIUM QUASI-STATIONARY STATE DUE TO A TEMPERATURE GRADIENT

I. GENERAL THEORY*

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We consider a system in a state of non-equilibrium due to the introduction of a temperature gradient. The essential problem of this paper is to determine, in their most general form, the fluctuation correlation functions for hydrodynamical fields. We use a notation which enables us to distinguish the contributions from the individual mechanisms: contributions from fluctuations in number density, momentum and energy; contributions appearing due to having taken into account fluctuations in sound velocity and the heat conductivity coefficient; and ones related with the presence of the temperature gradient.

1. Introduction

One of the essential problems of the theory of irreversible processes concerns the influence of various perturbations on the thermodynamical equilibrium of systems. Two kinds of perturbations – mechanical and thermal – are generally distinguished in the statistical thermodynamics of irreversible processes [1]. According to Kubo's terminology [2, 3], mechanical perturbations originate in the influence of external (e.g., electric) fields, an action that can be accounted for by including a term describing the interaction of the external field and the system into the Hamiltonian.

However, there exists a vast class of "thermal" perturbations, related with

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spatial inhomogeneities in the system. Their influence on the system is not directly accessible to an interpretation within the framework of Kubo's theory. The spatial inhomogeneities lead to the emergence of fluxes of matter, momentum and energy, tending to make the system homogeneous. Transport coefficients, such as the viscosity, diffusion and heat conductivity coefficients, are the result of perturbations of this kind.

On the microscopic level, processes involving mechanical perturbations differ essentially from processes due to thermal perturbations. On the macroscopic level, this distinction becomes inessential since all the transport coefficients irrespective of the type of perturbation can be expressed as integrals of the correlation functions of the microscopic fluxes (by the Green–Kubo formulae). Within the same framework, the fluctuational–dissipative theorem strictly related with the Onsager hypothesis [4] concerning the shape of fluctuation decay has successfully been extended to thermal perturbations. The hypothesis states that the behaviour of the system (or a part thereof) at non-equilibrium (albeit sufficiently close to equilibrium) is the same irrespective of whether its momentary state is due to the action of external forces or to a spontaneous fluctuation. This is of essential significance when it comes to establishing equations describing the evolution of systems with local inhomogeneities due to fluctuations. On the macroscopic level, non-equilibrium systems consisting of great numbers of identical atoms or molecules are described in terms of equations of motion of several macroscopic quantities. The form of these equations depends on what kind of system we are dealing with and on the conditions of its existence. It is at this point that Bogolubov's hierarchisation concept of relaxation times in non-equilibrium statistical thermodynamics becomes essential [5]. According to Bogolubov, a non-equilibrium system in its initial stage requires, in general, a great number of many-body distribution functions for its description. After a short time τ_c (of the order of intermolecular collisions), it attains a kinetical stage, characterized by a single-body distribution function. At this stage of description, kinetic equations related with the processes occurring during the time τ_r (of the order of the time of the free motion of a molecule between successive collisions) are established. Whereas the inhomogeneities arising due to fluctuations concern a system that is in the hydrodynamical stage (governed by the relaxation time τ_h). In simple fluids, within the Bogolyubov framework, the relaxation times fulfil the inequality $\tau_c \ll \tau_r \ll \tau_h$. Moreover, no processes of energy transfer between the translational and internal degrees of freedom are assumed to take place. In this way we neglect relaxation effects dependent on the microscopic structure of molecular fluids.

The system is moreover assumed to be sufficiently remote from its critical point for effects typical of near-criticality to be absent. The fundamentals of

the theory of effects occurring in fluids near the critical point have been proposed by Smoluchowski [6]. In recent years the theory has been considerably developed by Kociński [7]. With the above assumptions on the system, the hydrodynamical stage is characterized by the so-called normal distribution function of the number density of molecules, the momentum density, and the energy density. The preceding quantities are functions of the time and positions, and determine respectively the following hydrodynamical fields: the scalar fields of the number density of molecules and of the energy (temperature field), as well as the vector field of momentum density.

In simple liquids the fluctuations of the hydrodynamical fields are typically of the order of 10^3Å in size and thus greatly in excess of the intermolecular distances. They give rise to collective motions of great numbers of molecules setting free dissipative fluxes connected with viscosity and Joule–Lenz heat. The regions of inhomogeneity in the medium (determined by the size of the fluctuations) are very small compared with the size of the system as a whole, but are sufficiently large to admit of a description in terms of the laws of macroscopic physics: hydrodynamics and thermodynamics.

With regard to their size in space and the time-scale of their existence, the hydrodynamical field fluctuations are connected with a variety of phenomena occurring in the medium. Thus, studies of these fluctuations are a source of highly essential data concerning the system and especially the transport processes in the latter. Especial attention is given to fluctuations in number density [8] because the spectral density of their correlation function is proportional to the structural factor directly related with quantities that are measurable (light and neutron scattering). There are many ways of calculating the fluctuation correlation functions of the hydrodynamical fields leading to results of a form permitting their experimental verification. These methods are based on equations of motion, from simple phenomenological equations up to the equations of generalized statistical thermodynamics comprising effects of "memory" as well as renormalization of the transport coefficients. Reviews of the theoretical methods and respective experiments are due, e.g., to Berne and Pecora [9], Crosignani, Di Porto and Bertolotti [10], Lallemand [11] and Kielich [12].

Some years ago, a number of papers have appeared, dealing with the spectrum of hydrodynamical fluctuations in fluids at non-equilibrium stationary state. The results are discussed within the framework of light scattering theory. The state of non-equilibrium is obtained by imposing a temperature gradient, or a flow velocity gradient. In most cases, the authors apply methods of fluctuation hydrodynamics based on determining the equations of motion for the mean value of the respective variable [13–15], whereas others use the method involving an intermediate linear reaction [16, 17] or that of kinetic equation theory [18]. All these publications fall in two groups: in one, the

equations of motion are established first whereas the fluctuation correlation functions are calculated next, as well as the experimental consequences. In the other, a precise form of the equations of motion is assumed at the very start, and the procedure is restricted to the last two steps; this is justified inasmuch as in either case relationships derivable from the phenomenological hydrodynamical equations are used for calculating the correlation function. This, in fact, is the Landau–Lifshitz method, involving linearization of the hydrodynamical equations with respect to the steady state and supplementing the relationships thus obtained with stochastic terms, containing the stress tensor and heat flow vector. Finally, this leads to equations of the Langevin type.

It is our present aim to determine, in the most general manner, the fluctuation correlation functions for hydrodynamical fields in simple fluids. In section 2 we introduce the generalized Langevin equation of Grabert [19] using the method of projection operators. Next, on making certain assumptions, we obtain a set of equations of motion for the fluctuations of the hydrodynamical fields in atomic fluids. We use a notation (underlining certain expressions) which enables us to distinguish the contributions from the individual mechanisms. In section 3 we go over to variables k, ω in our formulae and calculate the respective fluctuation correlation functions of the hydrodynamical fields. Section 3, moreover, contains a description of the path followed by us when deriving the stochastic terms of the correlation functions for the equations of motion. Since the functional coefficients obtained are rather bulky in form, appendix A gives an appropriate tabulation aimed at abridging their notation. The results obtained with an accuracy to terms in q^2 when deriving the frequency dispersion equation are written out explicitly in appendix B.

2. Stochastic functions describing the hydrodynamical field fluctuations

The possibility of applying Langevin-like equations to the treatment of non-equilibrium fluctuations (non-equilibrium with respect to local equilibrium) was first considered by Keizer [20]. Subsequently, their applicability has been considered from different standpoints by Hinton [21], Onuki [22] and Ueyama [23]. Grabert [19], on the other hand, starts from Liouville's equation and applies the operator projection method to derive a generalized Langevin equation for fluctuations of macroscopic quantities on the level of generalized statistical thermodynamics. In the case of a simple atomic fluid of interest to us the equations take the following form:

$$\frac{\partial}{\partial t} \delta n = -\frac{1}{m} \sum_{\nu} \frac{\partial}{\partial x^{\nu}} \delta g^{\nu} , \tag{1}$$
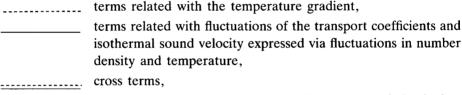
$$\frac{\partial}{\partial t}\,\delta g^{\nu} = -\sum_{\mu} \frac{\partial}{\partial x^{\mu}}\,[v^{\nu}\,\delta g^{\mu} + v^{\mu}\,\delta g^{\nu} - mv^{\nu}v^{\mu}\,\delta n] - \frac{\partial}{\partial x^{\nu}}\,\delta p$$

$$+ \frac{\partial}{\partial x^{\nu}}\left[\sum_{\mu}\frac{\partial v^{\mu}}{\partial x^{\mu}}\,(\delta\zeta - \tfrac{2}{3}\delta\eta) + (\zeta - \tfrac{2}{3}\eta)\,\frac{\partial}{\partial x^{\mu}}\,\delta v^{\mu}\right]$$

$$+ \sum_{\mu}\frac{\partial}{\partial x^{\mu}}\left[\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right)\delta\eta + \eta\left(\frac{\partial}{\partial x^{\mu}}\,\delta v^{\nu} + \frac{\partial}{\partial x^{\nu}}\,\delta v^{\mu}\right)\right]$$

$$- \sum_{\mu}\frac{\partial}{\partial x^{\mu}}\,\xi^{\nu\mu}\,, \tag{2}$$

$$\frac{\partial}{\partial t}\,\delta e = -\sum_{\nu}\frac{\partial}{\partial x^{\nu}}\,[v^{\nu}(\delta e + \delta p) + (\langle e\rangle + p)\,\delta v^{\nu}]$$

$$+ \sum_{\nu}\frac{\partial}{\partial x^{\nu}}\left[\frac{\partial T}{\partial x^{\nu}}\,\delta\kappa + \kappa\,\frac{\partial}{\partial x^{\nu}}\,\delta T\right]$$

$$+ \sum_{\nu,\mu}\frac{\partial}{\partial x^{\nu}}\left[v^{\nu}\frac{\partial v^{\mu}}{\partial x^{\mu}}\,(\delta\zeta - \tfrac{2}{3}\delta\eta) + (\zeta - \tfrac{2}{3}\eta)v^{\nu}\,\frac{\partial}{\partial x^{\mu}}\,\delta v^{\mu}\right.$$

$$\left. + (\zeta - \tfrac{2}{3}\eta)\,\frac{\partial v^{\mu}}{\partial x^{\mu}}\,\delta v^{\nu}\right]$$

$$+ \sum_{\nu,\mu}\frac{\partial}{\partial x^{\nu}}\left[\left(\frac{\partial v^{\nu}}{\partial x^{\mu}} + \frac{\partial v^{\mu}}{\partial x^{\nu}}\right)(v^{\mu}\,\delta\eta + \eta\,\delta v^{\mu})\right.$$

$$\left. + \eta v^{\mu}\left(\frac{\partial}{\partial x^{\mu}}\,\delta v^{\nu} + \frac{\partial}{\partial x^{\nu}}\,\delta v^{\mu}\right)\right]$$

$$- \sum_{\nu}\frac{\partial}{\partial x^{\nu}}\left[\sum_{\mu}\xi^{\nu\mu}v^{\mu} + \xi_{T}^{\nu}\right], \tag{3}$$

with: n the number density of atoms, g^{ν} the momentum density coordinate, e the energy density, p the pressure, v^{ν} the velocity coordinate, T the temperature, ζ the coefficient of the bulk viscosity (also referred to as second viscosity), η the dynamical viscosity coefficient (dynamical viscosity), κ the heat conduction coefficient, $\xi^{\nu\mu}$ the coordinate of stress tensor fluctuation, ξ_{T}^{ν} the coordinate of the fluctuation vector of the thermal energy flux, and m the atomic mass. The superscripts ν, μ denote Cartesian variables.

The above are linear equations of motion for the fluctuations in number density of atoms δn, in momentum density δg and in energy density δe. The fluctuations occur in a fluid in motion with the velocity $\boldsymbol{v}$, at non-equilibrium stationary state.

Let us consider a quiescent atomic fluid ($\boldsymbol{v} = \boldsymbol{0}$) in a weakly non-equilibrium, quasi-stationary state caused by a temperature gradient. Earlier, we had assumed the system to evolve towards the state of complete thermodynamical

equilibrium during a time much longer than all the relaxation times of fluctuations about the steady state. This enables us to deal with the quantities of interest as fulfilling, in the steady state, relations of the form specific for the state of equilibrium. It is our aim to derive the fluctuation spectrum of the hydrodynamical fields taking into account the greatest possible number of contributions, due to the effect of the temperature gradient on the viscosity coefficients, the heat conductivity coefficient, as well as the isothermal sound velocity (pressure). Moreover, we shall take into account the fluctuations of these quantities expressed in terms of fluctuations in number density and temperature. Within the above framework and for the sake of maximal generality we shall not restrict ourselves to the isothermal approximation but shall solve the set of all the five equations (1)–(3). In order to distinguish the individual contributions more easily, we have introduced the following underlinings:

---------------   terms related with the temperature gradient,

_____   terms related with fluctuations of the transport coefficients and isothermal sound velocity expressed via fluctuations in number density and temperature,

---------------   cross terms,

non-underlined are terms related with the basic fluctuations of the hydrodynamical fields.

To make eqs. (1)–(3) solvable we apply certain simple thermodynamical relations enabling us to express the fluctuations in energy density and pressure by way of fluctuations in temperature and number density of atoms [9]:

$$\delta e - \frac{e_{ss} + p_{ss}}{n_0} \delta n = -mn_0 c_V \left(\frac{\gamma - 1}{\alpha n_0} \delta n - \delta T \right), \tag{4}$$

$$\delta p = mc_T^2 (\delta n + \alpha n_0 \delta T), \tag{5}$$

where α is the volume coefficient of thermal dilatation, and γ the Poisson coefficient (the ratio c_p/c_v of the specific heat at constant pressure and at constant volume). The subscripts "ss" and "0" denote respectively steady state values and ones taken at complete thermodynamical equilibrium. Moreover, we express the fluctuations in momentum density in terms of fluctuations in the rate of flow δv:

$$\delta g^\nu = mn_0 \delta v^\nu. \tag{6}$$

The assumptions made when deriving eqs. (1)–(3) enable us to write the

transport coefficients, the temperature, the isothermal sound velocity c_T and the rate of flow in a given point of space r as follows:

$$f(r) = f_0 + \left(\frac{\partial f}{\partial T}\right) \nabla T \cdot r + \left(\frac{\partial f}{\partial T}\right) \delta T + \left(\frac{\partial f}{\partial n}\right) \delta n \, , \tag{7}$$

for f respectively equalling η, ζ, κ and c_T^2. Whereas for the temperature and velocity we have

$$T(r) = T_0 + \nabla T \cdot r + \delta T \, , \tag{8}$$

$$v_{ss}(r) = 0 \, . \tag{9}$$

For brevity, we introduce the following notation:

$$D_v = \frac{\zeta + \frac{4}{3}\eta}{mn_0} \quad \text{(longitudinal kinematic viscosity)} \, , \tag{10}$$

$$D_T = \frac{\kappa}{mn_0 c_p} \quad \text{(heat diffusion coefficient)} \, , \tag{11}$$

$$\Psi = \nabla \cdot \delta v \, , \tag{12}$$

$$\zeta' = \frac{\zeta}{mn_0} \, , \tag{13}$$

$$D_v' = 2 \frac{\zeta + \frac{2}{3}n}{mn_0} \, , \tag{14}$$

$$\xi' = \frac{1}{mn_0} \xi \, , \tag{15}$$

$$\xi_T' = \frac{1}{mn_0 c_v} \xi_T \, , \tag{16}$$

With regard to (4)–(16) and on introducing the operator nabla ∇ eqs. (1)–(3) become

$$\delta \dot{n} + n_0 \Psi = 0 \, , \tag{17}$$

$$\dot{\Psi} = -\frac{c_T^2}{n_0} \nabla^2 \delta n + D_v \nabla^2 \Psi - \alpha c_T^2 \nabla^2 \delta T - \frac{1}{n_0} \left(\frac{\partial c_T^2}{\partial T}\right)(\nabla T \cdot r) \nabla^2 \delta n$$

$$- \left(\frac{\partial D_v}{\partial T}\right)(\nabla T \cdot r) \nabla^2 \Psi - \alpha \left(\frac{\partial c_T^2}{\partial T}\right)(\nabla T \cdot r) \nabla^2 \delta T$$

$$+ \left(\frac{\partial \zeta'}{\partial T} \right) \nabla^2 (\nabla T \cdot r) \Psi - \alpha \left(\frac{\partial c_T^2}{\partial n} \right) \nabla^2 (\nabla T \cdot r) \, \delta n$$

$$- \alpha \left(\frac{\partial c_T^2}{\partial T} \right) \nabla^2 (\nabla T \cdot r) \, \delta T + \left(\frac{\partial D_v'}{\partial T} \right) \nabla (\nabla T \cdot r) \cdot \nabla \Psi$$

$$+ \left(\frac{\partial^2 \zeta'}{\partial T^2} \right) \nabla (\nabla T \cdot r) \cdot \nabla (\nabla T \cdot r) \Psi - \alpha c_T^2 \, \nabla^2 (\nabla T \cdot r)$$

$$- \alpha \left(\frac{\partial c_T^2}{\partial T} \right) (\nabla T \cdot r) \, \nabla^2 (\nabla T \cdot r) - \nabla \cdot \xi' \cdot \nabla , \tag{18}$$

$$\delta \dot{T} = - \frac{\gamma - 1}{\alpha} \Psi + \gamma D_T \, \nabla^2 \, \delta T + \left(\frac{\partial \gamma D_T}{\partial n} \right) (\nabla^2 T) \, \delta n + \left(\frac{\partial \gamma D_T}{\partial T} \right) (\nabla^2 T) \, \delta T$$

$$+ \frac{1}{3} \left(\frac{\partial \gamma D_T}{\partial n} \right) \nabla T \cdot \nabla \, \delta n - \frac{1}{3} \left(\frac{\partial \gamma D_T}{\partial T} \right) \nabla T \cdot \nabla \, \delta T$$

$$+ \frac{1}{3} \left(\frac{\partial \gamma D_T}{\partial T} \right) \nabla (\nabla T \cdot r) \cdot \nabla \, \delta T + \frac{1}{3} \left(\frac{\partial^2 \gamma D_T}{\partial T \, \partial n} \right) \nabla T \cdot \nabla (\nabla T \cdot r) \, \delta n$$

$$+ \frac{1}{3} \left(\frac{\partial^2 \gamma D_T}{\partial T^2} \right) \nabla T \cdot \nabla (\nabla T \cdot r) \, \delta T + \gamma D_T \, \nabla^2 T$$

$$+ \frac{1}{3} \left(\frac{\partial \gamma D_T}{\partial T} \right) \nabla (\nabla T \cdot r) \cdot \nabla T - \nabla \cdot \xi_T' . \tag{19}$$

Eqs. (17)–(19) form a set of three equations of the Langevin type of the hydrodynamical fluctuations occurring in the atomic fluid. The system is in a weakly non-equilibrium quasi-stationary state due to the presence of the temperature gradient. The latter has the meaning of an external generalized thermodynamical force.

3. Correlation functions of the hydrodynamical field fluctuations

The expressions (17)–(19) are linear equations, derivable from the phenomenological equations of hydrodynamics for momentary values of the hydrodynamical variables. Quite obviously, these equations differ from those describing equilibrium fluctuations in that they contain terms which take into account the influence of the temperature gradient and hydrodynamical fluctuations on the transport and sound velocity coefficients. One notes that, in contradistinction to the terms expressing the dependence on the temperature gradient, those related with the influence of the fluctuations on the transport and sound velocity coefficients do not occur as mutually independent quan-

tities. One moreover notes that eq. (18) contains no terms describing the influence of fluctuations in the transport coefficients. This is due to our assumption that the fluid does not flow as a whole, and the expressions in question always occur as products of the flow rate in the initial equation (2).

The set (17)–(19) will serve to determine the correlation function of hydrodynamical field fluctuations. To this aim, we rewrite the equations in matrix form:

$$\mathbf{M}\begin{pmatrix} \delta n \\ \Psi \\ \delta T \end{pmatrix} = - \begin{pmatrix} 0 \\ \nabla \cdot \boldsymbol{\xi}' \cdot \nabla \\ \nabla \cdot \boldsymbol{\xi}_T \end{pmatrix} + \mathbf{N} , \tag{20}$$

involving the matrices $\mathbf{M}$ and $\mathbf{N}$:

$$\mathbf{M} = \mathbf{A} + \mathbf{B}(\nabla T \cdot r)\, \nabla^2 + \mathbf{C}\, \nabla^2(\nabla T \cdot r) + \mathbf{D}\, \nabla(\nabla T \cdot r)\, \nabla + \mathbf{E}[\nabla(\nabla T \cdot r)]^2 , \tag{21}$$

$$\mathbf{N} = \mathbf{F}\, \nabla^2(\nabla T \cdot r) + \mathbf{G}(\nabla T \cdot r)\, \nabla^2(\nabla T \cdot r) + \mathbf{H}[\nabla(\nabla T \cdot r)]^2 , \tag{22}$$

where

$$\mathbf{A} = \begin{pmatrix} \dfrac{\partial}{\partial t} & n_0 & 0 \\[2ex] \dfrac{1}{n_0}\, c_T^2\, \nabla^2 & \dfrac{\partial}{\partial t} - D_v\, \nabla^2 & \alpha c_T^2\, \nabla^2 \\[2ex] 0 & \dfrac{1}{\alpha}\,(\gamma - 1) & \dfrac{\partial}{\partial t} - \gamma D_T\, \nabla^2 \end{pmatrix} ,$$

$$\mathbf{B} = \begin{pmatrix} 0 & 0 & 0 \\[2ex] \dfrac{1}{n_0}\left(\dfrac{\partial c_T^2}{\partial T}\right) & \left(\dfrac{\partial D_v}{\partial T}\right) & \alpha\left(\dfrac{\partial c_T^2}{\partial T}\right) \\[2ex] 0 & 0 & 0 \end{pmatrix} ,$$

$$\mathbf{C} = \begin{pmatrix} 0 & 0 & 0 \\[2ex] \alpha\left(\dfrac{\partial c_T^2}{\partial n}\right) & -\left(\dfrac{\partial \zeta'}{\partial T}\right) & \alpha\left(\dfrac{\partial c_T^2}{\partial T}\right) \\[2ex] -\left(\dfrac{\partial \gamma D_T}{\partial n}\right) & 0 & \left(\dfrac{\partial \gamma D_T}{\partial T}\right) \end{pmatrix} ,$$

$$\mathbf{D} = \begin{pmatrix} 0 & 0 & 0 \\[2ex] 0 & \left(\dfrac{\partial D_v'}{\partial T}\right) & 0 \\[2ex] \dfrac{1}{3}\left(\dfrac{\partial \gamma D_T}{\partial n}\right) & 0 & \dfrac{1}{3}(1+1)\left(\dfrac{\partial \gamma D_T}{\partial T}\right) \end{pmatrix} ,$$

$$
\mathbf{E} = - \begin{pmatrix} 0 & 0 & 0 \\ 0 & \left(\dfrac{\partial^2 \zeta'}{\partial T^2}\right) & 0 \\ \dfrac{1}{3}\left(\dfrac{\partial^2 \gamma D_T}{\partial T\, \partial n}\right) & 0 & \dfrac{1}{3}\left(\dfrac{\partial^2 \gamma D_T}{\partial T^2}\right) \end{pmatrix}, \quad
\mathbf{F} = \begin{pmatrix} 0 & & 0 \\ 0 & -\alpha c_T^2 & 0 \\ 0 & \gamma D_T & 0 \end{pmatrix},
$$

$$
\mathbf{G} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\alpha\left(\dfrac{\partial c_T^2}{\partial T}\right) & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad
\mathbf{H} = \frac{1}{3}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \left(\dfrac{\partial \gamma \partial_T}{\partial T}\right) & 0 \end{pmatrix}.
\tag{23}
$$

Prior to applying the Fourier transformation to eq. (20) we make an assumption, often used in quantum perturbation calculus. In order to ensure a slow evolution of the system towards equilibrium via quasi-stationary states we assume the temperature gradient to be an appropriately small quantity. Thus, the difference in temperature ΔT between the boundary region of the medium distant by L of the order of 1 cm is a quantity of the order of 1 K fulfilling the inequality $\Delta T/T \ll 1$. Thus, we are justified in writing

$$
T_{ss}(r) = T_0(r = 0) + \delta\tilde{T}\sin q \cdot r\,, \tag{24}
$$

where $q\,\delta\tilde{T} = \nabla T$, $q = 1/L$.

We consider a sample the dimensions L of which are much greater than the correlation range r and the free path of the hydrodynamical modes due to the fluctuations. We thus obtain non-zero contributions to the correlation function for $|r| \ll L$ only. For r-values satisfying this condition, the product $q \cdot r$ takes small values and (24) becomes a good approximation in (8). In addition, the above condition enables us to neglect the influence of boundary effects on the processes under consideration and permits the integration of (20) in the limits $(-\infty, +\infty)$. We now obtain the Fourier transform of (20) in the following general, compact form:

$$
\begin{pmatrix} \delta n_k \\ \Psi_k \\ \delta T_k \end{pmatrix} = \frac{1}{D(k, q)} \sum_{k'} \mathbf{M}_{k'}^{-1} \begin{pmatrix} 0 \\ k' \cdot \xi_{k'} \cdot k' \\ ik' \cdot \xi_{T,k'} \end{pmatrix}. \tag{25}
$$

To obtain the correlation function for the hydrodynamical fields we write the conjugate of the matrix (25):

$$
[\delta n_k^* \quad \Psi_k^* \quad \delta T_k^*] = \frac{1}{D^*(k, q)} \sum_{k''} [0 \quad k'' \cdot \xi_{k''}^* \cdot k'' \quad -ik'' \cdot \xi_{T,k''}](\mathbf{M}_{k''}^{-1})^*.
$$

$$
\tag{26}
$$

Next, multiplying (25) and (26) and taking the statistical average, we arrive at the correlation functions. Our results, when tabulated, assume the general form:

$$\begin{bmatrix} \langle \delta n_k \, \delta n_k^* \rangle \langle \delta n_k \, \Psi_k^* \rangle \langle \delta n_k \, \delta T_k^* \rangle \\ \langle \Psi_k \, \delta n_k^* \rangle \langle \Psi_k \, \Psi_k^* \rangle \langle \Psi_k \, \delta T_k^* \rangle \\ \langle \delta T_k \, \delta n_k^* \rangle \langle \delta T_k \, \Psi_k^* \rangle \langle \delta T_k \, \delta T_k^* \rangle \end{bmatrix} = \frac{1}{|D(k,q)|^2} \sum_{k',\,k''}$$

$$\begin{bmatrix} [\alpha'_{12}\alpha''_{12}\beta_{k',k''} - \alpha'_{13}\alpha''_{13}\beta_{T,k',k''}][\alpha'_{12}\alpha''_{22}\beta_{k',k''} - \alpha'_{13}\alpha''_{23}\beta_{T,k',k''}][\alpha'_{12}\alpha''_{32}\beta_{k',k''} - \alpha'_{13}\alpha''_{33}\beta_{T,k',k''}] \\ [\alpha'_{22}\alpha''_{12}\beta_{k',k''} - \alpha'_{23}\alpha''_{13}\beta_{T,k',k''}][\alpha'_{22}\alpha''_{22}\beta_{k',k''} - \alpha'_{23}\alpha''_{23}\beta_{T,k',k''}][\alpha'_{22}\alpha''_{32}\beta_{k',k''} - \alpha'_{23}\alpha''_{33}\beta_{T,k',k''}] \\ [\alpha'_{32}\alpha''_{12}\beta_{k',k''} - \alpha'_{33}\alpha''_{13}\beta_{T,k',k''}][\alpha'_{32}\alpha''_{22}\beta_{k',k''} - \alpha'_{33}\alpha''_{23}\beta_{T,k',k''}][\alpha'_{32}\alpha''_{32}\beta_{k',k''} - \alpha'_{33}\alpha''_{33}\beta_{T,k',k''}] \end{bmatrix} \cdot$$

$$(27)$$

The terms α'_{ij}, α''_{ij} are functions of the transport coefficients and their derivatives. On restricting ourselves to terms quadratic in q we get the respective functions in the form shown in appendix A.

The $\beta_{k',k''}$, $\beta_{T,k',k''}$ are functions of the stochastic correlation terms of the equations which describe, respectively, the fluctuation in velocity Ψ_k and in temperature δT_k:

$$\beta_{k',k''} \equiv \langle k' \cdot \xi_{k'} \cdot k' \; k'' \cdot \xi_{k''}^* \cdot k'' \rangle , \tag{28}$$

$$\beta_{T,k',k''} \equiv \langle k' \cdot \xi_{T,k'} \, \xi_{T,k''} \cdot k'' \rangle . \tag{29}$$

Let us assume that there are no correlations between the fluctuations of the stress tensor and thermal energy density flux vector. Thus, the cross correlation functions vanish. The correlation functions $\beta_{k',k''}$, $\beta_{T,k',k''}$, determined in ref. [24], – similarly to the elements α'_{ij}, α''_{ij} – are functions of the transport coefficients and their derivatives, dependent on q and the temperature. In ref. [24], the wave vectors k', k'' are shown to take the values

$$k', k'' = k \pm nq, \qquad n = \begin{cases} 0, 1, 2, & \text{for } \beta_{k',k''} , \\ 0, 1, 2, 3, & \text{for } \beta_{T,k',k''} . \end{cases} \tag{30}$$

Thus, the above correlation functions can now be written as

$$\left. \begin{array}{l} \beta_{k',k''} = \beta_{k+n'q,k+n''q} \equiv \beta_{n',l} \\ \beta_{T,k',k''} = \beta_{T,k+n'q,k+n''q} \equiv \beta_{T,n',l} \end{array} \right\} \quad \text{for } l = n'' - n' . \tag{31}$$

With an accuracy to terms quadratic in q we obtain [24]

$$B_{n',0} = 2k_B T m n_0 D_v (k + n'q)^4 \delta(\omega - \omega')$$
$$+ k_B \delta\tilde{T}^2 m n_0 \left(\frac{\partial D_v}{\partial T}\right)(k + n'q)^4 \delta(\omega' - \omega) \,,$$

$$\beta_{n'\pm1} = \mp k_B \delta\tilde{T}\left[2\eta\left(1 + \frac{\partial \ln \eta}{\partial \ln T}\right)(k + n'q)^2[k + (n' \pm 1)q]^2\right.$$
$$\left. + (\zeta - \tfrac{2}{3}\eta)\left(1 + \frac{\partial \ln(\zeta - \tfrac{2}{3}\eta)}{\partial \ln T}\right)(k + n'q)^2[k + (n' \pm 1)q]^2\right]\delta(\omega' - \omega) \,,$$

$$\beta_{n',\pm2} = \frac{(\delta\tilde{T})^2}{2} k_B\left[2\left(\frac{\partial n}{\partial T}\right)[(k + n'q)^2(k + (n' \pm 2)q)]^2\right.$$
$$\left. + \left(\frac{\partial(\zeta - \tfrac{2}{3}\eta)}{\partial T}\right)(k + n'q)^2(k + (n' \pm 2)q)^2\right]\delta(\omega' - \omega) \,, \tag{32}$$

$$\beta_{T,n',0} = 2k_B T^2 \kappa (k + n'q)^2 \delta(\omega' - \omega)$$
$$+ k_B \kappa \delta\tilde{T}^2\left(1 + 2\frac{\partial \ln \kappa}{\partial \ln T}\right)(k + n'q)\delta(\omega' - \omega) \,,$$

$$\beta_{T,n',\pm1} = \left[\mp i k_B T \kappa \delta\tilde{T}\left(2 + \frac{\partial \ln \kappa}{\partial \ln T}\right)(k + n'q)(k + (n' \pm 1)q)\right.$$
$$\left. \mp i\tfrac{3}{4}k_B \kappa \frac{\delta\tilde{T}^3}{T}\left(\frac{\partial \ln \kappa}{\partial \ln T}\right)(k + n'q)(k + (n' \pm 1)q)\right]\delta(\omega' - \omega) \,,$$

$$\beta_{T,n',\pm2} = -\tfrac{1}{2}k_B \kappa(\delta T)^2\left(1 + 2\frac{\partial \ln \kappa}{\partial \ln T}\right)(k + n'q)(k + (n' \pm 2)q)\delta(\omega' - \omega) \,.$$

In order to write $[|D(k, q)|^2]^{-1}$ in the generally accepted form we have to solve the frequency dispersion equation

$$D(k, q, s) = 0 \,, \tag{33}$$

where $D(k, q, s)$ is the value of the determinant of the Fourier transform of the matrix **M** of eq. (20).

The solutions of (33) take one form or another for different values of k. This is so because, according to the order of accuracy assumed, certain terms do or do not occur in the solution depending on the value of k. The strict solution of this equation for the case under consideration is to be found in ref. [24]. For k in the optical range, i.e., for $k \approx 10^5$ cm^{-1}, and for an accuracy restricted to the first terms in q^2, we obtain (see appendix B):

$$[|D(k, q)|^2]^{-1} = [|D(k)|^2]^{-1}\left\{1 - 2\left[\frac{(D_T k^2)^2}{\omega^2 + (D_T k^2)^2}\left(G_1 - \frac{\omega}{D_T k^2}\,G_2\right)\right.\right.$$

$$+ \frac{\omega c_s k + c_s^2 k^2 + (\Gamma k^2)^2}{(\omega + c_s k)^2 + (\Gamma k^2)^2}\,(G_4 + G_5)$$

$$+ \frac{\omega \Gamma k^2}{(\omega + c_s k)^2 + (\Gamma k^2)^2}\,(G_6 + G_7 + G_8)$$

$$+ \frac{\omega c_s k - c_s^2 k^2 - (\Gamma k^2)^2}{(\omega - c_s k)^2 + (\Gamma k^2)^2}\,(G_5 - G_4)$$

$$\left.\left.+ \frac{\omega \Gamma k^2}{(\omega - c_s k)^2 + (\Gamma k^2)^2}\,(G_6 - G_7 + G_8)\right]\right\}. \tag{34}$$

The corrections G_i, $i = 1, 2, \ldots, 8$, are given in appendix B (eqs. (B.13)–(B.20)).

The essential result of our work resides in the relation (27), which summarizes the set all possible cases of the hydrodynamical field correlation functions.

A similar calculation procedure has been applied in refs. [13–15]. However, their authors have not performed systematical calculations taking into account the greatest possible number of contributions to the hydrodynamical field correlation function, restricting themselves to a discussion of the influence of the temperature gradient on the velocity of sound, the coefficients of viscosity, and the heat conductivity coefficient, and neglecting the fluctuations of these quantities. Also, they do not go beyond solving the dispersion equation with accuracy to the second order of perturbation calculus. Applying the isothermal approximation, they omit the changes in entropy; this leads to a set of initial equations containing no equation of motion for the fluctuations in temperature. Also, the correlation functions of the stochastic terms of the hydrodynamical equations used there are given a presentation more intuitive than resulting from thorough calculations. All this leads to the circumvention of certain conditions which amount to specific selection rules on the values of n' and n'' and eliminate arbitrariness in the construction of final expressions based on strict premissae.

4. Conclusion

We have considered a system in a state of non-equilibrium due to the introduction of a temperature gradient. We have assumed that all the conditions for this state to be stationary are satisfied. A system like this can be realized with a high degree of accuracy by surrounding the medium on either

side with reservoirs at two different temperatures giving a slight gradient, decaying slowly compared with the lifetimes of the processes taking place in the system.

We make use of hydrodynamical equations of the most general form:

(i) taking into account the influence of the temperature gradient on the viscosity coefficients η and ζ, the heat conductivity coefficient κ, and the sound velocity c_s;

(ii) including the fluctuations in sound velocity and heat conductivity coefficient expressed via fluctuations of the fundamental hydrodynamical fields – those of temperature and number density; and

(iii) not restricting ourselves to the isothermal approximation, and taking into consideration all three hydrodynamical fields; and

(iv) performing our calculations up to terms in q^2.

We have transformed the set of five equations to variables k, ω and have solved it analytically. We have expressed the hydrodynamical field fluctuations by way of stochastic functions with various wave vectors, resulting from our calculations. The functional coefficients that occur are dependent on the parameters characterizing the medium and on their derivatives with respect to temperature, density and pressure. The determination of the correlation function consisted primarily in solving the frequency dispersion equation and calculating the correlation functions for the stochastic terms of the initial equations. It is necessary to stress, as highly important in all cases, the dependence on the concrete value of the wave vectors, of the general form $k' = k + n'q$ (for the conjugate part, $k'' = k + n''q$). It is essential that the values taken by n' and n'' are a consequence of the form derived by us for the initial equations and are by no means but an attempt at generalizing the expressions indexated by the k. Similarly, the set of n' and n'' values occurring as indices at the correlation functions of the stochastic terms of the initial equations is the result of strict, mathematical operations and thus derives from a mathematical and physical necessity rather than from a bare possibility.

We have introduced distinctions between terms related with contributions of different types:

1. contributions from fluctuations in number density, momentum and energy;

2. contributions appearing due to having taken into account fluctuations in sound velocity and heat conductivity coefficient; and

3. contributions related with the presence of the temperature gradient.

Only contributions of the type 1, specific to equilibrium fluctuations, are found to occur independently. Thus cross terms, being products of contributions of the types 1, 3, and 2, 3 appear as well.

In part II, now in preparation, we shall discuss the influence of the above derived contributions on the spectrum of scattered light.

Appendix A

In tabulated form (see table I), we give the terms α'_{ij} occurring in eq. (27). The elements α''_{ij} are derived from the α'_{ij} by the interchange: $\alpha'_{ij} \rightarrow \alpha'^{*}_{ij}$, $k' \rightarrow k''$. Each of the functions α'_{ij} is the sum of products of the terms in the corresponding row and the appropriate expressions of the first row. For example,

$$\alpha'_{23} = -\alpha c_T^2 k^2 \delta(k'-k) + \alpha s (1 + 1 \left(\frac{\partial \ln c_T^2 k^2}{\partial T} \right) i \frac{\delta \tilde{T}}{2}$$

$$\times \left\{ \left[1 + 2 \frac{k \cdot q}{k^2} + \left(\frac{q}{k} \right)^2 \right] \delta[k' - (k + q)] \right.$$

$$\left. - \left[1 - 2 \frac{k \cdot q}{k^2} + \left(\frac{q}{k} \right)^2 \right] \delta[k' - (k - q)] \right\} .$$

Appendix B

The frequency dispersion equation has the form [23]

$$D(k, q, s) = s^3 + [D_v k^2 + \gamma D_T k^2 + i(a_5 - a_7) + a_6 + a_8] s^2$$

$$+ [\gamma c_T^2 k^2 + D_v k^2 \gamma D_T k^2 + D_v k^2 a_8 + \gamma D_T k^2 a_6 + a_6 a_8 + a_5 a_7$$

$$- i(a_1 + (\gamma - 1) a_2 - \gamma D_T k^2 a_5 - D_v k^2 a_7 - a_5 a_8 + a_7 a_6] s$$

$$+ \alpha n_0 c_T^2 k^2 a_4 + G^2 k^2 \gamma D_T k^2 - c_T^2 k^2 a_8 - a_1 a_7 + \alpha n_0 a_2 a_3$$

$$+ i(\alpha n_0 c_T^2 k^2 a_3 - c_T^2 k^2 a_7 - \gamma D_T k^2 a_1 - a_1 a_8 - \alpha n_0 a_2 a_4) = 0 ,$$

$$\text{(B.1)}$$

with:

$$a_1 = 2\delta \tilde{T} \left[\left(\frac{\partial c_T^2 k^2}{\partial T} \right) + \alpha n_0 \left(\frac{\partial c_T^2 k^2}{\partial n} \right) \right] \frac{k \cdot q}{k^2} , \tag{B.2}$$

$$a_2 = 2\delta \tilde{T} (1 + 1) \left(\frac{\partial c_T^2 k^2}{\partial T} \right) \frac{k \cdot q}{k^2} , \tag{B.3}$$

$$a_3 = 2\delta \tilde{T} \left(\frac{\partial \gamma D_T k^2}{\partial n} \right) \left[\frac{k \cdot q}{k^2} - \frac{1}{3} \left(\frac{q}{k} \right)^2 \right] , \tag{B.4}$$

$$a_4 = \frac{\delta \tilde{T}^2}{6} \left(\frac{\partial^2 \gamma D_T k^2}{\partial T \partial n} \right) \left(\frac{q}{k} \right)^2 , \tag{B.5}$$

Table I

	$\delta(k'-k)$	$i\dfrac{\delta\tilde{T}}{2}\left\{\left[1+2\dfrac{k\cdot q}{k^2}+\left(\dfrac{q}{k}\right)^2\right]\delta[k'-(k+q)]-\left[1-2\dfrac{k\cdot q}{k^2}+\left(\dfrac{q}{k}\right)^2\right]\delta[k'-(k-q)]\right\}$	$i\dfrac{\delta\tilde{T}}{2}\left\{\left[\dfrac{k\cdot q}{k^2}+\left(\dfrac{q}{k}\right)^2\right]\delta[k'-(k+q)]+\left[\dfrac{k\cdot q}{k^2}+\left(\dfrac{q}{k}\right)^2\right]\delta[k'(k-q)]\right\}$	$\dfrac{\delta\tilde{T}^2}{12}\left(\dfrac{q}{k}\right)^2\left[2\delta(k'-k)+\delta[k-(k+2q)]-\delta[k'-(k-2q)]\right]$
α'_{12}	$-n_0(s+\gamma D_T k^2)$	$n_0\left(\dfrac{\partial\gamma D_T k^2}{\partial T}\right)$	$\dfrac{1}{3}n_0(1+1)\left(\dfrac{\partial\gamma D_\gamma k^2}{\partial t}\right)$	$n_0\left(\dfrac{\partial^2\gamma D_T k^2}{\partial T^2}\right)$
α'_{13}	$-\alpha n_0 c_T^2 k^2$	$\alpha n(1+1)\left(\dfrac{\partial c_T^2 k^2}{\partial T}\right)$	0	0
α'_{22}	$s(s+\gamma D_T k^2)$	$-s\left(\dfrac{\partial\gamma D_T k^2}{\partial T}\right)$	$\dfrac{1}{3}(1+1)s\left(\dfrac{\partial\gamma D_T k^2}{\partial T}\right)$	$s\left(\dfrac{\partial^2\gamma D_T k^2}{\partial T^2}\right)$
α'_{23}	$-\alpha c_T^2 k^2$	$\alpha s(1+1)\left(\dfrac{\partial\ln c_T^2 k^2}{\partial T}\right)$	0	0
α'_{32}	$\dfrac{\gamma-1}{\alpha}s$	$n_0\left(\dfrac{\partial\gamma D_T k^2}{\partial n}\right)$	$\dfrac{1}{3}n_0\left(\dfrac{\partial\gamma D_T k^2}{\partial n}\right)$	$-3n_0\left(\dfrac{\partial^2\gamma D_T k^2}{\partial T\partial n}\right)$
α'_{33}	$c_T^2 k^2+s(s+D_v k^2)$	$s\left[\left(\dfrac{\partial D_v k^2}{\partial T}\right)-\left(\dfrac{\partial\zeta'k^2}{\partial T}\right)-\left(\dfrac{\partial c_T^2 k^2}{\partial T}\right)-\alpha n_0\left(\dfrac{\partial c_T^2 k^2}{\partial n}\right)\right]$	0	$-3s\left(\dfrac{\partial^2\zeta'k^2}{\partial T^2}\right)$

$$a_5 = 2\delta\tilde{T}\left(\frac{\partial D_v k^2}{\partial T}\right)\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} - \delta\tilde{T}\left(\frac{\partial D_v' k^2}{\partial T}\right)\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} - \frac{\delta\tilde{T}}{2}\left(\frac{\partial\zeta' k^2}{\partial T}\right)\left(\frac{q}{k}\right)^2, \quad \text{(B.6)}$$

$$a_6 = \frac{\delta\tilde{T}^2}{4}\left(\frac{\partial^2\zeta' k^2}{\partial T^2}\right)\left(\frac{q}{k}\right)^2, \quad \text{(B.7)}$$

$$a_7 = \frac{1}{3}\,\delta\tilde{T}(7+1)\left(\frac{\partial\gamma D_T k^2}{\partial T}\right)\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}, \quad \text{(B.8)}$$

$$a_8 = \frac{\delta\tilde{T}^2}{12}\left(\frac{\partial^2\gamma D_T k^2}{\partial T^2}\right)\left(\frac{q}{k}\right)^2. \quad \text{(B.9)}$$

In ref. [23], eq. (B.1) is solved by well known methods of perturbation calculus. On restricting ourselves to an accuracy determined by the order of the first terms quadratic in q we get, for $k \approx 10^5\ \text{cm}^{-1}$,

$$s_1 = -D_T k^2[1 + G_1 + \mathrm{i}G_2], \quad \text{(B.10)}$$

$$s_2 = (\mathrm{i}c_s k + \Gamma k^2)\left[1 + \frac{1}{\mathrm{i}c_s k + \Gamma k^2}(\mathrm{i}G_8 + G_4 + G_5 + \mathrm{i}G_6 + \mathrm{i}G_7)\right], \quad \text{(B.11)}$$

$$s_3 = (-\mathrm{i}c_s k + \Gamma k^2)\left[1 - \frac{1}{-\mathrm{i}c_s k + \Gamma k^2}(\mathrm{i}G_8 - G_4 + G_5 + \mathrm{i}G_6 - \mathrm{i}G_7)\right],$$
$$\text{(B.12)}$$

where

$$G_1 = (\gamma - 1)\frac{D_T k^2}{c_s^2 k^2}(D_T k^2 - D_v k^2), \quad \text{(B.13)}$$

$$G_2 = 4\left(1 - \frac{1}{\gamma}\right)\frac{\delta\tilde{T}}{c_s k}\left[\left(\frac{\partial c_s k}{\partial T}\right) - \alpha n_0\left(\frac{\partial c_s k}{\partial n}\right)\right]\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}, \quad \text{(B.14)}$$

$$G_3 = 2\delta\tilde{T}\frac{1}{\gamma}[1 + (\gamma - 1)]\left[\left(\frac{\partial c_s k}{\partial T}\right) + \alpha n_0\left(\frac{\partial c_s k}{\partial n}\right)\right]\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}, \quad \text{(B.15)}$$

$$G_4 = \frac{1}{c_s^2 k^2}[b_1(D_T k^2)^3 + b_2(D_T k^2)^2 D_v k^2 + b_3 D_T k^2(D_v k^2)^2 + (D_v k^2)^3], \quad \text{(B.16)}$$

$$G_5 = \delta\tilde{T}\left[1 + \left(1 - \frac{1}{\gamma}\right)\right]\left[\left(\frac{\partial c_s k}{\partial T}\right) + \frac{\alpha n_0}{\gamma}\left(\frac{\partial c_s k}{\partial n}\right)\right]\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}, \quad \text{(B.17)}$$

$$G_6 = \frac{1}{c_s^3 k^3} \left[b_4 (D_T k^2)^4 - b_5 (D_T k^2)^3 D_v k^2 + b_6 (D_T k^2 D_v k^2)^2 \right.$$

$$\left. - b_7 D_T k^2 (D_v k^2)^3 - (D_v k^4)^4 \right], \tag{B.18}$$

$$G_7 = \frac{\delta \tilde{T}}{c_s k} \left[(b_8 D_T k^2 - b_9 D_v k^2) \left(\frac{\partial c_s k}{\partial T} \right) \right.$$

$$\left. - (b_{10} D_T k^2 + b_{11} D_v k^2) \alpha n_0 \left(\frac{\partial c_s k}{\partial n} \right) \right] \frac{\mathbf{k} \cdot \mathbf{q}}{k^2} , \tag{B.19}$$

$$G_8 = \frac{1}{c_s k} \left[b_{12} (D_T k^2)^2 + b_{13} D_T D_v k^4 + \tfrac{1}{8} (D_v k^2)^2 \right]. \tag{B.20}$$

The coefficients b_i, $i = 1, 2, \ldots 13$, occurring in (B.13)–(B.20) are functions of the Poisson coefficient γ and have the form

$$b_1 = \tfrac{1}{16} (4\gamma^3 - 19\gamma^2 + 19\gamma + 4) , \tag{B.21}$$

$$b_2 = \tfrac{1}{8} (46\gamma^2 - 72\gamma + 19) , \tag{B.22}$$

$$b_3 = \tfrac{1}{8} (12\gamma - 19) , \tag{B.23}$$

$$b_4 = \tfrac{1}{64} (-\gamma^4 - 1348\gamma^3 - 2350\gamma^2 - 1156\gamma + 279) , \tag{B.24}$$

$$b_5 = \tfrac{1}{32} (1006\gamma^3 - 4142\gamma^2 + 3450\gamma - 578) , \tag{B.25}$$

$$b_6 = \tfrac{1}{32} (2126\gamma^2 + 4142\gamma - 1175) , \tag{B.26}$$

$$b_7 = \tfrac{1}{16} (503\gamma - 337) , \tag{B.27}$$

$$b_8 = - \left[3\gamma - (7 - 3 - 1) - 4(1 - 1) \frac{1}{\gamma} \right] , \tag{B.28}$$

$$b_9 = 3 \left[\frac{1}{\gamma} + \left(1 - \frac{1}{\gamma} \right) \right] , \tag{B.29}$$

$$b_{10} = 4 \left(1 - \frac{1}{\gamma} \right) , \tag{B.30}$$

$$b_{11} = \frac{3}{\gamma} , \tag{B.31}$$

$$b_{12} = 14\gamma^2 - 26\gamma + 7 , \tag{B.32}$$

$$b_{13} = \tfrac{1}{4} (16\gamma - 15) . \tag{B.33}$$

The underlinings are in accordance with the convention introduced by us in section 2.

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