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GENERALIZED TRANSPORT COEFFICIENTS IN A BINARY
He$_{0.65}$-Ne$_{0.35}$ MIXTURE

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Узагальнені коефіцієнти переносу бінарної суміші He$_{0.65}$-Ne$_{0.35}$

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Анотація. На основі рекуррентних співвідношень для функцій пам'яті означені $(\boldsymbol{k}, \omega)$-залежні коефіцієнти переносу бінарної суміші He$_{0.65}$-Ne$_{0.35}$. В якості базисного вибрано набір динамічних змінних, що об'єднує гідродинамічні густини разом з їх першими похідними. Обговорюється зв'язок між коефіцієнтами Онсагера, означеними на цьому базисі, та експериментально спостережними коефіцієнтами переносу.

Generalized transport coefficients in a binary He$_{0.65}$-Ne$_{0.35}$ mixture

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Abstract. On the basis of recursive relations for memory kernels the generalized $(\boldsymbol{k}, \omega)$-dependent transport coefficients are defined for a binary fluids and calculated for a binary He$_{0.65}$-Ne$_{0.35}$ mixture. Extended set of dynamic variables including both hydrodynamic densities and their first time derivatives are taken into consideration. Connection between Onzager coefficients defined on this basis and experimentally observed transport coefficients is discussed.

1. Introduction

An intensive investigation of binary systems (liquid mixtures, melts, polymer solutions) had been started more then 25 years ago and at present is being characterized by a considerable advance in understanding of many aspects of nature of the object mentioned above. Starting from the very beginning one should refer to papers by Bhatia et al. [1,2] where authors considered both static and dynamic properties (static and dynamic structure factors, thermodynamic values, Green - Kubo relations) of binary mixtures. Though their results had a good agreement with scattering experiments [3] in the domain of small wave numbers k and frequencies ω, it was challenging to extend the description out from the framework of pure hydrodynamic approach. Suchlike investigations were stimulated by discovery of "fast sound" phenomenon in mixtures having been enriched by lighter component [4–7], which could be interpretated as collective motion of lighter particles on background of heavier ones and obviously presents the collective excitation of kinetic origin.

Another reason of going out from hydrodynamic description followed from the development of computer methods for calculations of time correlation functions for binary mixtures what sets up the problem of theoretical study of the dynamics at finite values of wave-vector $\boldsymbol{k}$ and frequency ω what is in fact the problem of the generalized hydrodynamics. One should emphasize that this problem is very important from experimental point as well, because neutron scattering experiments (especially in mixtures with disparate masses in the species) are being carried out in such a domain of k where usual hydrodynamic description is not applicable any more.

During the last decade an essential progress in understanding of dynamic properties of fluids has been achieved in connection with the generalized collective modes approach [8–11]. The extension of this method on binary liquids in the parameter–free form has been undertaken very recently [12] what opened the way of construction of generalized hydrodynamics of mixtures [11]. In comparison with five–mode formalism of Ref. [4] the approach proposed in [12] has really no fitting parameters and is based only on Markovian approximation for higher-order memory kernels being very effective in case of an extended set of dynamic variables [13]. Ref. [12] gave us an answer to the question: what set of dynamic variables is appropriate for the correct description of binary mixtures dynamics for small and intermediate values of k and ω?

In parallel way the construction of generalized hydrodynamics of binary mixtures was going on [14,15]. The results of these studies were the explicit expressions for generalized thermodynamic quantities and transport coefficients which had been obtained in the rigorous statistical approach without any phenomenologic–based presumptions.

A logical completion of these investigations might be the calculation of generalized k, ω-dependent transport coefficients that leads us to nonlocal transport equations. There were proposed in the literature several methods for solving of this problem for fluids: mode-coupling theory [16,17], generalized kinetic theory for gases [18,19], formalism of memory functions [20,21] and generalized collective mode approach [11,22] as one of the versions of memory function formalism. The mode-coupling theory allows us to study nonanalytical $\sqrt{k}$ and $\sqrt{\omega}$–dependent corrections to the hydrodynamic transport coefficients appeared in the region of small wave-vectors and frequencies due to nonlinear fluctuations of coarse-grained variables. The methods of kinetic theory are limited by consideration of low-density systems. In present paper we shall dwell ourselves on the method of generalized collective modes applying recursive relations for higher-order memory functions [13].

The paper is organized as follows: in Section 2 we introduce dynamic variables which serve as basic set for construction of memory functions in the strict microscopic approach. Some words will be said about an advantage of our choice of dynamic variables. In Section 3 we extend initial set of hydrodynamic densities taking into consideration their first time derivatives. Then we apply recursive relations for higher-order memory kernels to obtain $k-$ and $\omega-$dependent transport coefficients. In the last Section some concluding remarks are made.

2. Equations of generalized hydrodynamics

Let us introduce the basic dynamic variables in the following way:

$$\hat{n}_a(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N_a} \exp(i\boldsymbol{k}\boldsymbol{r}_i), \qquad a = 1, 2 \qquad (1)$$

is the Fourier-transform of the ath partial number density;

$$\hat{p}^{\parallel}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{a=1}^{2} \hat{p}_a^{\parallel}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{a=1}^{2} \sum_{i=1}^{N_a} \frac{\boldsymbol{k}\boldsymbol{p}_i}{k} \exp(i\boldsymbol{k}\boldsymbol{r}_i) \qquad (2)$$

denotes the Fourier-transform of the longitudinal component of total momentum density;

$$\hat{\varepsilon}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \sum_{a=1}^{2} \sum_{i=1}^{N_a} \left(\frac{\boldsymbol{p}_i^2}{2m_a} + \frac{1}{2} \sum_{b=1}^{2} \sum_{j=1}^{N_b} V(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \right) \exp(i\boldsymbol{k}\boldsymbol{r}) \qquad (3)$$

is the Fourier–transform of energy density. It should be noted that the dynamic variables (1)-(3) obey conservation laws in the form

$$\dot{\hat{a}}_i(\boldsymbol{k}) = i\boldsymbol{k}\hat{\boldsymbol{I}}_i(\boldsymbol{k}) \,, \qquad (4)$$

where $\dot{\hat{a}}_i(\boldsymbol{k}) \equiv i\hat{L}\hat{a}_i(\boldsymbol{k})$, $i\hat{L}$ is a Liouville operator, and $\hat{\boldsymbol{I}}_i(\boldsymbol{k})$ denote the microscopic fluxes corresponding to the variables $\hat{a}_i(\boldsymbol{k})$:

$$\hat{\boldsymbol{I}}_{n_a}(\boldsymbol{k}) = \frac{1}{\sqrt{N_a}} \sum_{i=1}^{N_a} \frac{\boldsymbol{p}_i}{m_a} \exp(i\boldsymbol{k}\boldsymbol{r}_i) \,, \qquad (5)$$

$$\hat{I}_p^{\alpha\beta}(\boldsymbol{k}) \equiv \hat{\sigma}_{\alpha\beta}(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \left(\sum_{a=1}^{2} \sum_{i=1}^{N_a} \frac{p_i^\alpha p_i^\beta}{m_a} \exp(i\boldsymbol{k}\boldsymbol{r}_i) \right.$$

$$\left. -\frac{1}{2} \left(\sum_{a,b} \sum_{i,j} \right)' V'(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} P_{\boldsymbol{k}}(\boldsymbol{r}_i - \boldsymbol{r}_j) \exp(i\boldsymbol{k}\boldsymbol{r}_i) \right) , \qquad (6)$$

$$\hat{I}_\varepsilon^\alpha(\boldsymbol{k}) = \frac{1}{\sqrt{N}} \left(\sum_{a=1}^{2} \sum_{i=1}^{N_a} \frac{p_i^\alpha}{m_a} \left[\frac{\boldsymbol{p}_i^2}{2m_a} + \frac{1}{2} \sum_{b=1}^{2} \sum_{j \neq i=1}^{N_b} V(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \right] \exp(i\boldsymbol{k}\boldsymbol{r}_i) \right.$$

$$-\frac{1}{2} \left(\sum_{a,b} \sum_{i,j} \right)' V'(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \left(\frac{p_i^\alpha}{4m_a} + \frac{p_i^\beta}{4m_b} \right) \frac{(r_i^\alpha - r_j^\alpha)(r_i^\beta - r_j^\beta)}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \qquad (7)$$

$$\left. \times P_{\boldsymbol{k}}(\boldsymbol{r}_i - \boldsymbol{r}_j) \exp(i\boldsymbol{k}\boldsymbol{r}_i) \right),$$

where $P_{\boldsymbol{k}}(\boldsymbol{r}) = [1 - \exp(-i\boldsymbol{k}\boldsymbol{r})]/[i\boldsymbol{k}\boldsymbol{r}] \to 1$ when $k \to 0$.

In Ref. [15] one has shown that passing from conserved variables (1)-(3) to the following ones determined as

$$\hat{Y}_1(\boldsymbol{k}) \equiv \hat{n}(\boldsymbol{k}) = \sum_{a=1}^{2} \hat{n}_a(\boldsymbol{k}) \,, \qquad (8)$$

$$\hat{Y}_2(\boldsymbol{k}) \equiv \hat{\tilde{n}}_1(\boldsymbol{k}) = (1 - \mathcal{P}_n)\hat{n}_1(\boldsymbol{k}) \,, \qquad (9)$$

$$\hat{Y}_3(\boldsymbol{k}) \equiv \hat{p}^{\|}(\boldsymbol{k}) \,, \qquad (10)$$

$$\hat{Y}_4(\boldsymbol{k}) \equiv \hat{h}(\boldsymbol{k}) = (1 - \mathcal{P}_n - \mathcal{P}_{\tilde{n}_1})\hat{\varepsilon}(\boldsymbol{k}) \,, \qquad (11)$$

one can express the static structure factors of "density-density", "concentration-concentration", "density-concentration" as well as the other generalized thermodynamic quantities of the system only via correlation functions of variables (8)-(11) and their fluxes. In (8)-(11) $N = N_1 + N_2$ denotes the total particle number and Mori-like projecting operator $\mathcal{P}_a$ acts accordingly

$$\mathcal{P}_a \ldots = \left(\ldots, \hat{a}(-\boldsymbol{k}) \right) \left(\hat{a}(\boldsymbol{k}), \hat{a}(-\boldsymbol{k}) \right)^{-1} \hat{a}(\boldsymbol{k}) \,, \qquad (12)$$

with $a = \{n, \tilde{n}_1\}$. For a static correlation function $(\hat{a}(\boldsymbol{k}), \hat{a}(-\boldsymbol{k}))$ we used the notation

$$F_{ab}(k) = (\hat{a}(\boldsymbol{k}), \hat{a}(-\boldsymbol{k})) \equiv \langle \Delta\hat{a}(\boldsymbol{k})\Delta\hat{b}(-\boldsymbol{k}) \rangle_0, \qquad (13)$$

where

$$\Delta\hat{a}(\boldsymbol{k}) = \hat{a}(\boldsymbol{k}) - \langle \hat{a}(\boldsymbol{k}) \rangle_0$$

and $\langle \ldots \rangle_0$ means an averaging with an equilibrium distribution ρ_0 in grand canonical ensemble,

$$\rho_0 = \exp \left[\beta(\Omega - \hat{E} - \sum_{a=1}^{2} \mu_a \hat{N}_a) \right]. \qquad (14)$$

In (14) one has as ussual that $\beta = 1/k_B T$ is an inverse temperature, μ_a denote of chemical potentials, and $\Omega = \Omega(V, T, \mu_1, \mu_2)$ is the thermodynamic potential which depends on volume V, temperature T and chemical potentials μ_a.

Thus static structure factor "density-concentration" equals

$$S_{NC}(k) = F_{n_1 n}(k) - C_1 F_{nn}(k) \,, \qquad (15)$$

where $C_i = N_i/N$ denotes concentration of the i-th species and $F_{AB}(k)$ means corresponding static correlation functions (one can write down, for instance, relation between static structure factur "density–density" $S_{nn}(k) \equiv F_{nn}(k)$ and partial static structure factors $S_{n_i n_j}(k) = (\hat{n}_i(\boldsymbol{k}), \hat{n}_j(-\boldsymbol{k})), \{i, j\} = 1,2$, as follows: $F_{nn}(k) = C_1 S_{n_1 n_1}(k) + C_2 S_{n_2 n_2}(k) + 2\sqrt{C_1 C_2} S_{n_1 n_2}(k)$);

$$S_{CC}(k) = F_{n_1 n_1}(k) - 2C_1 F_{nn_1}(k) + C_1^2 F_{nn}(k) \qquad (16)$$

denotes "concentration-concentration" structure factor;

$$\theta(k) = \frac{N}{V} k_B T K_T(k) = \frac{F_{nn}(k) F_{\bar{n}_1 \bar{n}_1}(k)}{S_{CC}(k)}, \qquad (17)$$

where $K_T(k)$ means generalized compressibility;

$$\delta(k) = -\frac{S_{NC}(k)}{S_{CC}(k)} \qquad (18)$$

denotes generalized N–C dilatation factor [1,2];

$$c_V(k) = \frac{1}{k_B T^2} \left(F_{\varepsilon\varepsilon}(k) - \frac{F_{\bar{n}\varepsilon}^2(k)}{F_{nn}(k)} - \frac{F_{\bar{n}_1\varepsilon}^2(k)}{F_{\bar{n}_1\bar{n}_1}(k)} \right) \qquad (19)$$

means the generalized specific heat at constant volume. Variables (17)-(19) in the limit $k \to 0$ transfer to their thermodynamic values, accordingly:

$$\lim_{k\to 0} \theta(k) = \frac{N}{V} k_B T K_T = \frac{N}{V} k_B T \left(-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right) \right)_{T,N,C}, \qquad (20)$$

$$\lim_{k\to 0} \delta(k) = \frac{V_1 - V_2}{V}, \qquad (21)$$

$$\lim_{k\to 0} c_V(k) = c_{V,N,C_1}, \qquad (22)$$

where V_i denotes i-species volume, p denotes pressure and corresponding long-wave limits of (15)-(16) coincide with static structure factors of Bhatia–Thornton [1,2].

Using the method of nonequilibrium statistical operator [23] one can obtain the chain of equations for Laplace-transforms

$$\tilde{F}_{Y_i Y_j}(k, z) = \int_0^\infty \exp(-z\, t) F_{Y_i Y_j}(k, t)\, dt, \quad z = i\omega + \epsilon, \, \epsilon \to 0 \qquad (23)$$

of time correlation functions (TCF)

$$F_{Y_i Y_j}(k, t) = \left(\hat{Y}_i(\boldsymbol{k}), \, \exp(-i\hat{L}t) \hat{Y}_j(-\boldsymbol{k}) \right) \qquad (24)$$

in matrix form:

$$z\tilde{F}_{Y_i Y_j}(k, z) - i\Omega_{Y_i Y_l}(k)\tilde{F}_{Y_l Y_j}(k, z) + \tilde{\varphi}_{Y_i Y_l}(k, z)\tilde{F}_{Y_l Y_j}(k, z)$$

$$= F_{Y_i Y_j}(k, t = 0), \qquad (25)$$

where frequency matrix $i\Omega_{Y_i Y_j}(k)$ is determined as

$$i\Omega_{Y_i Y_j}(k) = \frac{\left(i\hat{L}\hat{Y}_i(\boldsymbol{k}), \, \hat{Y}_j(-\boldsymbol{k}) \right)}{\left(\hat{Y}_j(\boldsymbol{k}), \, \hat{Y}_j(-\boldsymbol{k}) \right)}, \qquad (26)$$

$\tilde{\varphi}_{Y_i Y_j}(k, z)$ is Laplace-transform of memory function

$$\varphi_{Y_i Y_j}(k, t) = \int_{-\infty}^{t} \exp(-\epsilon\tau) \Big((1 - \mathcal{P}_H) i\hat{L}\hat{Y}_i(\boldsymbol{k}),$$

$$\exp\left[-i(1 - \mathcal{P}_H)\hat{L}(1 - \mathcal{P}_H)\tau \right] i\hat{L}\hat{Y}_j(-\boldsymbol{k}) \Big) \left(\hat{Y}_j(\boldsymbol{k}), \hat{Y}_j(-\boldsymbol{k}) \right)^{-1} d\tau, \quad (27)$$

where

$$\mathcal{P}_H = \sum_{i=1}^{4} \mathcal{P}_{Y_i}, \, \mathcal{P}_{Y_i}\dots = \left(\dots, \hat{Y}_i(-\boldsymbol{k}) \right) \left(\hat{Y}_i(\boldsymbol{k}), \hat{Y}_i(-\boldsymbol{k}) \right)^{-1} \hat{Y}_i(\boldsymbol{k}) \quad (28)$$

denotes Mori projecting operator on hydrodynamic basis (8)-(11) and $\epsilon \to +0$ after thermodynamic transition $V \to \infty$, $N \to \infty$, $N/V = n = const$.

One should point out that according construction dynamic variables (8)-(11) are orthogonal: $\left(\hat{Y}_i(\boldsymbol{k}), \hat{Y}_j(-\boldsymbol{k}) \right) = \delta_{ij}\left(\hat{Y}_i(\boldsymbol{k}), \hat{Y}_i(-\boldsymbol{k}) \right)$, δ_{ij} is Kronecker delta-symbol. Transport equations for variables $\hat{Y}_i(\boldsymbol{k})$ look similarly to (25) (see next section).

Frequency matrixes (26) determine generalized thermodynamic values of binary mixture [15]; we shall not dwell our attention on this theme any more referring readers to [12,14,15]. Instead of it we shall study memory kernels (27) more thoroughly.

The Fourier transforms of memory functions (27) could be expressed via generalized kinetic (Onzager) coefficients in the standart way [14]:

$$\tilde{\varphi}_{Y_i Y_j}(k, \omega) = k^2 \tilde{\mathsf{L}}_{Y_i Y_j}(k, \omega) \frac{V/N}{\beta\, F_{Y_j Y_j}(k, 0)}, \qquad (29)$$

where generalized kinetic coefficients $\tilde{\mathsf{L}}_{Y_i Y_J}(k,\omega)$ are the Laplace transforms of time dependent functions

$$\mathsf{L}_{Y_i Y_j}(k,t) = \int\limits_{-\infty}^{t} \exp(-\epsilon\tau)\left((1-\mathcal{P})\dot{\hat{Y}}_i^{(1)}(\boldsymbol{k}), \exp\left[-(1-\mathcal{P})i\hat{L}\tau\right]\right.$$
$$\left. \times (1-\mathcal{P})\dot{\hat{Y}}_j^{(1)}(-\boldsymbol{k})\right) d\tau. \qquad (30)$$

Relations (29)-(30) allow us to introduce generalized (nonlokal) transport coefficients in a standart way having been determined them through kinetic coefficients $\tilde{\mathsf{L}}_{Y_i Y_j}(k,\omega)$. Then we have:

$$\tilde{\mathsf{L}}_{pp}^{||}(k,\omega) = \frac{4}{3}\eta(k,\omega) + \zeta(k,\omega) \qquad (31)$$

means generalized "longitudinal" viscousity, where $\eta(k,\omega)$ denotes generalized shear viscousity and $\zeta(k,\omega)$ is generalized bulk viscousity;

$$\tilde{\mathsf{L}}_{hh}(k,\omega) = T\lambda(k,\omega), \qquad (32)$$

where $\lambda(k,\omega)$ means generalized thermal conductivity;

$$\tilde{\mathsf{L}}_{nn} = D(k,\omega), \qquad (33)$$

where $D(k,\omega)$ denotes generalized interdiffusion coefficient;

$$\tilde{\mathsf{L}}_{nh}(k,\omega) = \tilde{\mathsf{L}}_{hn}(k,\omega) = D_T(k,\omega), \qquad (34)$$

where $D_T(k,\omega)$ denotes generalized thermal diffusion coefficient.

Transverse component of the stress tensor (6) determines shear viscousity $\eta(k,\omega)$ (cf. (31)):

$$\tilde{\mathsf{L}}_{pp}^{\perp}(k,\omega) = \eta(k,\omega). \qquad (35)$$

Besides (31)-(34) there are transport coefficients describing interaction between dissipative fluxes of the different tensor dimensions. For instance, generalized transport coefficient

$$\tilde{\mathsf{L}}_{ph}(k,\omega) = \tilde{\mathsf{L}}_{hp}(k,\omega) = \xi(k,\omega) \qquad (36)$$

describes cross–effect "thermal conductivity – viscousity" and

$$\tilde{\mathsf{L}}_{np}(k,\omega) = \tilde{\mathsf{L}}_{pn}(k,\omega) = \nu(k,\omega) \qquad (37)$$

defines correlations of diffusive and viscous dissipative fluxes.

Further simplification can be reached in Markovian approximation for memory kernels $\tilde{\varphi}_{Y_i Y_j}(k,\omega) \approx \tilde{\varphi}_{Y_i Y_j}(k,0) = \int\limits_0^{\infty} \varphi_{Y_i Y_j}(k,t)\, dt$. In this approximation in the limit $k \to 0$ memory kernels $\tilde{\varphi}_{Y_i Y_j}$ could be written as follows:

$$\tilde{\varphi}_{Y_i Y_j}(k \to 0, z \to 0) = k^2 \mathsf{L}_{Y_i Y_j} \frac{V/N}{\beta\, F_{Y_j Y_j}(k=0, t=0)}, \qquad (38)$$

$$\mathsf{L}_{Y_i Y_j} = \frac{\beta}{V} \int\limits_0^{\infty} \left(\Delta\hat{f}_{Y_i}, \exp(-i\hat{L}t)\Delta\hat{f}_{Y_j}\right)\, dt, \qquad (39)$$

where $\Delta\hat{f}_{Y_i} = \hat{f}_{Y_i} - \langle\hat{f}_{Y_i}\rangle_0$ mean fluctuations of dissipative fluxes $\hat{f}_{Y_i}$ determined by relations

$$\hat{I}_{Y_i}^d(\boldsymbol{k}) = (1-\mathcal{P}_H)i\hat{L}\hat{Y}_i(\boldsymbol{k}) = \dot{\hat{Y}}_i(\boldsymbol{k}) - i\Omega_{Y_i Y_j}(k)\hat{Y}_j(\boldsymbol{k}),$$

$$\hat{I}_{Y_i}^d(k \to 0) = i\boldsymbol{k}\,\hat{f}_{Y_i}. \qquad (40)$$

In hydrodynamic limit ($k \to 0$, $z \to 0$) transport coefficients (33)-(34) are known to be expressed via Kubo relations [1,3] while cross–effects transport coefficients (36)-(37), determined on the different tensor dimension fluxes, tend to zero in the complete conformity with Curie principle [23] being not observable in ordinary hydrodynamics.

Taking into account properties (28) of projecting operator $\mathcal{P}_H$ and expression (9) for $\hat{\bar{n}}_1(\boldsymbol{k})$ one might obtain besides (31)-(34) some auxiliary relations for other kinetic koefficients:

$$\mathsf{L}_{n\bar{n}_1} = \mathsf{L}_{\bar{n}_1 n} = A\mathsf{L}_{nn}; \quad \mathsf{L}_{\bar{n}_1 h} = \mathsf{L}_{h\bar{n}_1} = A\mathsf{L}_{nh}; \quad \mathsf{L}_{\bar{n}_1\bar{n}_1} = A^2\mathsf{L}_{nn}, \quad (41)$$

where factor A in long-wave limit could be expressed explicitly via thermodynamic quantities:

$$A = \frac{V\delta}{z_p K_T + V\delta^2} - \frac{1}{\delta_m} \qquad (42)$$

where

$$\delta_m = \frac{m_1 - m_2}{\bar{m}}; \qquad \bar{m} = m_1 C_1 + m_2 C_2 \equiv m_1 C_1 + m_2(1 - C_1),$$

$$z_p = \left(\frac{\partial\mu}{\partial C_1}\right)_{T,p,N}; \qquad \mu = \mu_1 - \mu_2. \qquad (43)$$

Note that transport coefficients (33)-(34) in the limit ($k \to 0$, $z \to 0$) are connected with **experimentally observed** coefficients of mutual diffusion $\mathcal{D}$ and thermal diffusion $\kappa\mathcal{D}$, where κ means thermal diffusion ratio. One can obtain these expressions, taking into account relations between Onzager coefficients constructed on partial number densities $\mathsf{L}_{n_i n_j}$, $\mathsf{L}_{n_j h}$, which could be presented in the form

$$\sum_{i=1}^{2} m_i \mathsf{L}_{n_i n_j} = 0, \quad \sum_{i=1}^{2} m_i \mathsf{L}_{n_i h} = 0, \tag{44}$$

and the fact that thermodynamic force $\nabla\left(\frac{\mu}{T}\right)$ could be written down in the terms of concentration C_1, temperature T and pressure p as follows:

$$\nabla\mu = \left(\frac{\partial\mu}{\partial C_1}\right)_{p,T} \nabla C_1 + \left(\frac{\partial\mu}{\partial T}\right)_{C_1,p} \nabla T + \left(\frac{\partial\mu}{\partial p}\right)_{C_1,T} \nabla p, \tag{45}$$

that gives us the well known form for observable dissipative flux $\langle\hat{f}_{n_1}\rangle_0$ [3,23]:

$$\langle\hat{f}_{n_1}\rangle_0 = -\frac{1}{m_1}\rho\mathcal{D}\left(\nabla C_1 + \frac{\kappa}{T}\nabla T + \frac{\kappa_p}{p}\nabla p\right). \tag{46}$$

In (46) $\mathcal{D} = \dfrac{\mathsf{L}_{nn}X^2}{\bar{m}S_{xx}}$ means mutual diffusion coefficients, where $X = \dfrac{m_2\tilde{m}}{m_2 - m_1}$, $\tilde{m} = \dfrac{m_1 m_2}{m_1 + m_2}$ means reduced mass, S_{xx} denotes "mass concentration–mass concentration" static structure factor, related with S_{CC} as follows: $S_{xx} = \dfrac{(m_1 m_2)^2}{\bar{m}^3}S_{CC}$, $\kappa\mathcal{D} = \dfrac{X}{\bar{m}}\left\{\mathsf{L}_{nh} + XT\left(\dfrac{\partial\mu}{\partial T}\right)_{C_1,p}\right\}$ denotes thermal diffusion coefficient, while $\kappa_p = pTS_{xx}\left(\dfrac{\partial\mu}{\partial p}\right)_{C_1,T}$ denotes barodiffusion coefficient.

It should be mentiond that the chain of equation for TCF (25) is not closed yet: one can write down the equation for memory kernels where the functions constructed on derivatives of hydrodynamic densities will be involved [24]. Hence, it is necessary to perform certain ansatz to calculate generalized transport coefficients (33)-(37) defined accordingly (29) via memory functions. To solve this problem and, consequently, to consider time–spatial dispersion of transport coefficients we shall extend the set of hydrodynamic variables (8)-(11) having included their derivatives and having redefined memory kernels on the basis of recursive relations for the dynamic variables of kinetic nature. This is a subject of the next section.

3. Extended set of dynamic variables and definition of the generalized transport coefficients.

To go out from the framework of hydrodynamics and to make possible the generalization of transport coefficients in domain of arbitrary values of $\boldsymbol{k}$ and ω let us include into the basic set of dynamic variables (8)-(11) their derivatives, namely

$$\hat{B}_i(\boldsymbol{k}) = i\hat{L}\hat{Y}_i^{(0)}(\boldsymbol{k}), \quad i = 1,\ldots,4. \tag{47}$$

Further step is to orthogonalize $\hat{B}_i(\boldsymbol{k})$ with respect to the hydrodynamic variables (here and afterwards we supply $\hat{Y}_i(\boldsymbol{k})$ from (8)-(11) with superscript (0) to differ them from kinetic variables – the derivatives of $\hat{Y}_i^{(0)}(\boldsymbol{k})$ – defined below):

$$\hat{Y}_i^{(1)}(\boldsymbol{k}) = (1 - \mathcal{P}_H)\hat{B}_i(\boldsymbol{k}) = (1 - \mathcal{P}_H)\dot{\hat{Y}}_i^{(0)}(\boldsymbol{k}). \tag{48}$$

We confine ourselves only by the first derivatives of hydrodynamic variables referring readers for studying the general case of higher derivatives to [13,27]. One has to remark that three variables from 8 of the set $\hat{Y}_i(\boldsymbol{k}) = \hat{Y}_i^{(0)}(\boldsymbol{k}) \bigotimes \hat{Y}_i^{(1)}(\boldsymbol{k})$, namely $\hat{Y}_3^{(0)}$, $\hat{Y}_1^{(1)}$, $\hat{Y}_2^{(1)}$, are not independent (it is easy to verify writing them down explicitly). Hence we ommit variable $\hat{Y}_2^{(1)} \equiv (1 - \mathcal{P}_H)i\hat{L}\hat{\tilde{n}}_1(\boldsymbol{k})$ and shall operate with 7 variables: four hydrodynamic $\hat{Y}_i^{(0)}(\boldsymbol{k}) = \left\{\hat{Y}_1^{(0)}(\boldsymbol{k}), \hat{Y}_2^{(0)}(\boldsymbol{k}), \hat{Y}_3^{(0)}(\boldsymbol{k}), \hat{Y}_4^{(0)}(\boldsymbol{k})\right\}$ (variables (8)-(11)) and three kinetic $\hat{Y}_i^{(1)}(\boldsymbol{k}) = \left\{\hat{Y}_1^{(1)}(\boldsymbol{k}), \hat{Y}_3^{(1)}(\boldsymbol{k}), \hat{Y}_4^{(1)}(\boldsymbol{k})\right\}$.

One has to point out that variables $\hat{Y}_i^{(1)}(\boldsymbol{k})$ are not mutualy orthogonal being orthogonal only with respect to $\hat{Y}_i^{(0)}(\boldsymbol{k})$. The procedure of "internal" ortogonalization of (48) leads $\hat{Y}_2^{(1)}(\boldsymbol{k})$ to become zero and this is the second reason for ommitting it.

Using method of nonequilibrium statistical operator (NSO) [23] we can write down the system of equations for Fourier–transforms

$$\langle\Delta\hat{Y}_i(\boldsymbol{k})\rangle^\omega = \int_{-\infty}^{\infty} \exp(i\omega t)\langle\Delta\hat{Y}_i(\boldsymbol{k})\rangle^t \, dt \tag{49}$$

of averaged over NSO dynamic variables – the chain of transport equa-

tions for the extended set:

$$
\begin{pmatrix}
M_{00}(k,\omega) & \vline & M_{01}(k) \\
\hline
M_{10}(k) & \vline & M_{11}(k,\omega)
\end{pmatrix}
\begin{pmatrix}
\langle \Delta \hat{Y}^{(0)}(\boldsymbol{k}) \rangle^{\omega} \\
\hline
\langle \Delta \hat{Y}^{(1)}(\boldsymbol{k}) \rangle^{\omega}
\end{pmatrix} = 0 \,, \quad (50)
$$

where subblocks of the matrix in the left-hand side are of the following structure:

$$
M_{00}^{4\times4}(k,\omega) =
\begin{pmatrix}
i\omega & 0 & -i\Omega_{np}(k) & 0 \\
0 & i\omega & -i\Omega_{\bar{n}_1 p}(k) & 0 \\
-i\Omega_{pn}(k) & -i\Omega_{p\bar{n}_1}(k) & i\omega & -i\Omega_{ph}(k) \\
0 & 0 & -i\Omega_{hp}(k) & i\omega
\end{pmatrix} \quad (51)
$$

denotes hydrodynamic matrix of 4×4 − dimension;

$$
M_{01}^{4\times3}(k) =
\begin{pmatrix}
-1 & 0 & 0 \\
-i\Omega_{21}^{(01)}(k) & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix} \quad (52)
$$

means matrix of 4×3 − dimension;

$$
M_{10}^{3\times4}(k) =
\begin{pmatrix}
\Gamma_{11}(k) & \Gamma_{12}(k) & 0 & \Gamma_{14}(k) \\
0 & 0 & \Gamma_{33}(k) & 0 \\
\Gamma_{41}(k) & \Gamma_{42}(k) & 0 & \Gamma_{44}(k)
\end{pmatrix} \quad (53)
$$

is 3×4 − dimension matrix. In (51)-(53) we have used the definitions for frequency matrixes (26), constructed on whole set $\hat{Y}_i(\boldsymbol{k}) = \hat{Y}_i^{(0)}(\boldsymbol{k}) \bigotimes \hat{Y}_i^{(1)}(\boldsymbol{k})$, taking into account nonorthogonality of variables $\hat{Y}_i^{(1)}(\boldsymbol{k})$. One can easily prove that corresponding elements of the subblock $M_{01}(k)$ reduce to units (exept the element $-i\Omega_{21}^{(01)}(k)$) while the elements of $M_{10}(k)$ can be written down as follows:

$$
\Gamma_{ij}(k) = i\Omega_{ij}^{(10)}(k) = \frac{\left(\dot{\hat{Y}}_i^{(1)}(\boldsymbol{k}), \hat{Y}_j^{(0)}(-\boldsymbol{k}) \right)}{\left(\hat{Y}_j^{(0)}(\boldsymbol{k}), \hat{Y}_j^{(0)}(-\boldsymbol{k}) \right)}\,. \quad (54)
$$

The last equations for $i, j \neq 2$ could be presented as

$$
\Gamma_{ij}(k) = -\frac{\left(\hat{Y}_i^{(1)}(\boldsymbol{k}), \hat{Y}_j^{(1)}(-\boldsymbol{k}) \right)}{\left(\hat{Y}_j^{(0)}(\boldsymbol{k}), \hat{Y}_j^{(0)}(-\boldsymbol{k}) \right)}\,. \quad (55)
$$

What about kinetic subblock $M_{11}(k,\omega)$, in Markovian approximation it has the form

$$
M_{11}(k,\omega) =
$$
$$
\begin{pmatrix}
i\omega + \tilde{\varphi}_{11}^{(1)}(k,0) & -i\Omega_{13}^{(1)}(k) + \tilde{\varphi}_{13}^{(1)}(k,0) & \tilde{\varphi}_{14}^{(1)}(k,0) \\
-i\Omega_{31}^{(1)}(k) + \tilde{\varphi}_{31}^{(1)}(k,0) & i\omega + \tilde{\varphi}_{33}^{(1)}(k,0) & -i\Omega_{34}^{(1)}(k) + \tilde{\varphi}_{34}^{(1)}(k,0) \\
\tilde{\varphi}_{41}^{(1)}(k,0) & -i\Omega_{43}^{(1)}(k) + \tilde{\varphi}_{43}^{(1)}(k,0) & i\omega + \tilde{\varphi}_{44}^{(1)}(k,0)
\end{pmatrix},
$$
$$
(56)
$$

with elements

$$
i\Omega_{ij}^{(1)}(k) = \sum_l \left(\dot{\hat{Y}}_i^{(1)}(\boldsymbol{k}), \hat{Y}_l^{(1)}(-\boldsymbol{k}) \right) \left(\hat{Y}^{(1)}(\boldsymbol{k}), \hat{Y}^{(1)}(-\boldsymbol{k}) \right)_{lj}^{-1}\,, \quad (57)
$$

$$
\tilde{\varphi}_{ij}^{(1)}(k,\omega) = \int_{-\infty}^{\infty} \exp(-i\omega t)\, \varphi_{ij}^{(1)}(k,t)\, dt\,, \quad (58)
$$

where

$$
\varphi_{ij}^{(1)}(k,t) = \sum_l \int_{-\infty}^{t} \exp(-\epsilon\tau) \left((1-\mathcal{P})\dot{\hat{Y}}_i^{(1)}(\boldsymbol{k}), \exp\left[-(1-\mathcal{P})i\hat{L}\tau \right] \right.
$$
$$
\left. \times\, (1-\mathcal{P})\dot{\hat{Y}}_l^{(1)}(-\boldsymbol{k}) \right) \left(\hat{Y}^{(1)}(\boldsymbol{k}), \hat{Y}^{(1)}(-\boldsymbol{k}) \right)_{lj}^{-1} d\tau \quad (59)
$$

denote memory kernels constructed on basis $\hat{Y}_i^{(1)}(\boldsymbol{k})$, where projecting operator $\mathcal{P}$ consists of two terms:

$$
\mathcal{P} = \mathcal{P}_H + \mathcal{P}^{(1)} \equiv \mathcal{P}^{(0)} + \mathcal{P}^{(1)} \quad (60)
$$

with Mori-like projecting operators $\mathcal{P}^{(0)} \equiv \mathcal{P}_H$ (see eqn. (28)) defined on hydrodynamic basis (8)-(11) and $\mathcal{P}^{(1)}$ defined as

$$
\mathcal{P}^{(1)} \ldots = \sum_{i,j} \left(\ldots, \hat{Y}_i^{(1)}(-\boldsymbol{k}) \right) \left(\hat{Y}^{(1)}(\boldsymbol{k}), \hat{Y}^{(1)}(-\boldsymbol{k}) \right)_{ij}^{-1} \hat{Y}_j^{(1)}(\boldsymbol{k})\,. \quad (61)
$$

From (59)-(61) immediately follows that $\left(1 - \mathcal{P}^{(0)} - \mathcal{P}^{(1)} \right) \dot{\hat{Y}}_i^{(0)}(\boldsymbol{k}) \equiv 0$ so memory kernels remain only in the subblock $M_{11}(k,\omega)$.

Note that the Markovian approximation for memory kernels constructed on derivatives of hydrodynamic densities is well grounded because these memory functions are damping more rapidly than TCF of hydrodynamic variables [10,13].

Now we have prepared everything for solution to the problem how to introduce the generalized transport coefficients. Having solved the second equation of (50) with respect to $\langle \Delta \hat{Y}_i^{(1)}(\boldsymbol{k}) \rangle^\omega$ and substituting obtained result into the first equation one can write down the following matrix relation:

$$\left(M_{00}(k,\omega) - M_{01}(k)\, M_{11}^{-1}(k,\omega)\, M_{10}(k) \right)\, \langle \Delta \hat{Y}_i^{(0)}(\boldsymbol{k}) \rangle^\omega = 0 \;, \qquad (62)$$

where from it is easy to indentify $\tilde{\varphi}^{(0)}(k,\omega)$:

$$\tilde{\varphi}^{(0)}(k,\omega) = -M_{01}(k)\, M_{11}^{-1}(k,\omega)\, M_{10}(k)\,. \qquad (63)$$

The last equations, being the result of recursive relations procedure, has its general meaning what allows one to introduce the generalized transport coefficients of any system as quick as extended set of dynamic variables was taken into consideration. For instance, in Ref. [27] the generalized coefficients of simple Lennard–Jones liquid have been evaluated taking into account derivatives of hydrodynamic densities up to the third order.

Now using (29) one can calculate k- and ω–dependent kineic coefficients $\mathsf{L}_{ij}(k,\omega)$ related with generalized transport coefficients $\eta(k,\omega)$, $\zeta(k,\omega, D(k,\omega), D_T(k,\omega), \lambda(k,\omega), \xi(k,\omega)$ and $\nu(k,\omega)$.

On figure (1) we have presented k-dependence of transport coefficients at $\omega = 0$ and on figures (2)-(5) ω-dependence of transport coefficients (accordingly- their real and imiginary parts) at fixed values of wave–vector k. As input data we have used MD simulation results of Ref. [12], namely: static correlation functions, constructed on the basic set of partial densities and derivatives of total momentum and total energy densities

$$\hat{\mathcal{y}}_i(\boldsymbol{k}) = \{\hat{n}_1(\boldsymbol{k}, \hat{n}_2(\boldsymbol{k}), \hat{p}_1^{||}(\boldsymbol{k}), \hat{p}_2^{||}(\boldsymbol{k}), \hat{\varepsilon}(\boldsymbol{k}), \dot{\hat{p}}^{||}(\boldsymbol{k}), \dot{\hat{\varepsilon}}(\boldsymbol{k})\} \qquad (64)$$

and hydrodynamic relaxation times, defined accordingly

$$\tau_{\mathcal{y}_i \mathcal{y}_j}(k) = \frac{\int\limits_0^\infty F_{\mathcal{y}_i \mathcal{y}_j}(k,t)\, dt}{F_{\mathcal{y}_i \mathcal{y}_j}(k,0)}. \qquad (65)$$

The expressions for transport equations (cf. (50)), constructed on basic set (64) as well as the form of transition matrix $\mathcal{L}$ from (64) to the variables $\hat{Y}_i(\boldsymbol{k})$ are presented in the Appendix. We would like to emphasize
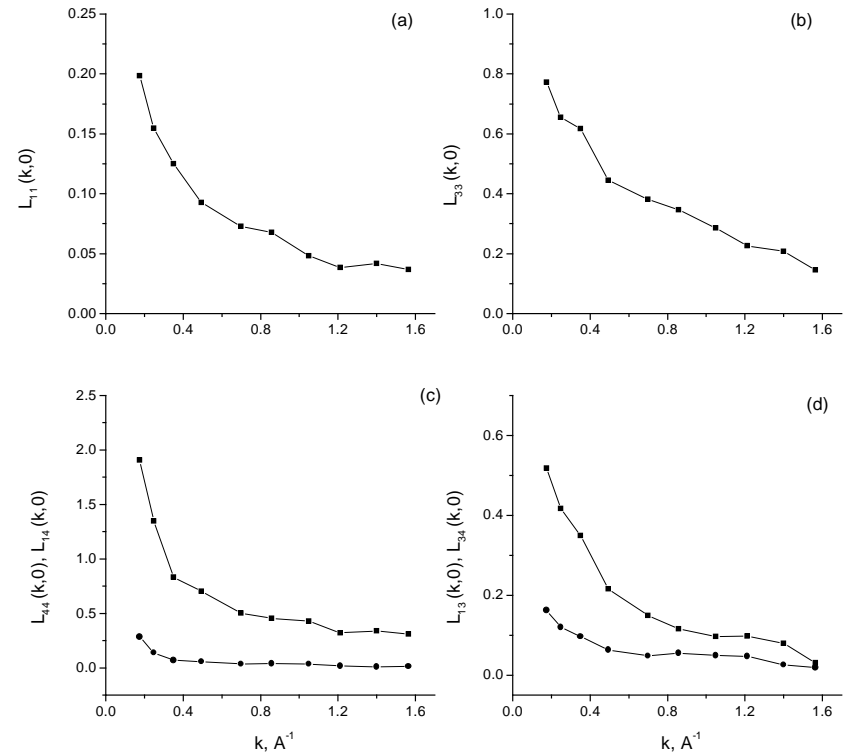

Figure 1. Kinetic coefficients $\mathsf{L}_{11}(k,0)$, $\mathsf{L}_{33}(k,0)$, $\mathsf{L}_{44}(k,0)$ (squares), $\mathsf{L}_{14}(k,0)$ (circles), $\mathsf{L}_{34}(k,0)$ (squares), $\mathsf{L}_{13}(k,0)$ (circles) as functions of k.
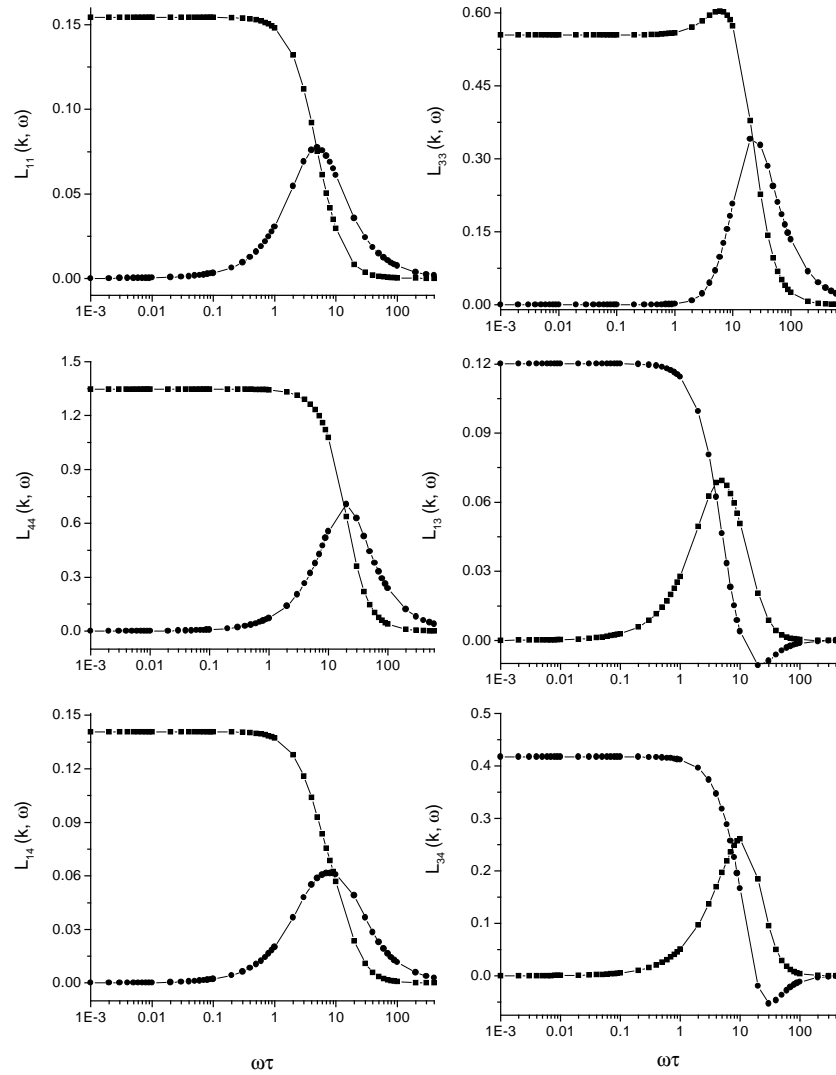
Figure 2. $k = 0.247 \mathring{A}^{-1}$. Real (squares) and image (circles) parts of kinetic coefficients $\mathsf{L}_{ij}(k,\omega)$ as functions of $\omega\tau$.
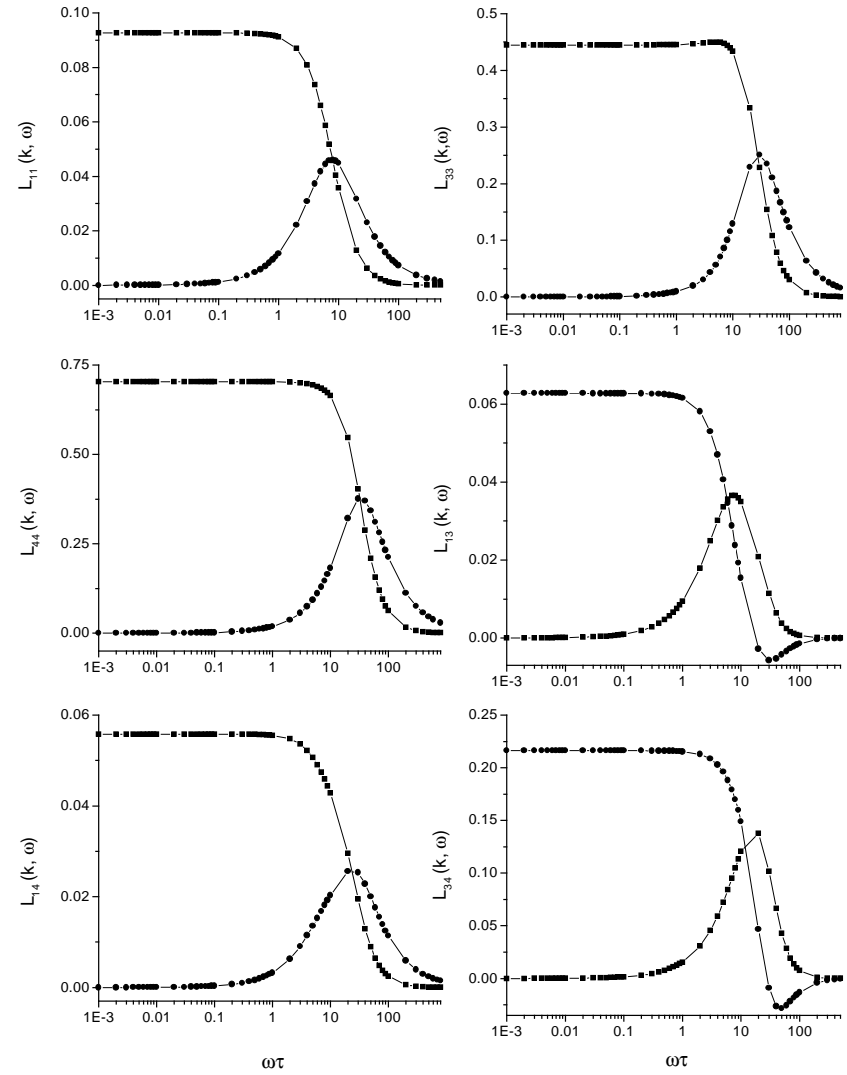
Figure 3. $k = 0.494 \mathring{A}^{-1}$. Real (squares) and image (circles) parts of kinetic coefficients $\mathsf{L}_{ij}(k,\omega)$ as functions of $\omega\tau$.
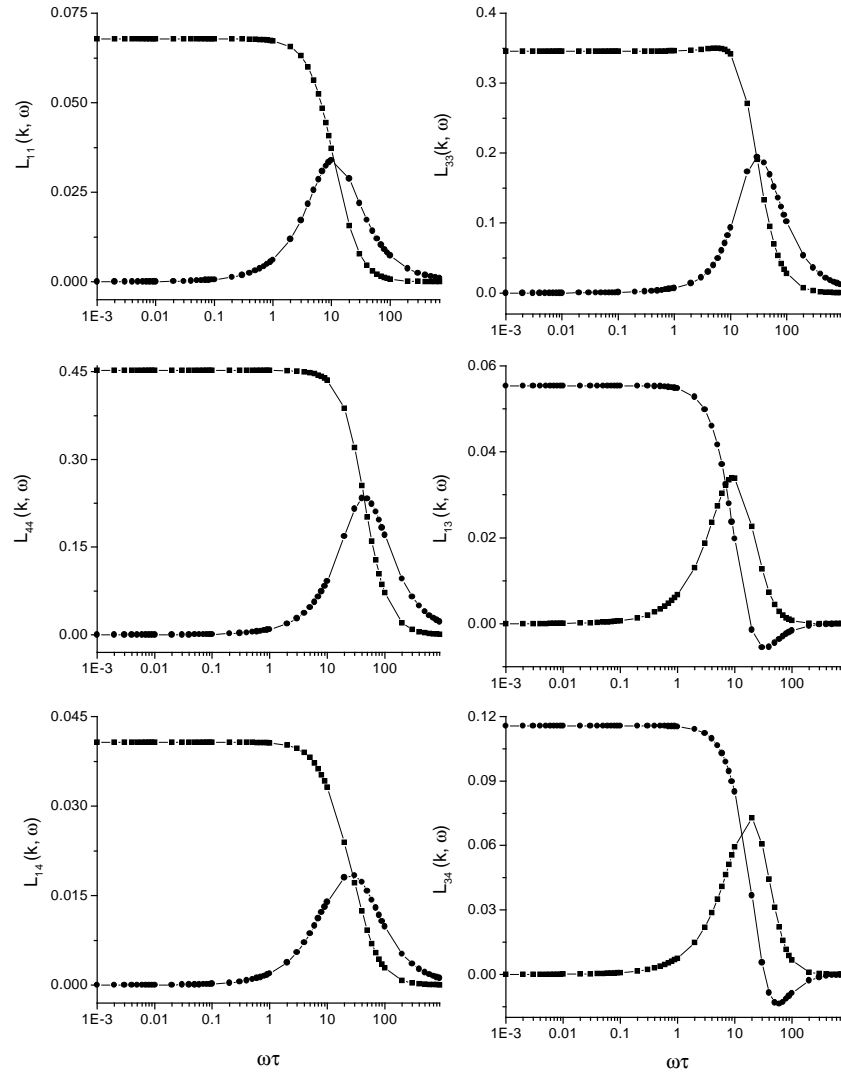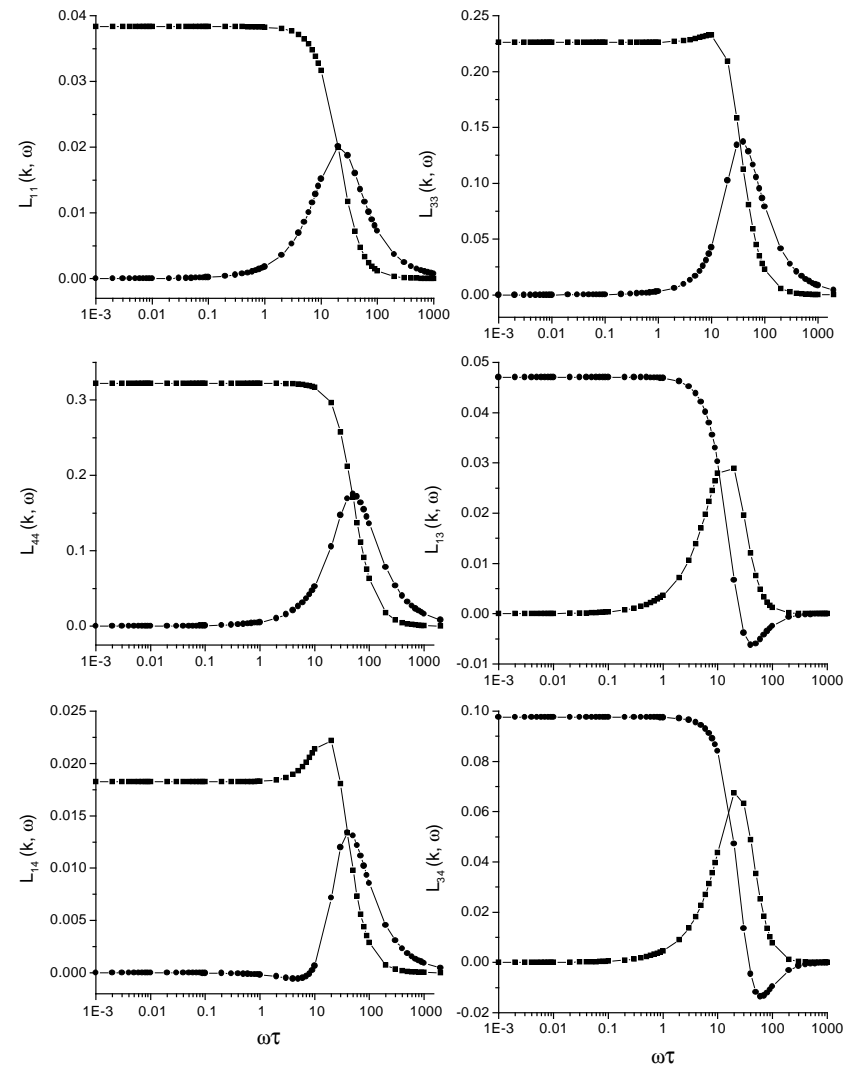
Figure 4. $k = 0.856\mathring{A}^{-1}$. Real (squares) and image (circles) parts of kinetic coefficients $\mathsf{L}_{ij}(k,\omega)$ as functions of $\omega\tau$.

Figure 5. $k = 1.211\mathring{A}^{-1}$. Real (squares) and image (circles) parts of kinetic coefficients $\mathsf{L}_{ij}(k,\omega)$ as functions of $\omega\tau$.

once more that none approximation except Markovian was done during calculation of memory functions which, as one can see from Appendix, reduce to evaluation of higher order static correlation functions. Hence, our approach indeed appears to be parameter–free.

MD simulations have been performed for a gas mixture of $He_{0.65}$-$Ne_{0.35}$ at a number density n=0.0186 $\mathring{A}^{-3}$ at temperature T=39.3 K. The system of 864 particles interacting through Aziz-potentials [25,26] at constant volume has been considered.

¿From figure (1)-(5) one can see that process of heat transfer is the dominant in comparison with the others (value of $\lambda(k,0)$ is one order larger then interdiffusion and thermal diffusion coefficients and is three times as much as longitudnial viscousity). The profile of thermal diffusion coefficient is much smoother then $\lambda(k,0)$ and $D(k,0)$ and becomes negligible already at $k = 0.4\mathring{A}^{-1}$. It means that behaviour of temperature conductivity coefficient $\chi(k,0) = \lambda(k,0) - \dfrac{D_T^2(k,0)}{D(k,0)}$ (it is exactly coefficient $\chi(k,\omega)$ to be measured in heat transfer experiments) reflects the main features of heat conductivity being only slightly shiffted because of interdiffusion and thermal diffusion processes. From fig. (1) one can observe coefficients $\xi(k,0)$, $\nu(k,0)$ (their imiginary parts) appear to be comparative with longitudnial viscousity and interdiffusion coefficient respectively. On the other hand, they tend to zero when $k \to 0$, though we can not obtain this due to limited volume of simulation box.

Inspecting fig. (2)-(4) one can see that real parts of transport coefficients have character relaxation behaviour from their maximum values at $\omega = 0$ to infinitesimal values when ω becomes large. On the contrary, their imiginary parts increase from zero at $\omega = 0$ to maximum in the vicinity of fast sound frequency (see [12]) renormalizing sound dispersion and shifting sound peak of dynamic structure factor to the right.

Transport coefficient $\xi(k,\omega)$ and $\nu(k,\omega)$ that describe fluxes with different tensor dimensiality have pure imiginary parts at $\omega = 0$ as it should be according Curie principle. One can see that their imiginary parts tend to zero from below changing their signs at frequencies where corresponding real parts become of the maximum values. So their behaviour resembles the behaviour of cross-effect transport coefficient and bulk viscosity in simple liquid [27]. The common feature of all transport coefficients is decreasing of their values (both real and imiginary parts) with growth of k.

An availability of a small peak in longitudnial viscosity $4/3\eta(k,\omega) + \zeta(k,\omega)$ at low values of wave–vector as well as appearance of similar peak in thermal diffusion coefficient at intermidiate values of k in our opinion

is the only result of our restriction by the first derivatives of the dynamic variables in recursive relations. As has been already said a further extention of our method on case of higher derivatives is straightforward and could be the subject of further research.

Note, that generalized transport coefficients in the domain of small wave–vectors have Lorentz form [28] like TCF in Markovian approximation [10].

4. Conclusion

In the present paper we have presented the method of calculation of time–spatial dispersion of transport coefficients. Nonlocality of obtained transport coefficients is a result of consistent description of kinetics and hydrodynamics of the system (an initial set of transport equations for hydrodynamic variables has been extended at the expence of including kinetic variables). Taking into consideratin kinetic variables makes Markovian approximation for the memory kernels well grounded because memory functions constructed on derivatives of hydrodynamic densities are known to relax in time more rapidly then corresponding hydrodynamic time correlation functions [13]. At the same time it would be interesting to include the second derivatives into our set of dynamic variables. It corresponds to 7–modes approximation for TCF in the theory of simple fluids [10] and should improve the whole recursive procedure because the convergence of calculations grows with extending of the basic set of variables.

Another way of introducing generalized transport coefficients is application of the mode–coupling theory. As one has already said this method allows us to calculate nonanalytical corrections to the transport coefficients explicitly. Thus, one can obtain $\sqrt{k}$–dependence of cross–effect coefficients $\xi(k,0$, $\nu(k,0)$ in hydrodynamic region, while kinetic theory of simple fluids give us behaviour linear in k. However the limiting frame of mode–coupling theory is requirement for k to be small. On the other hand, MD simulations are restricted by the box volume that is - by k from below. It is challenging to invastigate just this intermediate region of wave–vectors to answer to the question whether including into consideration higher fluctuations and higher derivatives of dynamic variables are equivalent procedures.

It would be interesting to investigate time–spatial dispersion of transport coefficients of other binary mixtures, such as Ar-Kr, Ar-Xe, where the mass ratio of heavier to lighter component is not so large as in present case to possess enough statistics about behaviour of these coefficients.

For instance, slow decreasing of transport coefficients in k in the intermediate domain of wave–vector (see Fig.(1) could be the result of such a masses ratio. Quite different systems are polymers, where the molecular masses of species are about the same.

All problems mentioned here could be the subject of a separate study which authors hope to carry out in future.

Appendix

Transport equations (50), constructed on the set of partial densities (64), in Markovian approxiamtion can be written down in the matrix form [10]:

$$i\omega\langle\Delta\hat{y}_i(\boldsymbol{k})\rangle^\omega + T_{ij}(k)\langle\Delta\hat{y}_j(\boldsymbol{k})\rangle^\omega = 0, \tag{A.1}$$

where the dynamic matrix $T_{ij}(k) = -i\Omega_{y_i y_j}(k) + \tilde{\varphi}_{y_i y_j}(k,0)$ can be expressed via matrix $F_{y_i y_j}(k) = \left(\hat{y}_i(\boldsymbol{k}), \hat{y}_j(-\boldsymbol{k})\right)$ of corresponding static correlation functions and the inverse matrix to $\tilde{F}_{y_i y_j}(k) = \int_0^\infty F_{y_i y_j}(k,t)\, dt$ as follows:

$$T_{ij}(k) = \sum_{l=1}^7 F_{y_i y_l}(k)\left[\tilde{F}(k)\right]^{-1}_{y_l y_j}, \tag{A.2}$$

where matrix of relaxation times $\tilde{F}_{y_i y_j}(k)$ can be presented as:

$$\tilde{F}_{y_i y_j}(k) =$$

$$\begin{pmatrix}
\tau_{n_1 n_1}F_{n_1 n_1} & \tau_{n_1 n_2}F_{n_1 n_2} & \frac{\imath m_1}{k}F_{n_1 n_1} & \frac{\imath m_2}{k}F_{n_1 n_2} & \tau_{n_1\varepsilon}F_{n_1\varepsilon} & 0 & -F_{n_1\varepsilon} \\
\tau_{n_1 n_2}F_{n_1 n_2} & \tau_{n_2 n_2}F_{n_2 n_2} & \frac{\imath m_1}{k}F_{n_1 n_2} & \frac{\imath m_2}{k}F_{n_2 n_2} & \tau_{n_1\varepsilon}F_{n_2\varepsilon} & 0 & -F_{n_2\varepsilon} \\
\frac{-\imath m_1}{k}F_{n_1 n_1} & \frac{-\imath m_1}{k}F_{n_1 n_2} & 0 & 0 & \frac{\imath m_1}{k}F_{n_1\varepsilon} & -F^{\|}_{p_1 p_1} & 0 \\
\frac{-\imath m_2}{k}F_{n_1 n_2} & \frac{-\imath m_2}{k}F_{n_2 n_2} & 0 & 0 & \frac{\imath m_2}{k}F_{n_2\varepsilon} & -F^{\|}_{p_2 p_2} & 0 \\
\tau_{n_1\varepsilon}F_{n_1\varepsilon} & \tau_{n_2\varepsilon}F_{n_2\varepsilon} & \frac{-\imath m_1}{k}F_{n_1\varepsilon} & \frac{-\imath m_2}{k}F_{n_2\varepsilon} & \tau_{\varepsilon\varepsilon}F_{\varepsilon\varepsilon} & 0 & -F_{\varepsilon\varepsilon} \\
0 & 0 & F^{\|}_{p_1 p_1} & F^{\|}_{p_2 p_2} & 0 & 0 & -F^{\|}_{\dot{p}\varepsilon} \\
F_{n_1\varepsilon} & F_{n_2\varepsilon} & 0 & 0 & F_{\varepsilon\varepsilon} & F^{\|}_{\dot{p}\varepsilon} & 0
\end{pmatrix}. \tag{A.3}$$

Here we have used definition (65) for corresponding relaxation times τ while the other elements could be expressed via static correlation functions $F_{y_i y_j}(k)$. One can see from (A.1)-(A.3) that memory functions, constructed on basic set (64), are expressed only via static correlation functions and relaxation times without any complex time dependence through projecting technique (unlike memory kernels (59)), so they turn out to be quite simple functions for MD simulations.

Transition matrix $\mathcal{L}_{ij}(k)$ from the set $\hat{Y}_i(\boldsymbol{k})$ to the variables $\hat{y}_i(\boldsymbol{k})$ can be presented as follows:

$$\mathcal{L}_{ij}(k) = \frac{\partial Y_i(k)}{\partial y_j(k)} = \begin{bmatrix}
1 & 1 & 0 & 0 & 0 & 0 & 0 \\
\mathcal{L}_{21} & \mathcal{L}_{22} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 1 & 0 & 0 & 0 \\
\mathcal{L}_{41} & \mathcal{L}_{42} & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & \mathcal{L}_{53} & \mathcal{L}_{54} & 0 & 0 & 0 \\
\mathcal{L}_{61} & \mathcal{L}_{62} & 0 & 0 & \mathcal{L}_{65} & 1 & 0 \\
0 & 0 & \mathcal{L}_{73} & \mathcal{L}_{74} & 0 & 0 & 1
\end{bmatrix}. \tag{A.4}$$

In (A.4) we have the following nonzero elements (except $\mathcal{L}_{11} = \mathcal{L}_{12} = \mathcal{L}_{33} = \mathcal{L}_{34} = \mathcal{L}_{45} = \mathcal{L}_{66} = \mathcal{L}_{77} = 1$):

$$\mathcal{L}_{21}(k) = \frac{\partial\tilde{n}_1(k)}{\partial n_1(k)} = 1 - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}, \tag{A.5}$$

$$\mathcal{L}_{22}(k) = \frac{\partial\tilde{n}_1(k)}{\partial n_2(k)} = -\frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}, \tag{A.6}$$

$$\mathcal{L}_{41}(k) = \frac{\partial h(k)}{\partial n_1(k)} = -\frac{(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\mathcal{L}_{11} - \frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}(-\boldsymbol{k})_1\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}(-\boldsymbol{k})_1\right)}\mathcal{L}_{21} =$$

$$-\frac{(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))} - \frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}\left\{1 - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\right\}, \tag{A.7}$$

$$\mathcal{L}_{42}(k) = \frac{\partial h(k)}{\partial n_2(k)} = -\frac{(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\mathcal{L}_{12}(k) - \frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}\mathcal{L}_{22}(k) =$$

$$(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))^{-1}\left\{\frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)} - (\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))\right\}, \tag{A.8}$$

$$\mathcal{L}_{53}(k) = \imath k\left\{\frac{1}{m_1} - \frac{1}{\bar{m}}\right\}, \tag{A.9}$$

$$\mathcal{L}_{54}(k) = \imath k\left\{\frac{1}{m_2} - \frac{1}{\bar{m}}\right\}, \tag{A.10}$$

$$\mathcal{L}_{61}(k) = -\frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k})\right)}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\mathcal{L}_{11}(k) - \frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}\mathcal{L}_{21}(k)$$

$$- \frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right)}{\left(\hat{h}(\boldsymbol{k}), \hat{h}(\boldsymbol{k})\right)}\mathcal{L}_{41}(k), \tag{A.11}$$

where

$$\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k})\right) = \frac{\imath k}{\beta}\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right) = \frac{\imath k}{\beta}\left\{C_1 - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\right\},$$

$$\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right) = \left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{\varepsilon}(-\boldsymbol{k})\right) - \frac{\imath k}{\beta}\frac{(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}$$

$$-\frac{\imath k}{\beta}\left\{C_1 - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\right\}\frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)},$$

$$\mathcal{L}_{62}(k) = -\frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k})\right)}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}\mathcal{L}_{12}(k) - \frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)}\mathcal{L}_{22}(k)$$

$$- \frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right)}{\left(\hat{h}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right)}\mathcal{L}_{42}(k), \tag{A.12}$$

$$\mathcal{L}_{65}(k) = -\frac{\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right)}{\left(\hat{h}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right)}, \tag{A.13}$$

$$\mathcal{L}_{73}(k) = \mathcal{L}_{74}(k) = -\frac{\left(\dot{\hat{h}}(\boldsymbol{k}), \hat{p}^{\|}(-\boldsymbol{k})\right)}{\left(\hat{p}^{\|}(\boldsymbol{k}), \hat{p}^{\|}(-\boldsymbol{k})\right)} = -\frac{\beta}{\bar{m}}\left(\dot{\hat{p}}^{\|}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right). \tag{A.14}$$

In its turn,

$$\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right) = (\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k})) - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))^2}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))},$$

$$\left(\hat{h}(\boldsymbol{k}), \hat{h}(-\boldsymbol{k})\right) = (\hat{\varepsilon}(\boldsymbol{k}), \hat{\varepsilon}(-\boldsymbol{k})) - \frac{(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))^2}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))} - \frac{\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)^2}{\left(\hat{\tilde{n}}_1(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right)},$$

$$\left(\hat{\varepsilon}(\boldsymbol{k}), \hat{\tilde{n}}_1(-\boldsymbol{k})\right) = (\hat{\varepsilon}(\boldsymbol{k}), \hat{n}_1(-\boldsymbol{k})) - \frac{(\hat{n}_1(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))\,(\hat{\varepsilon}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}{(\hat{n}(\boldsymbol{k}), \hat{n}(-\boldsymbol{k}))}.$$

Acknowledgement

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