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Generalized thermodynamic and transport properties. I. Simple liquids

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We propose a method by which the generalized transport properties and coefficients at all wavelengths and frequencies can be obtained by inversion of an exact kinetic equation. The necessary data are the density-density, energy-energy, and density-energy time correlation functions, which can be obtained by molecular-dynamics simulation. In addition, also the coupling between viscous stress tensor and energy flux vector can be obtained without approximation. This allows one to check the validity of the Markov assumption in a straightforward way. As a first test case, the theory is applied to liquid argon in two thermodynamic states. For this system, we calculate and discuss generalized thermodynamic (enthalpy, specific heats, and thermal expansion) and transport properties (longitudinal viscosity, thermal conductivity).

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I. INTRODUCTION

Generalized hydrodynamics extends from the macroscopic to the microscopic scale the domain of ordinary hydrodynamics. Retaining the form of the Navier-Stokes equations, it describes how the thermodynamic properties and transport coefficients depend on distance and time scales typical of the microscopic structure and dynamics of the fluids. With this extension, one will then be able to predict, for example, the momentum with which neutrons are scattered at various angles by a fluid. In the study of liquids since 1965, the generalized hydrodynamics theory [1–6] has been developed by many authors. At the same time, computer simulations started their enormous increase in scope and applications [7–9]. In addition, the neutron scattering technique [10,11] was continuously improved, complemented, after 1990, by inelastic x-ray scattering [11,12]. From a theoretical point of view, an important reference is the paper by de Schepper *et al.* [13], which stimulated and inspired a large part of the work reported here. Despite the fact that the core of the theory was the same as that in the classical works [1–6], the elegant development of the arguments was full of implications, not all of them completely realized and exploited in our opinion.

The authors [13] suggested to adopt a base of microscopic variables that includes fluctuations of density, n, longitudinal velocity, u, energy, e, longitudinal stress tensor, σ, and longitudinal heat flux, q. They showed that only three independent time correlation functions (cf's), namely the density-density, density-energy, and energy-energy cf, are sufficient to derive the entire set of microscopic hydrodynamic cf's. As a test, the method was applied to the Lennard-Jones (LJ) fluid at one thermodynamic state. For this system, a number of k-dependent thermodynamic functions were calculated: the enthalpy per particle, the generalized thermal expansion coefficient, the generalized specific heat at constant volume and pressure, and the generalized ratio of specific heats. The k-dependent transport properties (at $\omega = 0$) also also obtained, but using the Markov approximation and assuming that the three fundamental time cf's can be described by the sum of five complex exponentials. By means of a diagonalization procedure, de Schepper *et al.* [13] obtained the five k-dependent eigenvalues: two (also complex conjugate for higher k values) were related to the two kinetic real modes at small k values, while the remaining three were a direct extension of the heat mode (always real) and complex acoustic modes. For the latter, the common real part corresponded to the sound damping and the conjugate imaginary part to the sound dispersion.

The authors also introduced five k-dependent orthonormal linear combinations of the five microscopic quantities described above. The advantage of this procedure is that the temperature replaces energy in the basis set, and with the three new orthonormal density-density, density-temperature, and temperature-temperature cf's, it is possible to describe all the transport properties of the fluids. In addition, they obtained an exact kinetic equation that relates the Laplace transform of the new orthonormal cf's with all the transport properties and hence transport coefficients (see Appendixes A and B of Ref. [13]).

Another interesting approach to the same issues is that of generalized collective modes (GCM) of Mryglod *et al.* [14]: the starting point was practically the same as that in [13], with the exact kinetic equation described above, although the set of variables was not normalized. Assuming the Markov approximation for the memory functions of the cf's obtained from the hydrodynamic variables (density, current, and energy, and their time derivative), by means of a diagonalization procedure the authors obtained the above cf's as a linear combination of complex exponential terms, as in Ref. [13]. The first application was made for the LJ fluid at the same thermodynamic state as in Ref. [13] in the five-, seven-, and nine-variable approximations (note that the five-variable approximation must coincide with the approximate procedure of Ref. [13]). The method was also applied to the transverse modes, to binary and multicomponent mixtures, to a magnetic and polar fluid, and more recently to single-particle dynamics

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[15] and to the transverse modes of the TIP4P model of water [16]. According to the authors [14], increasing the number of variables led to more accurate results, even though the used cf's are not independent. However, as will be shown in the following, although the approach of Mryglod *et al.* may account for the k,ω dependence of the coupling between viscous stress and energy flux, at least for not too high k values (not in the Gaussian regime), it is impossible to check if the results actually converge to the "exact" ones.

The kinetic equation mentioned above inspired the methodological approach we outline in Sec. II of this paper. Our most remarkable result is that in the frequency domain (and hence, in principle, in the time domain) it is possible to obtain an *exact* expression for the transport properties and coefficients at all k and frequency values, *without* the need of the Markov approximation or any other restrictive hypothesis. This result is attained from the three density-density, density-temperature, and temperature-temperature correlation functions, after a simple linear transformations of the density-density, density-energy, and energy-energy cf's calculated by molecular-dynamics (MD) simulation. The exact solution also allows one to test the Markov approximation, as it gives not only the generalized longitudinal viscosity, thermal conductivity, and generalized ratio of specific heats at all k's and frequencies, but also the generalized transport coefficients. It is worth observing that the latter are usually obtained with use of the Markov approximation.

Section II F is devoted to a discussion of a memory function approach that leads to an interesting and simple connection of the second- and third-order memory functions of the density-density and temperature-temperature cf's with the two corresponding k,ω-dependent transport coefficients, especially in the proper physical limit. Note that the coupling between viscous stress and energy flux can also be obtained without approximation, as well as the free-streaming limit. This regime, where the cf's gradually change from a complex exponential to a Gaussian-like behavior, can be treated with the same procedure, as the method is general and not restricted to a functional fitting type.

To conclude, we remark that despite the enormous amount of work in this field, many questions are still not answered satisfactorily, and a more detailed description of the theoretical problems over the whole k-value regime is of interest [17,18]. Also, the experimental neutron and x-ray scattering results, which become more and more accurate [19,20], still need to be explained. For instance, it is worth remarking that the data of the dynamic structure factor can be interpreted in two seemingly equivalent ways, which correspond to focusing on viscous or thermal effects. At present, no experimental technique allows us to complement the data of density fluctuations with those of energy or temperature fluctuations, which could be used to resolve this ambiguity. However, experimental results of the dynamic structure factor are matched by molecular simulation to such an accuracy that those concerning energy or temperature cf's can also be considered reliable.

The availability of a broad range of cf's for a wide spectrum of k,ω, in its turn, demands a theoretical framework that has to be general and, possibly, free from approximations. This paper attempts to propose a viable theoretical scheme for simple liquids, while its extension to molecular liquids is presented in the following paper. The method is outlined in Sec. II, with formal details collected in the appendixes. The results of generalized thermodynamic properties and k- and ω-dependent transport coefficients are presented and discussed in the following section. Section IV presents a summary and the main conclusions.

II. THEORETICAL BACKGROUND FOR SIMPLE LIQUIDS

A. Fundamental definitions

We consider a three-dimensional fluid of N particles interacting through a potential $\Phi(r)$ [13]. The time-evolution operator that replaces the position and velocity of an arbitrary particle α at $t = 0$ by its position and velocity at time t is $e^{\widehat{L}t}$, where $\widehat{L}$ is the Liouville operator defined as

$$\widehat{L} = \sum_{\alpha=1}^{N} \mathbf{v}_\alpha \cdot \frac{\partial}{\partial \mathbf{r}_\alpha} - \frac{1}{M} \sum_{\alpha=1,\alpha\neq\beta}^{N} \frac{\partial \Phi_{\alpha\beta}(r_{\alpha\beta})}{\partial \mathbf{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha}. \tag{2.1}$$

The five wave vector (k) microscopic quantities $a_m(\mathbf{k})$ are given by

$$a_m(k) = \frac{1}{\sqrt{N}} \sum_{\alpha=1}^{N} A_{\alpha,m}(\mathbf{k})\, e^{-\imath \mathbf{k}\cdot\mathbf{r}_\alpha}. \tag{2.2}$$

In Eqs. (2.2), $m = 1,\ldots,5$ refers to the density, longitudinal velocity, energy, longitudinal stress tensor, and longitudinal heat-flux fluctuations, respectively.

The quantities $A_\alpha^{(m)}(\mathbf{k})$ are defined as follows:

$$A_{\alpha,1}(\mathbf{k}) = 1, \tag{2.3}$$

$$A_{\alpha,2}(\mathbf{k}) = \mathbf{v}_\alpha \cdot \frac{\mathbf{k}}{k}, \tag{2.4}$$

$$A_{\alpha,3}(\mathbf{k}) = \frac{1}{2} M \mathbf{v}_\alpha^2 + \frac{1}{2} \sum_{\beta=1,\beta\neq\alpha}^{N} \Phi_{\alpha\beta}(r_{\alpha\beta}), \tag{2.5}$$

$$A_{\alpha,4}(\mathbf{k}) = \left[\mathbf{v}_\alpha \cdot \frac{\mathbf{k}}{k}\right]^2 + \frac{i}{2Mk^2} \times \sum_{\beta=1,\beta\neq\alpha}^{N} \mathbf{k}\cdot \frac{\partial \Phi_{\alpha\beta}(r_{\alpha\beta})}{\partial \mathbf{r}_{\alpha\beta}} [e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha\beta}} - 1], \tag{2.6}$$

$$A_{\alpha,5}(\mathbf{k}) = \frac{1}{2}\left[M \mathbf{v}_\alpha^2 + \sum_{\beta=1,\beta\neq\alpha}^{N} \Phi_{\alpha\beta}(r_{\alpha\beta})\right] \mathbf{v}_\alpha \cdot \frac{\mathbf{k}}{k} + \frac{i}{2k} \sum_{\beta=1,\beta\neq\alpha}^{N} \mathbf{v}_\alpha \cdot \frac{\partial \Phi_{\alpha\beta}(r_{\alpha\beta})}{\partial \mathbf{r}_{\alpha\beta}} [e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha\beta}} - 1]. \tag{2.7}$$

The correlation functions (cf's) of interest are

$$F_{ml}(k,t) = \langle a_m(\mathbf{k})^* e^{\widehat{L}t}\, a_l(\mathbf{k})\rangle = \langle a_m(\mathbf{k})^*\, a_l(\mathbf{k},t)\rangle, \tag{2.8}$$

with $m,l = 1,\ldots,5$. $F_{ml}(k,t)$ are 25 cf's with initial values $V_{ml}(k) \equiv F_{ml}(k,0)$ and symmetry condition $F_{ml}(k,t) = F_{lm}(k,t)$. Then, the (5,5) matrix of the initial values $V_{ml}(k)$ contains only nine nonvanishing terms (the other initial values are zero for different parity):

The conservation laws for $l = 1,2,3,4,5,$

$$F_{2l}(k,t) = \frac{i}{k}\,\frac{\partial}{\partial t}F_{1l}(k,t), \tag{2.9}$$

$$F_{4l}(k,t) = \frac{i}{k}\,\frac{\partial}{\partial t}F_{2l}(k,t), \tag{2.10}$$

$$F_{5l}(k,t) = \frac{i}{k}\,\frac{\partial}{\partial t}F_{3l}(k,t), \tag{2.11}$$

reduce the nonvanishing initial values to seven and the different cf's $F_{ml}(k,t)$ to twelve. Applying Eqs. (2.9) and (2.11), we have $F_{22}(k,t) = F_{14}(k,t), F_{25}(k,t) = F_{34}(k,t)$, and $F_{23}(k,t) = F_{15}(k,t)$, so that $V_{22}(k) = V_{14}(k)$ and $V_{25}(k) = V_{34}(k)$.

Note that the remaining 12 cf's $F_{ml}(k,t)$ are not independent, because from the conservation laws it is possible to obtain nine additional relations, five connecting the first time derivative and four the second time derivative to the simple functions. In conclusion, within the 25 $F_{ml}(k,t)$, only three are independent, that is, $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$, while all the other cf's can be obtained from these three basic functions.

B. Orthonormal linear transformation

As is well known, in generalized hydrodynamics (as well as in any other approach based on memory functions) it is advantageous to deal with a set of mutually orthogonal variables. This reduction can be achieved by introducing five k-dependent orthonormal linear combinations $b_m(k)$ of the five microscopic quantities $a_m(k)$ of Eq. (2.2):

$$b_m(k) = \sum_{l=1}^{5} U_{ml}(k)\; a_l(k), \tag{2.12}$$

which satisfy the orthonormal conditions $\langle [b_m(k)]^* b_l(k)\rangle = \delta_{ml}$.

The (5×5) matrix $\underline{U}(k)$ is related to matrix $\underline{V}(k)$ by $\underline{U}^T(k)\underline{U}(k) = \underline{V}^{-1}(k)$.

A successive orthogonalization of n, u, e, σ, and q defines the matrix $\underline{U}(k)$, whose elements as a function of $V_{ml}(k)$ and of thermodynamic parameters are reported in Appendix A.

C. Generalized hydrodynamics and $G_{ml}(k,t)$

We start with the 25 cf's $G_{ml}(k,t)$ defined as follows:

$$G_{ml}(k,t) = \langle [b_m(k)]^* b_l(k,t)\rangle. \tag{2.13}$$

The cf's $G_{ml}(k,t)$ can readily be calculated from the relevant $F_{ij}(k,t)$, and the expressions of the four fundamental functions G_{11}, G_{22}, G_{13}, and $G_{33}(k,t)$ are given by Eqs. (3.16)–(3.18) of Ref. [21].

In generalized hydrodynamics, it is impossible to connect the above time cf's to the transport properties, *in the time domain*, without approximations. In contrast, this is possible *in the frequency domain*, through the exact kinetic equations (derived in Appendix B),

$$z\,\tilde{G}_{ml}(k,z) = -\sum_{r=1}^{5} H_{mr}(k,z)\;\tilde{G}_{rl}(k,z)\; + \delta_{ml}, \tag{2.14}$$

where $H_{mr}(k,z)$ are the elements of the matrix

$$\underline{H}(k,z) = \begin{vmatrix} 0 & if_{un}(k) & 0 & 0 & 0 \\ if_{un}(k) & 0 & if_{uT}(k) & if_{u\sigma}(k) & 0 \\ 0 & if_{uT}(k) & 0 & 0 & if_{Tq}(k) \\ 0 & if_{u\sigma}(k) & 0 & z_\sigma(k,z) & iz_{q\sigma}(k,z) \\ 0 & 0 & if_{Tq}(k) & iz_{q\sigma}(k,z) & z_q(k,z) \end{vmatrix} \tag{2.15}$$

and are derived and defined in the same appendix. In this matrix, there are four k-dependent characteristic frequencies [defined by Eqs. (B6)–(B9)] and three (k,z)-dependent transport parameters [Eqs. (B10)–(B11)]. Now, solving the linear system of Eq. (2.14), it is possible to obtain all the $\tilde{G}_{ml}(k,z)$ as a function of these four frequencies and three (k,z)-dependent transport parameters. Notice that the three functions $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ and their Laplace transform are sufficient to calculate all the $\tilde{G}_{ml}(k,z)$. We report in the following only the result for the Laplace transform of the three fundamental functions [the results for the other independent $\tilde{G}_{ml}(k,z)$ are reported in Appendix C]. We obtain

$$\tilde{G}_{11}(k,z) = \frac{[z + z_T(k,z)][z + z_\phi(k,z)] + [f_{uT}(k) + \Delta(k,z)]^2}{D(k,z)}, \tag{2.16}$$

$$\tilde{G}_{13}(k,z) = \frac{-f_{un}(k)[f_{uT}(k) + \Delta(k,z)]}{D(k,z)}, \tag{2.17}$$

$$\tilde{G}_{33}(k,z) = \frac{[z^2 + f_{un}(k)^2 + zz_\phi(k,z)]}{D(k,z)}, \tag{2.18}$$

with

$$\Delta(k,z) = -\frac{f_{u\sigma}(k)\; f_{Tq}(k)\; z_{q\sigma}(k,z)}{D_1(k,z)}, \tag{2.19}$$

$$z_\phi(k,z) = \frac{f_{u\sigma}(k)^2\;[z + z_q(k,z)]}{D_1(k,z)}, \tag{2.20}$$

$$z_T(k,z) = \frac{f_{Tq}(k)^2\;[z + z_\sigma(k,z)]}{D_1(k,z)}, \tag{2.21}$$

and

$$\begin{aligned} D(k,z) = {} & z[z + z_T(k,z)][z + z_\phi(k,z)] \\ & + f_{un}(k)^2[z + z_T(k,z)] + z[f_{uT}(k) + \Delta(k,z)]^2. \end{aligned} \tag{2.22}$$

In Eqs. (2.19)–(2.21),

$$D_1(k,z) = [z + z_\sigma(k,z)][z + z_q(k,z)] + z_{q\sigma}(k,z)^2. \tag{2.23}$$

The standard problem of generalized hydrodynamics is to obtain information on sound propagation and dispersion, and on transport properties (viscosities and thermal diffusivity). From the experimental point of view, however, scattering experiments provide data of the structure factor, $S(k,\omega) \propto \mathrm{Re}\{\tilde{G}_{11}(k,z)\}$. With these data only, it is impossible to obtain all seven quantities of matrix $\underline{H}(k,z)$, the four frequencies and the three complex quantities, which are connected directly to the transport properties. Hence, to obtain this information on transport properties, it is usually necessary to resort to a model for the memory functions [5,6] (viscoelastic model, two exponential model, etc.). By MD simulation, on the contrary, it is possible to calculate all three cf's density-density, density-energy, and energy-energy directly, $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$, and, by orthonormal transformations, the three cf's $G_{11}(k,t)$, $G_{13}(k,t)$, and $G_{33}(k,t)$; note that in the last cf's the index 3 relates to temperature, so that $G_{33}(k,t)$ is the normalized temperature-temperature fluctuation. In conclusion, in MD "experiments," with the above-mentioned three cf's one can perform the inversion of Eqs. (2.16)–(2.18) to obtain the three quantities $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$, together with the four generalized frequencies, without approximations and models.

If the higher-order cf's, with m or $l = 4,5$, are eliminated, Eq. (2.14) reduces to

$$z\ \tilde{G}_{ml}(k,z) = -\sum_{r=1}^{3} H^{(h)}_{mr}(k,z)\ \tilde{G}_{rl}(k,z)\ +\delta_{ml}, \tag{2.24}$$

with $\underline{H}^h$, the hydrodynamic matrix, defined as follows:

$$\underline{H}^{(h)}(k,z) = \begin{bmatrix} 0 & i f_{un}(k) & 0 \\ i f_{un}(k) & z_\phi(k,z) & i[f_{uT}(k)+\Delta(k,z)] \\ 0 & i[f_{uT}(k)+\Delta(k,z)] & z_T(k,z) \end{bmatrix}. \tag{2.25}$$

The comparison with the standard hydrodynamic model leads to the following generalizations:

$$z_\phi(k,z) = \frac{k^2\ \eta_L(k,z)}{\rho}, \tag{2.26}$$

where $\eta_L(k,z)$ is the generalized longitudinal viscosity;

$$z_T(k,z) = \ k^2\ \frac{\lambda(k,z)\ M}{\rho\ c_V(k)}, \tag{2.27}$$

with $\lambda(k,z)$ the generalized thermal conductivity; and

$$\gamma(k,z) = 1 + \frac{[f_{uT}(k)+\Delta(k,z)]^2}{f_{un}(k)^2} \tag{2.28}$$

the generalized ratio of specific heats. In the hydrodynamic model (h) it is assumed that the z dependence of these three properties can be neglected, so that $\tilde{G}_{11}(k,\omega) = \frac{S(k,\omega)}{S(k)}$ becomes a sum of three Lorentzians that correspond to the three eigenmodes of matrix $\underline{H}^{(h)}(k)$.

D. Generalized transport properties

To obtain an explicit expression of the three functions $z_{\sigma}(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$, it is convenient to rewrite Eqs. (2.16)–(2.18) using the three new complex variables:

$$\widetilde{n}_\phi(k,z) \equiv \frac{1}{z+z_\phi(k,z)}, \tag{2.29}$$

$$\widetilde{n}_T(k,z) \equiv \frac{1}{z+z_T(k,z)}, \tag{2.30}$$

$$\widetilde{f}_{uT}(k,z) \equiv f_{uT}(k)+\Delta(k,z). \tag{2.31}$$

Using these functions, Eqs. (2.16)–(2.18) become

$$\tilde{G}_{11}(k,z) = \frac{1+\widetilde{n}_\phi(k,z)\widetilde{n}_T(k,z)\widetilde{f}_{uT}(k,z)^2}{\mathrm{den}(k,z)}, \tag{2.32}$$

$$\tilde{G}_{13}(k,z) = \frac{-f_{un}(k)\widetilde{n}_\phi(k,z)\widetilde{n}_T(k,z)\widetilde{f}_{uT}(k,z)}{\mathrm{den}(k,z)}, \tag{2.33}$$

$$\tilde{G}_{33}(k,z) = \frac{[z+f_{un}(k)^2\widetilde{n}_\phi(k,z)]\widetilde{n}_T(k,z)}{\mathrm{den}(k,z)}, \tag{2.34}$$

where

$$\mathrm{den}(k,z) = z + f_{un}(k)^2\widetilde{n}_\phi(k,z) + z\ \widetilde{n}_\phi(k,z)\widetilde{n}_T(k,z)\widetilde{f}_{uT}(k,z)^2. \tag{2.35}$$

Combining the three equations above, we can derive

$$\tilde{G}_{11}(k,z)\ \tilde{G}_{33}(k,z) - \tilde{G}_{13}(k,z)^2 \equiv \Gamma_{13}(k,z) = \frac{\widetilde{n}_T(k,z)}{\mathrm{den}(k,z)}. \tag{2.36}$$

Then from Eq. (2.34), we obtain

$$\begin{aligned}\widetilde{n}_\phi(k,z) &= \frac{1}{f_{un}(k)^2}\ \frac{\tilde{G}_{33}(k,z) - z\Gamma_{13}(k,z)}{\Gamma_{13}(k,z)} \\ &= \frac{1}{f_{un}(k)^2}\ \frac{\Delta_{13}(k,z)}{\Gamma_{13}(k,z)}.\end{aligned} \tag{2.37}$$

Replacing Eqs. (2.36) and (2.37) in Eq. (2.33), we have

$$\widetilde{f}_{uT}(k,z) = \frac{-f_{un}(k)\ \tilde{G}_{13}(k,z)}{\Delta_{13}(k,z)}, \tag{2.38}$$

and from Eq. (2.32),

$$\widetilde{n}_T(k,z) = \frac{\Delta_{13}(k,z)}{1-z\ \tilde{G}_{11}(k,z)} \equiv \frac{\Delta_{13}(k,z)}{\Gamma_{11}(k,z)}. \tag{2.39}$$

Using Eqs. (2.29)–(2.31), it is now possible to calculate $\Delta(k,z)$, $z_\phi(k,z)$, and $z_T(k,z)$ as a function of the three Laplace transforms $\tilde{G}_{11}(k,z)$, $\tilde{G}_{13}(k,z)$, and $\tilde{G}_{33}(k,z)$,

$$\Delta(k,z) = \widetilde{f}_{uT}(k,z) - f_{uT}(k) = \frac{-f_{un}(k)\ \tilde{G}_{13}(k,z)}{\Delta_{13}(k,z)} - f_{uT}(k), \tag{2.40}$$

$$z_\phi(k,z) + z = \frac{1}{\widetilde{n}_\phi(k,z)} = \frac{f_{un}(k)^2\Gamma_{13}(k,z)}{\Delta_{13}}, \tag{2.41}$$

$$z_T(k,z) + z = \frac{1}{\widetilde{n}_T(k,z)} = \frac{\Gamma_{11}(k,z)}{\Delta_{13}(k,z)}. \tag{2.42}$$

The three (k,z)-dependent transport properties $z_{q\sigma}(k,z)$, $z_\sigma(k,z)$, and $z_q(k,z)$ of matrix (2.15) can now be expressed as follows:

$$\begin{aligned}&\frac{z_{q\sigma}(k,z)}{f_{u\sigma}(k)\ f_{Tq}(k)} \\ &\quad= \frac{-\Delta(k,z)}{[z_\phi(k,z)\ z_T(k,z)+\Delta(k,z)^2]} \\ &\quad= \frac{[f_{un}(k)\tilde{G}_{13}(k,z)+f_{uT}(k)\Delta_{13}(k,z)]\Delta_{13}(k,z)}{D_{q\sigma}(k,z)},\end{aligned} \tag{2.43}$$

$$\frac{z_\sigma(k,z)+z}{f_{u\sigma}(k)^2} = \frac{z_T(k,z)}{[z_\phi(k,z)\; z_T(k,z)+\Delta(k,z)^2]} = \frac{[\Gamma_{11}(k,z)-z\Delta_{13}(k,z)]\Delta_{13}(k,z)}{D_{q\sigma}(k,z)}, \tag{2.44}$$

$$\frac{z_q(k,z)+z}{f_{Tq}(k)^2} = \frac{z_\phi(k,z)}{[z_\phi(k,z)\; z_T(k,z)+\Delta(k,z)^2]} = \frac{[f_{un}(k)^2\Gamma_{13}(k,z)-z\Delta_{13}(k,z)]\Delta_{13}(k,z)}{D_{q\sigma}(k,z)}, \tag{2.45}$$

where

$$D_{q\sigma}(k,z) = [\Gamma_{11}(k,z)-z\Delta_{13}(k,z)][f_{un}(k)^2\Gamma_{13}(k,z)-z\Delta_{13}(k,z)] + [f_{un}(k)\tilde{G}_{13}(k,z)+f_{uT}(k)\Delta_{13}(k,z)]^2. \tag{2.46}$$

As shown in Sec. III B, from the short time behavior and the initial values of these functions, also the generalized thermodynamic properties $h(k)$, $\alpha(k)$, $c_P(k)$, $c_V(k)$, and therefore $\gamma(k)$ can be calculated [see Eqs. (3.3)–(3.8)].

In conclusion, we have obtained exact and explicit expressions for all elements of matrix (2.15), which can be calculated from the three cf's $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ through the transforms $G_{11}(k,z)$, $G_{13}(k,z)$, and $G_{33}(k,z)$. This result is the main original contribution of the present paper.

E. Physical interpretation of transport properties and limiting cases

In a number of interesting cases, the three generalized parameters $\eta_L(k,z)$, $\lambda(k,z)$, and $\gamma(k,z)$ can be related to the transform of the MD cf's in a clearer way.

To achieve this result, it is convenient using $\tilde{G}_{22}(k,z)$, the transform of the longitudinal current cf, instead of that of the density-density cf, $\tilde{G}_{11}(k,z)$. Using Eq. (C4), we obtain

$$\eta_L(k,z) = \frac{\rho}{k^2}\left\{\frac{1}{\tilde{G}_{22}(k,z)}\left[1-\frac{\delta_{13}(k,z)}{1+\delta_{13}(k,z)}\right]-z-\frac{f_{un}(k)^2}{z}\right\}, \tag{2.47}$$

$$\lambda(k,z) = \frac{\rho c_V(k)}{k^2M}\left\{\frac{1}{\tilde{G}_{33}(k,z)}\left[1-\frac{\delta_{13}(k,z)}{1+\delta_{13}(k,z)}\right]-z\right\}, \tag{2.48}$$

and

$$\gamma(k,z)-1 = \left[\frac{\delta_{13}(k,z)}{z\,\tilde{G}_{13}(k,z)[1+\delta_{13}(k,z)]}\right]^2, \tag{2.49}$$

where

$$\delta_{13}(k,z) = \frac{z^2\tilde{G}_{13}(k,z)^2}{f_{un}(k)^2\tilde{G}_{22}(k,z)\tilde{G}_{33}(k,z)}. \tag{2.50}$$

The equations above show that $\eta_L(k,z)$ is related to $\tilde{G}_{22}(k,z)$, the transform of the longitudinal current cf, being mostly determined by its memory function. In a similar way, $\lambda(k,z)$ is connected to the temperature-temperature correlations, as this parameter also is related to its memory function of $\tilde{G}_{33}(k,z)$. As to $\gamma(k,z)$, this parameter reflects density-temperature correlations, being ruled by $\tilde{G}_{13}(k,z)$.

The connection between transport properties and the Laplace transform of the correlation functions becomes more apparent when the condition $|\delta_{13}(k,z)| \ll 1$ is fulfilled. In this case, we obtain

$$\mathrm{Re}\{\eta_L(k,z)\} \cong \frac{\rho}{k^2}\mathrm{Re}\left\{\frac{1}{\tilde{G}_{22}(k,z)}\right\}, \tag{2.51}$$

$$\mathrm{Re}\{\lambda(k,z)\} \cong \frac{\rho c_V(k)}{k^2M}\mathrm{Re}\left\{\frac{1}{\tilde{G}_{33}(k,z)}\right\} \tag{2.52}$$

and $\gamma(k,z)-1 \cong 0$.

From a physical point of view, this condition corresponds to a liquid with a small generalized thermal expansivity $\gamma(k)-1\alpha \propto (k)^2 \ll 1$ and relatively small temperature-density coupling, that is, relatively small cross correlation between stress tensor and longitudinal heat-flux fluctuations, $|\Delta(k,z)| \simeq 0$.

A sort of opposite limiting behavior is observed if the conditions

$$z_{q\sigma}(k,z)=0, \quad |\Delta(k,z)| \ll f_{uT}(k) \quad \text{or} \quad \gamma \gg 1 \tag{2.53}$$

are verified. This means that the coupling between the stress-tensor and heat-flux fluctuations becomes negligible, but the specific-heat ratio is much greater than 1. In this case, also the calculation of the elements of the matrix (2.15) can be simplified. We have

$$\tilde{f}_{uT}(k,z) \cong f_{uT}(k) = \left[\frac{V_{22}(k)}{V_{11}(k)}[\gamma(k)-1]\right]^{\frac{1}{2}} k. \tag{2.54}$$

From the relations among the basic functions $G_{11}(k,z)$, $G_{13}(k,z)$, and $G_{33}(k,z)$,

$$\tilde{G}_{33}(k,z)-z\,[\tilde{G}_{11}(k,z)\tilde{G}_{33}(k,z)-\tilde{G}_{13}(k,z)^2] \equiv \Delta_{13}(k,z) = \frac{-f_{un}(k)\,\tilde{G}_{13}(k,z)}{f_{uT}(k)} \tag{2.55}$$

and

$$f_{un}(k)^2\tilde{G}_{22}(k,z)\tilde{G}_{33}(k,z)+z^2\tilde{G}_{13}(k,z)^2 = \frac{-z\,f_{un}(k)\,\tilde{G}_{13}(k,z)}{f_{uT}(k)} = z\Delta_{13}(k,z), \tag{2.56}$$

we can rewrite Eqs. (2.47) and (2.48) as

$$\eta_L(k,z) = \frac{\rho}{k^2}\left\{\frac{1}{\tilde{G}_{22}(k,z)}\left[1+\frac{z\,f_{uT}(k)\tilde{G}_{13}(k,z)}{f_{un}(k)}\right]-z-\frac{f_{un}(k)^2}{z}\right\}, \tag{2.57}$$

$$\lambda(k,z) = \frac{\rho M}{k^2c_V(k)}\left\{\frac{1}{\tilde{G}_{33}(k,z)}\left[1+\frac{z\,f_{uT}(k)\tilde{G}_{13}(k,z)}{f_{un}(k)}\right]-z\right\}. \tag{2.58}$$

In other words, in this case $G_{13}(k,t)$ becomes the fundamental function.

F. Memory functions approach

A very useful and frequently used approach involves the memory functions [5,6,19,22]. From a Laplace transform of a normalized cf $N(t)$, we obtain the respective memory function by the relation

$$\widetilde{N}(z) = \frac{1}{z + \widetilde{M}(z)}, \tag{2.59}$$

where $\widetilde{M}(z) = M(t=0)\widetilde{N}_1(z)$ and $\widetilde{N}_1(z)$ is the Laplace transform of the normalized memory function of order 1, $N_1(t)$, of the correlation function $N(t)$. Applying this relation to the autocorrelation functions $G_{11}(k,t)$ and $G_{33}(k,t)$, we obtain

$$\widetilde{N}_{11,1}(k,z) = \frac{\widetilde{M}_{11,1}(k,z)}{f_{un}(k)^2} = \frac{1}{z + \widetilde{M}_{11,2}(k,z)}, \tag{2.60}$$

where

$$\widetilde{M}_{11,2}(k,z) = z_\phi(k,z) + \frac{\widetilde{f}_{uT}(k,z)^2}{z + z_T(k,z)} \tag{2.61}$$

and

$$\widetilde{G}_{33}(k,z) = \frac{1}{z + \widetilde{M}_{33,1}(k,z)}, \tag{2.62}$$

where

$$\widetilde{M}_{33,1}(k,z) = z_T(k,z) + \frac{z\ \widetilde{f}_{uT}(k,z)^2}{z^2 + z\ z_\phi(k,z) + f_{un}(k)^2}. \tag{2.63}$$

Note the different order of the $G_{11}(k,t)$ and $G_{33}(k,t)$ cf's with respect to the memory function formalism and the transport coefficients: $\widetilde{M}_{11,2}(k,z)$, the memory function of order 2 of $G_{11}(k,t)$, has $z_\phi(k,z)$ at the same order as $z_T(k,z)$ of $\widetilde{M}_{33,1}(k,z)$, the memory function of order 1 of $G_{33}(k,t)$. From this point of view, $G_{22}(k,t)$ behaves as $G_{33}(k,t)$ does. In fact, from Eq. (C4) we obtain

$$\widetilde{G}_{22}(k,z) = \frac{1}{z + \widetilde{M}_{22,1}(k,z)} = \frac{1}{z + \widetilde{M}_{11,2}(k,z) + f_{un}(k)^2/z}. \tag{2.64}$$

It is worth pushing the procedure one step further: as a consequence of Eqs. (2.19)–(2.23), with a simple calculation, finally we obtain

$$\widetilde{N}_{11,2}(k,z) = \frac{\widetilde{M}_{11,2}(k,z)}{f_{u\sigma}(k)^2 + \widetilde{f}_{uT}(k,0)^2} = \frac{1}{z + \widetilde{M}_{11,3}(k,z)}, \tag{2.65}$$

where

$$\widetilde{M}_{11,3}(k,z) = z_\sigma(k,z)\frac{1 + \widetilde{A}_n(k,z)}{1 + \widetilde{A}_d(k,z)} \tag{2.66}$$

with

$$\widetilde{A}_n(k,z) = \frac{f_{un}(k)^2 f_{uT}(k)^2}{f_{u\sigma}(k)^2 z_\sigma(k,z)} \frac{z + z_\sigma(k,z) + 2\,z\,z_{q\sigma}(k,z)\,\{f_{u\sigma}(k)/[f_{uT}(k)f_{Tq}(k)]\}}{z\ [z + z_q(k,z)] + f_{Tq}(k)^2} \tag{2.67}$$

and

$$\widetilde{A}_d(k,z) = \frac{f_{uT}(k)^2}{f_{u\sigma}(k)^2} \frac{D_1(k,z) - 2\ z_{q\sigma}(k,z)\ f_{u\sigma}(k)f_{Tq}(k)/f_{uT}(k)}{z\ [z + z_q(k,z)] + f_{Tq}(k)^2}. \tag{2.68}$$

Moreover, for the memory functions of $G_{33}(k,t)$, we obtain

$$\widetilde{N}_{33,1}(k,z) = \frac{\widetilde{M}_{33,1}(k,z)}{f_{Tq}(k)^2 + \widetilde{f}_{uT}(k,0)^2} = \frac{1}{z + \widetilde{M}_{33,2}(k,z)}, \tag{2.69}$$

where

$$\widetilde{M}_{33,2}(k,z) = z_q(k,z)\frac{1 + z\ \widetilde{B}_n(k,z)}{1 + z\ \widetilde{B}_d(k,z)} \tag{2.70}$$

with

$$\widetilde{B}_n(k,z) = \frac{f_{u\sigma}(k)^2 f_{uT}(k)^2}{f_{Tq}(k)^2 z_q(k,z)} \frac{z + z_q(k,z) + 2\,z\,z_{q\sigma}(k,z)\,\{f_{Tq}(k)/[f_{uT}(k)f_{u\sigma}(k)]\}}{[z + z_\sigma(k,z)][z^2 + f_{un}(k)^2] + z\ f_{u\sigma}(k)^2} \tag{2.71}$$

and

$$\widetilde{B}_d(k,z) = \frac{f_{uT}(k)^2}{f_{Tq}(k)^2} \frac{D_1(k,z) - 2\,z_{q\sigma}(k,z)\,f_{u\sigma}(k)f_{Tq}(k)/f_{uT}(k)}{[z + z_\sigma(k,z)][z^2 + f_{un}(k)^2] + z\ f_{u\sigma}(k)^2}. \tag{2.72}$$

III. RESULTS AND DISCUSSION

A. Simulation details

Two thermodynamic states of argon have been simulated, at $T = 88$ and 200 K and a corresponding density of $\rho = 1.3$ and 1.4 g/cm^3. In all cases, 864 atoms have been used and the length of the runs, after a long equilibration time, has been about 2 ns [23]. We calculated a range of time correlation functions between the microscopic variables defined in Eqs. (2.3)–(2.7), namely, $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and

$F_{33}(k,t)$ and also $F_{43}(k,t)$, $F_{44}(k,t)$, and $F_{55}(k,t)$. The latter three functions have been used as a check of the accuracy of our results. The values of k ranged from $k \simeq 1.8\ \text{nm}^{-1}$ to $k \simeq 300\ \text{nm}^{-1}$, while the correlation time was significantly larger than that required for the functions to vanish in the noise.

B. Initial values $V_{ml}(k)$ and generalized thermodynamic functions

As a consequence of the theory of critical phenomena, some of the seven functions $V_{ml}(k)$ of matrix $\underline{V}(k)$ are connected to the generalized thermodynamic properties:

$$V_{13}(k) = h(k)S(k) - k_B T^2 \alpha(k), \tag{3.1}$$

$$V_{33}(k) = [k_B T^2 c_P(k) + h(k)^2 S(k) - 2k_B T^2 \alpha(k) h(k)], \tag{3.2}$$

where $S(k) \equiv V_{11}(k$ is the structure factor). Moreover, the mean-square longitudinal velocity is connected to the initial value of the longitudinal current $\frac{k_B T}{M} = V_{22}(k)$, and the generalized enthalpy per particle is defined as

$$h(k) = -\frac{1}{V_{22}(k)\,k^2} \lim_{t\to 0} \frac{\partial^2}{\partial t^2} F_{13}(k,t) = \frac{V_{34}(k)}{V_{22}(k)}. \tag{3.3}$$

The remaining properties are the generalized thermal expansion coefficient, $\alpha(k)$, and the generalized specific heat at constant pressure, $c_P(k)$. We obtain

$$\alpha(k) = \frac{h(k)\ V_{11}(k) - V_{13}(k)}{k_B T^2}, \tag{3.4}$$

$$c_p(k) = \frac{h(k)^2 V_{11}(k) - 2\ h(k) V_{13}(k) + V_{33}(k)}{k_B T^2}. \tag{3.5}$$

Furthermore, from the thermodynamic equation,

$$c_V(k) = c_P(k) - \frac{k_B T^2 \alpha(k)^2}{S(k)}, \tag{3.6}$$

it is possible to calculate the generalized specific heat at constant volume,

$$c_v(k) = \frac{V_{33}(k) - \frac{V_{13}(k)^2}{V_{11}(k)}}{k_B T^2}, \tag{3.7}$$

and hence the generalized ratio of the specific heats,

$$\gamma(k) = 1\ + \frac{[h(k)\ V_{11}(k) - V_{13}(k)]^2}{V_{11}(k)\left[V_{33}(k) - \frac{V_{13}(k)^2}{V_{11}(k)}\right]}. \tag{3.8}$$

It is also necessary to add the two functions

$$V_{44}(k) = -\frac{1}{k^2} \lim_{t\to 0} \frac{\partial^2}{\partial t^2} F_{22}(k,t), \tag{3.9}$$

$$V_{55}(k) = -\frac{1}{k^2} \lim_{t\to 0} \frac{\partial^2}{\partial t^2} F_{33}(k,t), \tag{3.10}$$

which will be used in $f_{u\sigma}(k)$ and $f_{Tq}(k)$ [see Eqs. (B8) and (B9)]. In conclusion, except for the two last functions, the five generalized properties $S(k)$, $h(k)$, $\alpha(k)$, $c_V(k)$, and $c_P(k)$ can be calculated by a proper combination of $V_{11}, V_{22}, V_{13}, V_{33}$, and V_{34}.

The generalized thermodynamic functions for argon at 88 and 200 K are shown in Fig. 1. At the higher temperature, these functions depend on k in a more smooth fashion and their values are in good agreement with the corresponding values obtained in Refs. [13] and [24] for the same thermodynamic state. In particular, for $k > 15\,\text{nm}^{-1}$, the correlation between $S(k)$ and $\alpha(k)$ is remarkable, and is due [see Eq. (3.4)] to the flat behavior of $h(k)$ and the proportionality of $S(k)$ and $V_{13}(k)$ for these values of k. On the contrary, at low k's also $h(k)$ affects $\alpha(k)$ and is responsible of the increasing $\alpha(k)$ for $k \to 0$.

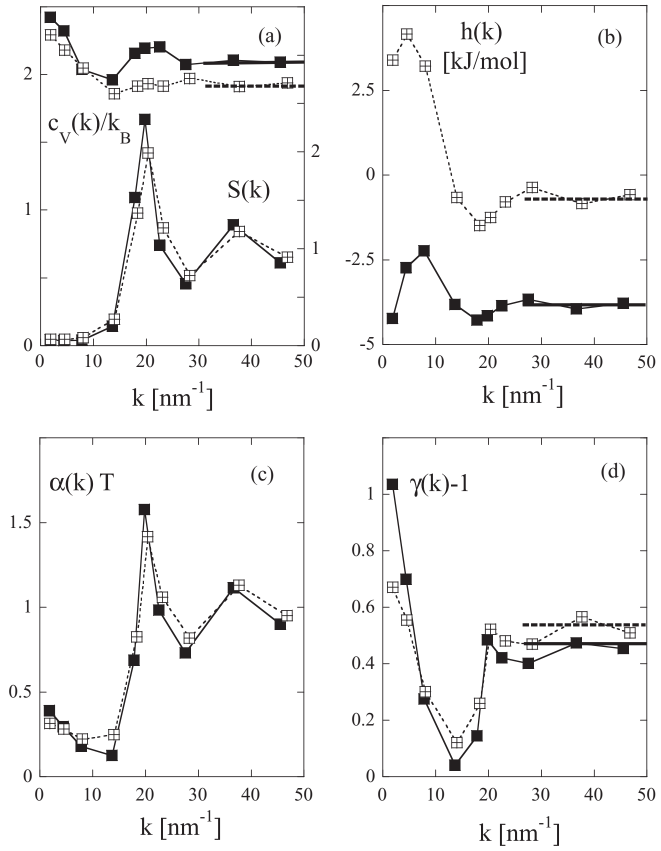

FIG. 1. Generalized thermodynamic functions for argon: black squares, $T = 88$ K; white crossed squares, $T = 200$ K; the horizontal thick full and dashed lines relate to $k \to \infty$ values.

In its turn, the behavior of $h(k)$ [see Eq. (3.3)] is completely determined by $V_{43}(k)$, $V_{22}(k)$ being constant. At low k and at $T = 200$ K, $h(k)$ is positive, denoting the prevalence of the kinetic term, while at lower temperature $h(k)$ is always negative, denoting the prevalence of the potential term. Note also the great increase of $\gamma(k)$ for $k \to 0$, especially at lower temperature.

As remarked in Ref. [24], the $k \to \infty$ values differ from the corresponding ideal-gas values because the liquid system interacts via a potential that does not vanish in this limit. The ideal-gas limits are $h^{(G)} = 5k_B T/2$, $c_V^{(G)} = 3k_B/2$, and $\gamma^{(G)} = 5/3$. This difference is evident in the quantities that are potential-dependent such as $h(k)$, $c_V(k)$, and $\gamma(k)$, the only exception being $\alpha(k)T$, where a cancellation of terms leads to the ideal-gas limit value $[\alpha(k)T \to 1]$ in Eq. (3.4) also in the liquid case $[h(\infty) - V_{13}(\infty) = k_B T]$.

C. Generalized transport coefficients (k dependence)

The aim of this subsection is to discuss the k dependence of the transport coefficients [see Eqs. (2.40)–(2.45)] in the $\omega \to 0$

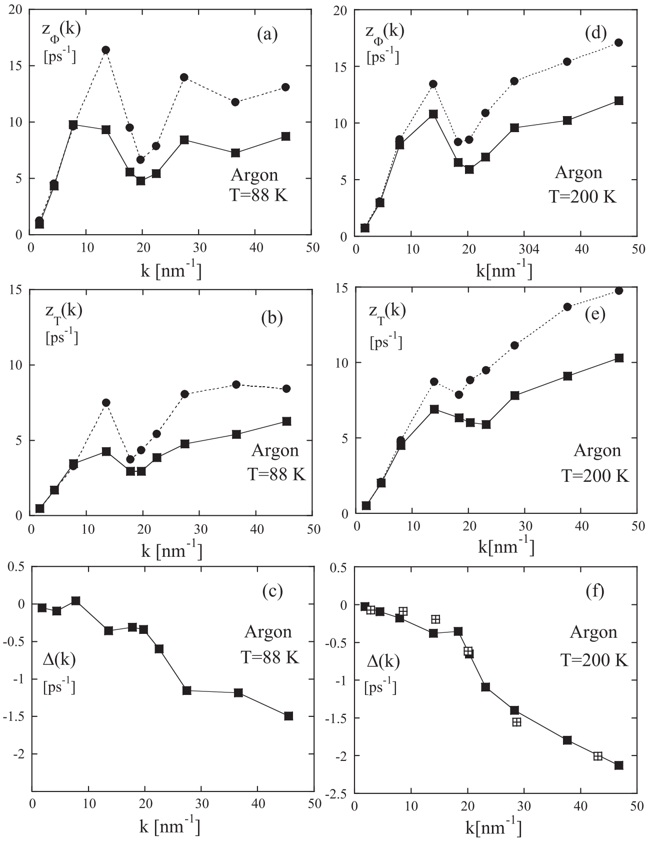

FIG. 2. Generalized transport coefficients of argon at $\omega = 0$. (a) and (d) $z_\phi(k)$, (b) and (e) $z_T(k)$, (c) and (f) $\Delta(k)$; the full circles in the $z_\phi(k)$ and $z_T(k)$ plot refer to approximate values obtained for $\Delta(k) = 0$. The crossed squares reported for $\Delta(k)$ at $T = 200$ K are calculated from the results of Ref. [25] (see text).

limit. It is worth recalling that the results we obtain with the theory outlined in the previous sections are not connected with a linear combination of complex Lorentzian components, as in Ref. [13] or other possible models. Rather, the generalized hydrodynamic transport properties are obtained by inverting exact algebraic relations for the Laplace transform of the three fundamental cf's $G_{11}(k,t)$, $G_{13}(k,t)$, and $G_{33}(k,t)$, calculated from the density-density, density-energy, and energy-energy cf's. In fact, also the transforms of the cross cf's $\Delta(k,z)$ and $z_{q\sigma}(k,z)$ can be obtained "exactly" from simulation data.

$z_\phi(k,0)$, $z_T(k,0)$, and $\Delta(k,0)$ are shown in Fig. 2. The first two functions are proportional to generalized viscosity and thermal conductivity, respectively, while the last can be considered a measure of the coupling between stress and heat currents. $z_\phi(k,0)$ and $z_T(k,0)$ increase almost linearly at low k's to produce a peak that ends with a minimum at the k of the maximum of $S(k)$. The k dependence is more apparent if these functions are calculated assuming $\Delta(k,0) = 0$. In fact, the results diverge as soon as k reaches $\simeq$10 nm^{-1}, see Fig. 2. This is where $\Delta(k,0)$ starts decreasing much more rapidly than $f_{uT}(k) = f_{un}(k)\,[\gamma(k) - 1]^{\frac{1}{2}}$, so that the condition of the second limiting case discussed in Sec. II E is no longer fulfilled. In conclusion, at intermediate and high k values it is not correct to neglect the contribution of the cross correlation term, $\Delta(k,0)$.

A dynamical coupling coefficient between stress and heat currents [$\bar{\xi}(k,0) \propto -\Delta(k,0)\, c_V(k)/k^2$] has also been computed for the LJ fluid by Mryglod and Omelyan (Ref. [25]) from simulation results, at a thermodynamic state very close to our own at $T = 200$ K. The results obtained from our data of $c_V(k)$ and $\Delta(k,0)$ show a good agreement with those of Ref. [25]. The coefficient $\bar{\xi}(k,0)$ has a large increase at low k's, then a minimum at the k value corresponding to the maximum of $S(k)$, and a similar oscillation at higher k's around a value roughly an order of magnitude lower than the value at low k's. The corresponding results at $T = 88$ K show a similar trend with a minimum at $k \sim 10$ nm^{-1} roughly one-half of that corresponding to the maximum of $S(k)$. To compare more quantitatively the two results, in Fig. 2 the values of $\Delta(k,0)$ calculated combining our results of $z_{q\sigma}(k,0)$ with $c_V(k)$ of Ref. [24] and $\bar{\xi}(k,0)$ of Ref. [25] are reported for seven k values. The agreement is satisfactory, apart for some points at low k, where the magnitude of this quantity decreases and the error in the calculation of this coefficient becomes higher.

In Fig. 3, the values of $z_\sigma(k,0)$, $z_q(k,0)$, and $z_{q\sigma}(k,0)$ calculated from Eqs. (2.43)–(2.45) are reported. The first two quantities increase as a function of k with an oscillation at $k \sim 20$ nm^{-1}, and also $z_{q\sigma}(k,0)$ at higher temperature shows a small maximum at this k value. The latter quantity at 88 K increases with k, after a small minimum at low k values. For $T = 200$ K, the three quantities show a reasonable agreement

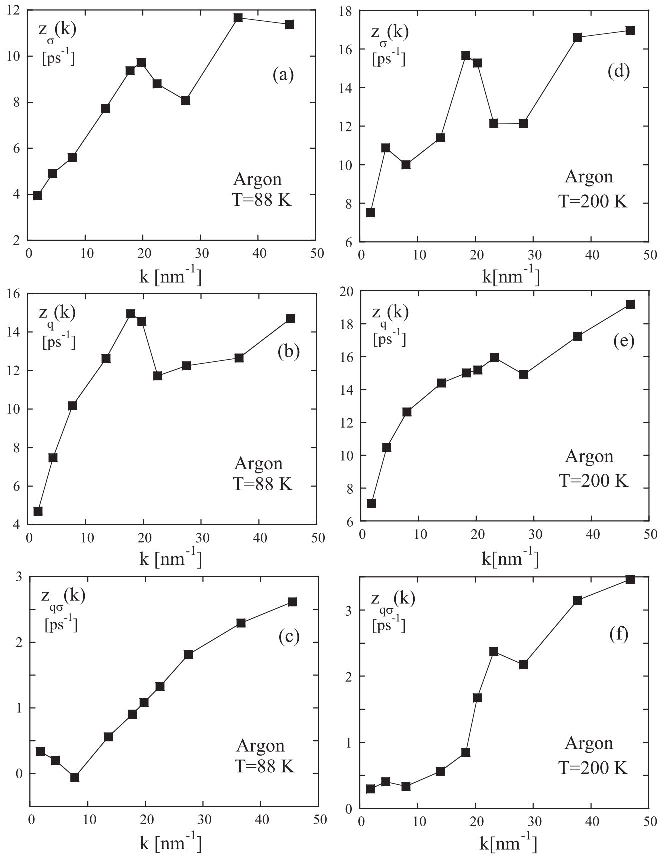

FIG. 3. Generalized transport coefficients of argon at $\omega = 0$. (a) and (d) $z_\sigma(k)$, (b) and (e) $z_q(k)$, (c) and (f) $z_{q\sigma}(k)$.

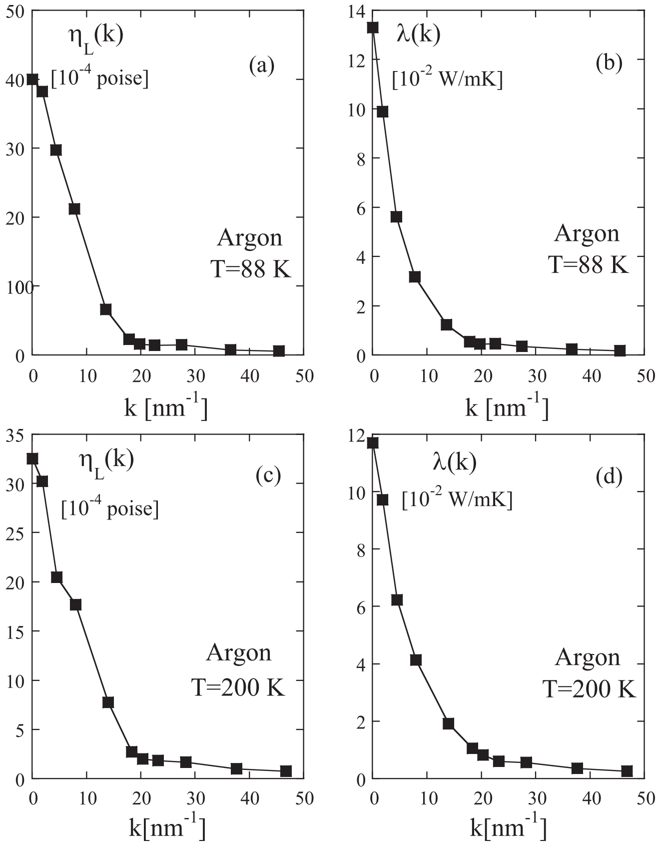

FIG. 4. Generalized transport properties of argon at two temperatures. (a) and (c) longitudinal viscosity, $\eta_L(k)$; (b) and (d) thermal conductivity, $\lambda(k)$.

with the results of Ref. [13] in the same thermodynamic state. Note that the results of Ref. [13] are obtained assuming that $F_{ij}(k,t)$ can be expressed in terms of the eigenmodes as a sum of five exponentials and neglecting the dependence of the three parameters on the frequency. This is correct only if the decay time of the cf's $J_\sigma(k,t)$, $J_q(k,t)$, and $J_{q\sigma}(k,t)$, which are related via Laplace transform to $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ (see Appendix B), is shorter than that of $G_{ij}(k,t)$. In other words, $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$ are the results of a fitting procedure, which means that these parameters perform a sort of mean of $J_\sigma(k,t)$, $J_q(k,t)$, and $J_{q\sigma}(k,t)$ over the time scale in which the $G_{ij}(k,t)$ decay to zero.

The generalized longitudinal viscosity, $\eta_L(k)$, and thermal conductivity, $\lambda(k)$, obtained from Eqs. (2.26) and (2.27), are reported in Fig. 4. Both functions decay rapidly and monotonically as a function of k, consistently with the behavior of the "parent" coefficients $z_\phi(k,0)$ and $z_T(k,0)$ shown in Fig. 2. The values at $k = 0$ are calculated from the Green-Kubo relations and the results are in reasonable agreement with the experimental data [26,27]. The viscosity and thermal conductivity of argon change slightly (10%–20%) in the two thermodynamic states despite their large difference of temperature, and this is due to a compensation effect of the density contribution (the density at $T = 200$ K is 1.4 g/cm^3 versus 1.3 g/cm^3 at $T = 88$ K), in perfect agreement with experimental results.

Finally, note that from relations (2.19)–(2.21) and (2.43)–(2.45) in the $k \to 0$ limit, $z_{q\sigma}(k,0)$ must tend to zero as k, $\Delta(k,0)$ as k^3, $z_\Phi(k,0)$ and $z_T(k,0)$ as k^2, while $z_\sigma(k,0)$ and $z_q(k,0)$ tend to finite values $z_\sigma(0,0) = \{[f_{u\sigma}(k)^2/k^2]\rho/\eta_L(k)\}_{k\to 0}$ and $z_q(0,0) = \{[f_{Tq}(k)^2/k^2]\rho c_V(k)/M\lambda(k)\}_{k\to 0}$, respectively. As we can see from Figs. 2 and 3, these limits are respected with just a little deviation for $k \to 0$ especially in $z_{q\sigma}(k,0)$, likely due to some residual computational inaccuracy.

D. Generalized spectra of transport coefficients (ω dependence)

From the exact kinetic Eq. (2.14) and using Eqs. (2.40)–(2.45), it is possible to obtain, for all k values, the Laplace transforms and then the time dependence of all the transport properties, without approximation or intermediate models. An important consequence is that this procedure can be used to test the validity of the Markovian hypothesis that consists of neglecting the z (or ω) dependence of the three quantities $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ in the low frequency range. As noted in the preceding paragraph, this is correct only if $\tilde{G}_{ij}(k,z)$ decays completely in the same frequency range in which the three quantities $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ can be assumed frequency-independent.

An example of this situation is shown in Fig. 5 for argon at $k \simeq 265$ nm^{-1}. Note that for very high values of k, the shape of the $F_{ij}(k,t)$ [or $G_{ij}(k,t)$] cf's is practically Gaussian

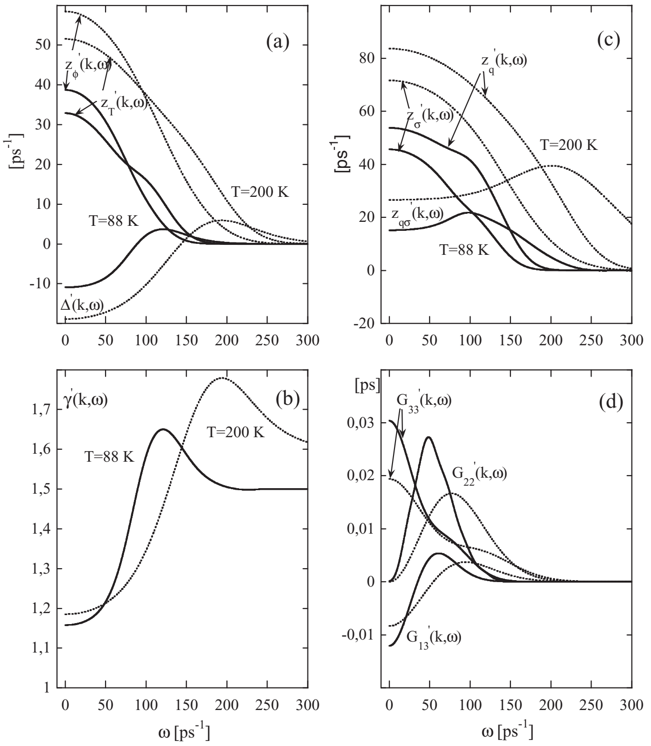

FIG. 5. Generalized spectra of the transport properties, of the ratio of specific heats, and of the three cf's $G_{22}(k,t)$, $G_{13}(k,t)$, and $G_{33}(k,t)$ in the free-streaming limit, $k \simeq 265$ nm^{-1}, at $T = 88$ K (full lines) and $T = 200$ K (broken lines): (a) Real part of $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$; (b) real part of $\gamma(k,z)$; (c) real part of $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$; (d) real part of $\tilde{G}_{22}(k,z)$, $\tilde{G}_{13}(k,z)$, and $\tilde{G}_{33}(k,z)$.

or a time derivative of a Gaussian [28]. The six transport properties for argon at the two temperatures are reported in parts (a) and (c) of the figure, while the spectra of the three fundamental cf's $G_{22}(k,t)$, $G_{13}(k,t)$, and $G_{33}(k,t)$ are shown in part (d). The spectra of these functions are essentially zero beyond $\omega \sim 125$ ps^{-1} at 88 K and $\omega \sim 200$ ps^{-1} at 200 K. In the same frequency range, the real part of $z_\sigma(k,z)$ and $z_q(k,z)$ decays roughly 20%–10% at 88 K and 60%–40% at 200 K. Moreover, the real part of $z_{q\sigma}(k,z)$ shows a flat behavior with a small maximum at $\omega \sim 110$ ps^{-1} at 88 K and $\omega \sim 220$ ps^{-1} at 200 K. This means that the Markovian approximation is not accurate at high k, especially in the high temperature state. Furthermore, the values of $z_{q\sigma}(k,z)$ are not negligible. In fact, the values of the real part of $z_\sigma(k,z)$ and $z_q(k,z)$, calculated by Eqs. (2.44) and (2.45) assuming $\Delta(k,z) = 0$, are 10%–15% higher than that of Fig. 5(c), for $\omega = 0$, as it happens for $z_\phi(k,z)$ and $z_T(k,z)$, see Fig. 2.

In Fig. 5(b), we report the real part of $\gamma(k,z)$ defined by Eq. (2.28). Note that the values reported in Fig. 1(d) relate to the $\omega \to \infty$ limit (or $t \to 0$) for the definitions (3.3) and (3.8), so that this limit (1.5–1.55) must coincide with the values at high k's of Fig. 1(d) and actually does. Note also that $\gamma(k,\omega \to \infty) = \gamma(k) \neq \gamma(k,0)$, because in Eq. (3.8) there are only quantities calculated at $t = 0$ or $t \to 0$ and in this limit $\Delta(k,\omega \to \infty) \to 0$, hence the real part of $\gamma(k,z)$ has an ω-dispersion behavior starting from $\gamma(k,\omega = 0)$ and reaching $\gamma(k)$ for $\omega \to \infty$ (or $t \to 0$). At lower frequencies, $\gamma(k,z)$ is determined also by the $\Delta(k,z)$ contribution [see Eq. (2.28)]. In fact, its form is similar to that of the real part of $\Delta(k,z)$ [see the corresponding maximum in the Fig. 5(a)].

Given that the Markovian hypothesis is not correct at high k's for argon, we report in Fig. 6 the analogous results for the k value ($k \simeq 20$ nm^{-1}), where $S(k)$ has its maximum. At $T = 200$ K, the cf's $G_{ij}(k,t)$ decay in the range of 15 ps^{-1}, while in the same range $z_\phi(k,z)$ and $z_T(k,z)$ decay only 5%–10% and the real part of $z_{q\sigma}(k,z)$ is roughly flat, so that the three functions may be considered ω-independent. This is the reason why the results of Ref. [13], if properly scaled, are in good accord with our results. The ω dependence of the real part of $\Delta(k,z)$ can be compared with the theoretical prediction shown in Fig. 6(d) of Ref. [25], taking into account that because of different definitions, the sign is opposite and the value must be scaled. Doing so, the shape is in quite good agreement, especially in the case of the five-mode approximation. Note that in Ref. [25] (Figs. 6 and 7), only the theoretical prediction for the frequency dependence of $\bar{\xi}(k,z) \propto -\Delta(k,z)$ is reported. In fact, the authors could not obtain the exact simulation results (as for generalized shear viscosity and thermal conductivity) for $\bar{\xi}(k,z) \propto -\Delta(k,z)$, as we do in the present paper.

For $T = 88$ K, the results are similar, apart for a relatively large increase (20%–30%) of $z'_q(k,\omega)$ in the low-ω region that leads to a corresponding decrease of $z'_T(k,\omega)$ (and then of thermal conductivity) for $\omega \to 0$. Another observation is that the variation of the amplitude of the real part of $\Delta(k,z)$ is smaller than at $T = 200$ K, while the effect on the real part of $\gamma(k,z)$ is more pronounced, probably due to the smaller value of $f_{uT}(k) = f_{un}(k)[\gamma(k) - 1]^{0.5}$, being $f_{un}(k) \propto T^{0.5}$. In the case of $z'_q(k,\omega)$, the Markovian assumption is more correct at $T = 200$ K, because at $T = 88$ K it rapidly increases in the low ω region.

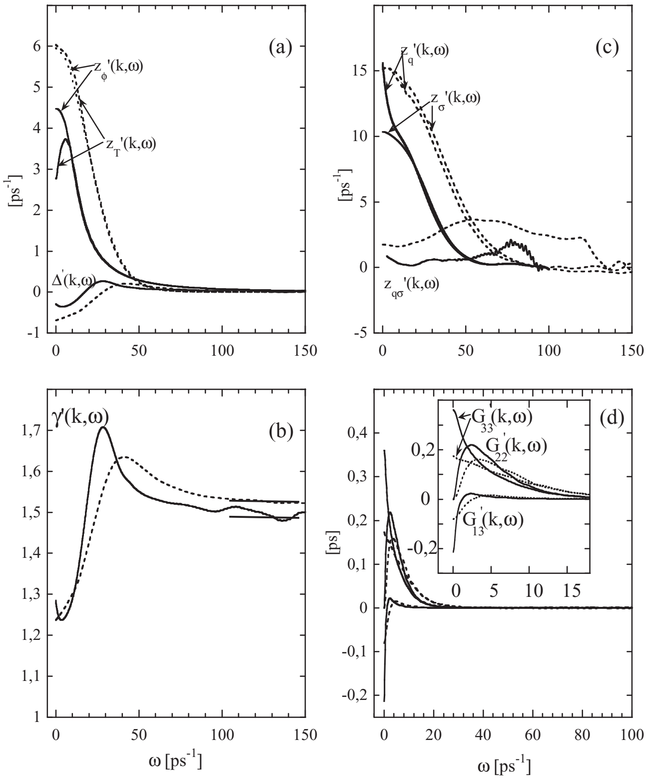

FIG. 6. Generalized spectra of the transport properties, of the ratio of the specific heats, and of the three fundamentals cf's $G_{22}(k,t)$, $G_{13}(k,t)$, and $G_{33}(k,t)$, at the k of the peak of $S(k)$, $k \simeq 20$ nm^{-1}, at $T = 88$ K (full lines) and $T = 200$ K (broken lines), and for $k \simeq 20$ nm^{-1} : (a) Real part of $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$; (b) real part of $\gamma(k,z)$; (c) real part of $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$; (d) real part of $\tilde{G}_{22}(k,z)$, $\tilde{G}_{13}(k,z)$, and $\tilde{G}_{33}(k,z)$. The inset shows the low frequency region.

IV. CONCLUSIONS

We have presented an approach that provides an explicit solution of the exact kinetic equations (2.14) in the frequency and wavelength domain.

The data necessary to implement this approach are the three independent density-density, $F_{11}(k,t)$; density-energy, $F_{13}(k,t)$; and energy-energy, $F_{33}(k,t)$ time correlation functions. They are most easily obtained in an MD simulation, but theoretical or experimental data could also be used, provided they cover a time span large enough to allow an accurate Laplace transformation.

In fact, orthonormal combinations of the Laplace transforms of the three basic cf's $[G_{ij}(k,z)]$ are the functions that enter Eqs. (2.14) as input. With a basis of five variables, the matrix $H_{mr}(k,z)$ that enters Eq. (2.14) contains elements that are related to generalized thermodynamic properties (e.g., enthalpy, thermal expansivity, and heat capacities), and are given by proper combinations of the initial values of the three cf's mentioned above.

The matrix $H_{mr}(k,z)$ also contains frequency-dependent functions, related to generalized transport coefficients such as longitudinal viscosity, thermal conductivity, and ratio of specific heats. Solving Eq. (2.14) leads to explicit expressions for these quantities, which offers the additional advantage of testing the reliability of the common assumptions usually made to calculate generalized transport parameters. Among them are the Markov approximation, which amounts to considering frequency independent the generalized transport coefficients until the spectra $G_{ij}(k,z)$ essentially vanish, and the approximation of assuming negligible the coupling between stress tensor and energy flux fluctuations.

When our approach is applied to the LJ fluid (argon), it turns out that the latter approximation is not correct, as the parameter that measures the coupling $[\Delta(k,0)]$ is actually negligible only in the limit of $k = 0$, at 88 and 200 K. This approximation becomes even less accurate as k increases, except for the k range around the maximum of $S(k)$. The range of wavelengths where the maximum of $S(k)$ is corresponds to longer-lived positional correlations. In its turn, this leads to relatively slowly decaying time correlation functions and then to spectra that vanish more quickly. This explains why, if the Markov approximation is adopted, one obtains more accurate results for k in the range of the peak of $S(k)$ rather than in the free-streaming limit. On the same basis, higher temperatures worsen the Markov approximated results, with the possible exception of $z'_q(k,\omega)$. In any case, the most important factor for the reliability of the Markov assumption remains the distance scale of the correlations, as measured by k, at least for the LJ fluid.

Moreover, the exact calculation of the generalized thermodynamic coefficients allows one to resolve the ambiguity on the relative role [essentially due to $\gamma(k)$] of the viscous and thermal contribution to $S(k,\omega)$, which is the only experimentally measurable physical quantity [17–20].

Confidence in the simulation results is based on their agreement with experimental data. This is achieved for the thermal conductivity [26], as well as for the longitudinal viscosity [27], calculated from the Green-Kubo relations at $k = 0$. The latter is also in accord with recent results from a very long simulation of the LJ fluid [29].

As a final remark, we note that Appendix D details an alternative route to the results described in this paper. This alternative approach leads to a higher accuracy in the high frequency region, at the cost of computing twelve $F_{ij}(k,t)$ cf's instead of three. In the same appendix we show that it is possible to write an alternative definition of generalized longitudinal viscosity and thermal conductivity. This permits us to obtain a correct definition of the generalized bulk viscosity [23] for argon and simple liquids, and can be extended to molecular liquids as well. With this definition, bulk viscosity remains positive at all k's, unlike what was reported for the LJ fluid [25] and, recently, for liquid metals [30].

APPENDIX A: ELEMENTS OF THE ORTHONORMAL TRANSFORMATION MATRIX

For the nine elements $U_{ml}(k)$, we obtain

$$U_{11}(k) = [V_{11}(k)]^{-\frac{1}{2}} = [S(k)]^{-\frac{1}{2}}, \tag{A1}$$

$$U_{22}(k) = [V_{22}(k)]^{-\frac{1}{2}} = \left[\frac{k_B T}{m}\right]^{-\frac{1}{2}}, \tag{A2}$$

$$U_{33}(k) = \left[V_{33}(k) - \frac{V_{13}(k)^2}{V_{11}(k)}\right]^{-\frac{1}{2}} = [k_B T^2 c_V(k)]^{-\frac{1}{2}}, \tag{A3}$$

$$U_{31}(k) = -U_{33}(k)\frac{V_{13}(k)}{V_{11}(k)} = U_{33}(k)\left[\frac{k_B T^2 \alpha(k)}{S(k)} - h(k)\right], \tag{A4}$$

$$U_{44}(k)^2 = V_{44}(k) - \frac{V_{11}(k)V_{34}(k)^2 - 2V_{13}(k)V_{14}(k)V_{34}(k) + V_{33}(k)V_{14}(k)^2}{V_{11}(k)V_{33}(k) - V_{13}(k)^2} = V_{44}(k) - \left(\frac{k_B T}{m}\right)^2 \frac{\gamma(k)}{S(k)}, \tag{A5}$$

$$U_{43}(k) = -U_{44}(k)\,\frac{V_{11}(k)V_{34}(k) - V_{13}(k)V_{14}(k)}{V_{11}(k)V_{33}(k) - V_{13}(k)^2} = -U_{44}(k)\frac{k_B T}{m S(k)}\frac{\alpha(k)}{c_V(k)}, \tag{A6}$$

$$U_{41}(k) = -U_{44}(k)\,\frac{V_{33}(k)V_{14}(k) - V_{13}(k)V_{34}(k)}{V_{11}(k)V_{33}(k) - V_{13}(k)^2} = -U_{44}(k)\frac{k_B T}{m S(k)}\frac{[c_P(k) - \alpha(k)h(k)]}{c_V(k)}, \tag{A7}$$

$$U_{55}(k) = \left[\frac{V_{22}(k)V_{55}(k) - V_{25}(k)^2}{V_{22}(k)}\right]^{-\frac{1}{2}} = \left[V_{55}(k) - \frac{k_B T}{m}h(k)^2\right]^{-\frac{1}{2}}, \tag{A8}$$

$$U_{52}(k) = -U_{55}(k)\frac{V_{25}(k)}{V_{22}(k)} = -U_{55}(k)h(k). \tag{A9}$$

APPENDIX B: EXACT KINETIC EQUATIONS FOR THE LAPLACE TRANSFORM OF THE CF'S OF ORTHONORMAL QUANTITIES

We resume here, for the reader's convenience, part of the appendix A of [13]. The Laplace transforms of the $G_{ml}(k,t)$ are

$$\tilde{G}_{ml}(k,z) = \langle b_m(k) \mid b_l(k,z)\rangle \tag{B1}$$

with

$$|b_l(k,z)\rangle = \frac{1}{z-\widehat{L}}|b_l(k)\rangle. \tag{B2}$$

Equation (B2) can be written as

$$z\;|b_l(k,z)\rangle = \widehat{L}\;|b_l(k,z)\rangle + |b_l(k)\rangle. \tag{B3}$$

Defining the projection operators,

$$P = \sum_{l=1}^{5} |b_l(k)\rangle\langle b_l(k)|, \tag{B4}$$

$$P_\perp = 1 - P, \tag{B5}$$

applying both operators to Eq. (B3), and eliminating $P_\perp\,|b_l(k,z)\rangle$ and using the definition (B5), we obtain the exact kinetic equation Eq. (2.14), which involves the matrix $H_{mr}(k,z)$; see Eq. (2.15).

The elements of the matrix that do not depend on frequency are given by the initial value of the relevant correlation functions, so they are related to the generalized thermodynamic functions:

$$f_{un}(k) = \left[\frac{V_{22}(k)}{V_{11}(k)}\right]^{\frac{1}{2}} k, \tag{B6}$$

$$f_{uT}(k) = \left[\frac{V_{22}(k)}{V_{11}(k)}\,[\gamma(k)-1]\right]^{\frac{1}{2}} k, \tag{B7}$$

$$f_{u\sigma}(k) = \left[\frac{V_{44}(k)}{V_{22}(k)} - \frac{V_{22}(k)}{V_{11}(k)}\gamma(k)\right]^{\frac{1}{2}} k, \tag{B8}$$

$$f_{Tq}(k) = \left[V_{11}(k)\frac{V_{55}(k) - V_{22}(k)\;h(k)^2}{V_{33}(k)V_{11}(k) - V_{13}(k)^2}\right]^{\frac{1}{2}} k. \tag{B9}$$

The matrix $H_{mr}(k,z)$ also contains frequency-dependent functions, related to transport coefficients and defined by

$$z_\sigma(k,z) = \int_0^\infty dt\; e^{-zt}\;\; J_\sigma(k,t), \tag{B10}$$

$$z_q(k,z) = \int_0^\infty dt\; e^{-zt}\;\; J_q(k,t), \tag{B11}$$

$$z_{q\sigma}(k,z) = \int_0^\infty dt\; e^{-zt}\;\; J_{q\sigma}(k,t) + i \leqslant \langle b_5(k)|\widehat{L}|b_4(k)\rangle, \tag{B12}$$

where

$$J_\sigma(k,t) \equiv -\langle b_4(k)|\widehat{L}P_\perp e^{tP_\perp\widehat{L}P_\perp} P_\perp\widehat{L}|b_4(k)\rangle, \tag{B13}$$

$$J_q(k,t) \equiv -\langle b_5(k)|\widehat{L}P_\perp e^{tP_\perp\widehat{L}P_\perp} P_\perp\widehat{L}|b_5(k)\rangle, \tag{B14}$$

$$J_{q\sigma}(k,t) \equiv i\langle b_5(k)|\widehat{L}P_\perp e^{tP_\perp\widehat{L}P_\perp} P_\perp\widehat{L}|b_4(k)\rangle. \tag{B15}$$

Note that when the time scale on which $J_\sigma(k,t)$, $J_q(k,t)$, and $J_{q\sigma}(k,t)$ decay to zero is shorter than that of the functions $G_{ij}(k,t)$, the z dependence of the transport coefficients $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ can be neglected. As a consequence, we obtain

$$z_\sigma(k) = \int_0^\infty dt\;\; J_\sigma(k,t), \tag{B16}$$

$$z_q(k) = \int_0^\infty dt\;\; J_q(k,t), \tag{B17}$$

$$z_{q\sigma}(k) = \int_0^\infty dt\;\; J_{q\sigma}(k,t) + i\,\langle b_5(k)|\,\widehat{L}\,|b_4(k)\rangle\,. \tag{B18}$$

This approximation is equivalent to assuming that a transport coefficient, which must go to zero when $\omega \to \infty$, has a flat behavior in the low-ω range, in which the spectra of the fundamental functions $G_{ij}(k,t)$ decay to zero, so that it is possible to use the $\omega = 0$ value for this coefficient in Eqs. (B10)–(B11). This approximation, expressed equivalently in the time regime, is usually referred to as the Markov assumption (see also Ref. [4], p. 969).

APPENDIX C: CORRELATION FUNCTIONS CALCULATED FROM TRANSPORT PARAMETERS

According to Eqs. (2.24), the $\widetilde{G}_{ml}(k,z)$ are calculated as a function of the three generalized parameters $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$,

$$\widetilde{G}_{12}(k,z) = \frac{-if_{un}(k)[z+z_T(k,z)]}{D(k,z)}, \tag{C1}$$

$$\widetilde{G}_{14}(k,z) = -\frac{f_{un}(k)}{f_{u\sigma}(k)}\frac{z_\phi(k,z)[z+z_T(k,z)] + \Delta(k,z)\widetilde{f}_{uT}(k,z)}{D(k,z)}, \tag{C2}$$

$$\widetilde{G}_{15}(k,z) = \frac{if_{un}(k)\{f_{uT}(k)[z+z_T(k,z)] - z\widetilde{f}_{uT}(k,z)\}}{f_{Tq}(k)D(k,z)}, \tag{C3}$$

$$\widetilde{G}_{22}(k,z) = \frac{iz}{f_{un}(k)}\widetilde{G}_{12}(k,z) = \frac{z[1-z\widetilde{G}_{11}(k,z)]}{f_{un}(k)^2} = \frac{z[z+z_T(k,z)]}{D(k,z)}, \tag{C4}$$

$$\widetilde{G}_{23}(k,z) = \frac{iz}{f_{un}(k)}\widetilde{G}_{13}(k,z) = -i\frac{z\widetilde{f}_{uT}(k,z)}{D(k,z)}, \tag{C5}$$

$$\widetilde{G}_{24}(k,z) = \frac{iz}{f_{un}(k)}\widetilde{G}_{14}(k,z) = -iz\frac{z_\phi(k,z)[z+z_T(k,z)] + \Delta(k,z)\widetilde{f}_{uT}(k,z)}{f_{u\sigma}(k)D(k,z)}, \tag{C6}$$

$$\widetilde{G}_{25}(k,z) = \frac{iz}{f_{un}(k)}\widetilde{G}_{15}(k,z) = -\frac{z}{f_{Tq}(k)}\frac{f_{uT}(k)[z+z_T(k,z)] - z\widetilde{f}_{uT}(k,z)}{D(k,z)}, \tag{C7}$$

$$\widetilde{G}_{34}(k,z) = \frac{\Delta(k,z)[z^2 + f_{un}(k)^2] - z z_\phi(k,z) f_{uT}(k)}{f_{u\sigma}(k) D(k,z)}, \quad \text{(C8)}$$

$$i\widetilde{G}_{35}(k,z) = \frac{z_T(k,z)[z^2 + f_{un}(k)^2 + z z_\phi(k,z)] + z\Delta(k,z)\widetilde{f}_{uT}(k,z)}{f_{Tq}(k)D(k,z)}, \quad \text{(C9)}$$

$$\begin{aligned} f_{u\sigma}(k)^2 D(k,z)\widetilde{G}_{44}(k,z) &= z z_\phi(k,z)[z^2 + f_{un}(k)^2 + f_{uT}(k)^2] \\ &\quad + [z^2 + f_{un}(k)^2][z_\phi(k,z) z_T(k,z) + \Delta(k,z)^2], \end{aligned} \quad \text{(C10)}$$

$$\begin{aligned} f_{u\sigma}(k)\ \ f_{Tq}(k) D(k,z)\widetilde{G}_{45}(k,z) &= iz\Delta(k,z)[z^2 + f_{un}(k)^2 + f_{uT}(k)^2] \\ &\quad + iz f_{uT}(k)[z_\phi(k,z) z_T(k,z) + \Delta(k,z)^2], \end{aligned} \quad \text{(C11)}$$

$$\begin{aligned} f_{Tq}(k)^2 D(k,z)\widetilde{G}_{55}(k,z) &= z z_T(k,z)[z^2 + f_{un}(k)^2 + f_{uT}(k)^2] \\ &\quad + z^2[z_\phi(k,z) z_T(k,z) + \Delta(k,z)^2], \end{aligned} \quad \text{(C12)}$$

where

$$\begin{aligned} D(k,z) = {} & z[z + z_T(k,z)][z + z_\phi(k,z)] \\ & + f_{un}(k)^2[z + z_T(k,z)] + z\widetilde{f}_{uT}(k,z)^2. \end{aligned} \quad \text{(C13)}$$

The symmetry property $\widetilde{G}_{ml}(k,z) = \widetilde{G}_{lm}(k,z)$ and Eqs. (2.16)–(2.18) define the remaining elements $\widetilde{G}_{11}(k,z)$, $\widetilde{G}_{13}(k,z)$, and $\widetilde{G}_{33}(k,z)$. Apart from the functions $\widetilde{G}_{12}(k,z)$ and $\widetilde{G}_{22}(k,z)$ easily connected to $\widetilde{G}_{11}(k,z)$ and the functions $\widetilde{G}_{23}(k,z)$, $\widetilde{G}_{24}(k,z)$, and $\widetilde{G}_{25}(k,z)$ that can readily be obtained from the functions $\widetilde{G}_{13}(k,z)$, $\widetilde{G}_{14}(k,z)$, and $\widetilde{G}_{15}(k,z)$, the other ten functions may be divided into the following three groups: the three fundamental functions $\widetilde{G}_{11}(k,z)$, $\widetilde{G}_{13}(k,z)$, and $\widetilde{G}_{33}(k,z)$, the four intermediate functions $\widetilde{G}_{14}(k,z)$, $\widetilde{G}_{15}(k,z)$, $\widetilde{G}_{34}(k,z)$, and $\widetilde{G}_{35}(k,z)$ that involve only one second time derivative of a_2 and a_3, and the three functions $\widetilde{G}_{44}(k,z)$, $\widetilde{G}_{45}(k,z)$, and $\widetilde{G}_{55}(k,z)$ that involve two second time derivatives of a_2 and a_3. These three groups can be considered as corresponding to low, intermediate, and high order in frequency, respectively.

APPENDIX D: TRANSPORT PARAMETERS AND INTERMEDIATE AND HIGH FREQUENCY ORDER CF'S

In this appendix, we explore the possibility of defining the transport properties by means of intermediate or high frequency order cf's according to the scheme outlined in the previous appendix. Note that

$$\begin{aligned} \frac{\widetilde{G}_{24}(k,z)}{\widetilde{G}_{22}(k,z)} = \frac{\widetilde{G}_{14}(k,z)}{\widetilde{G}_{12}(k,z)} &= -\frac{i}{f_{u\sigma}(k)} z_\phi(k,z) \\ &\quad - \frac{i}{f_{u\sigma}(k)}\Delta(k,z)\frac{\widetilde{f}_{uT}(k,z)}{z + z_T(k,z)}, \end{aligned} \quad \text{(D1)}$$

and

$$\begin{aligned} \frac{\widetilde{G}_{35}(k,z)}{\widetilde{G}_{33}(k,z)} &= -\frac{i}{f_{Tq}(k)} z_T(k,z) - \frac{i}{f_{Tq}(k)}\Delta(k,z) \\ &\quad \times \frac{z\widetilde{f}_{uT}(k,z)}{[z^2 + f_{un}(k)^2 + z z_\phi(k,z)]}. \end{aligned} \quad \text{(D2)}$$

From these two equations and Eqs. (2.26) and (2.27), it is possible to obtain an alternative definition of generalized longitudinal viscosity and thermal conductivity,

$$\begin{aligned} \frac{k^2\eta_L(k,z)}{\rho} &= z_\phi(k,z) \\ &= i f_{u\sigma}(k)\frac{\widetilde{G}_{24}(k,z)}{\widetilde{G}_{22}(k,z)} + \frac{\Delta(k,z)}{f_{un}(k)}\frac{z\widetilde{G}_{13}(k,z)}{\widetilde{G}_{22}(k,z)}, \end{aligned} \quad \text{(D3)}$$

$$\begin{aligned} \frac{k^2\lambda(k,z)M}{\rho c_V(k)} &= z_T(k,z) \\ &= i f_{Tq}(k)\frac{\widetilde{G}_{35}(k,z)}{\widetilde{G}_{33}(k,z)} + \frac{\Delta(k,z)}{f_{un}(k)}\frac{z\widetilde{G}_{13}(k,z)}{\widetilde{G}_{33}(k,z)}. \end{aligned} \quad \text{(D4)}$$

By means of two additional intermediate order functions [$\widetilde{G}_{34}(k,z)$ and $\widetilde{G}_{25}(k,z)$], we can write

$$\frac{\Delta(k,z)}{f_{un}(k) f_{u\sigma}(k)} = \frac{f_{un}(k)\widetilde{G}_{22}(k,z)\widetilde{G}_{34}(k,z) - iz\widetilde{G}_{13}(k,z)\widetilde{G}_{24}(k,z)}{f_{un}(k)^2\widetilde{G}_{22}(k,z)\widetilde{G}_{33}(k,z) + z^2\widetilde{G}_{13}(k,z)^2}, \quad \text{(D5)}$$

$$\frac{\Delta(k,z)}{f_{un}(k) f_{Tq}(k)} = \frac{f_{un}(k)\widetilde{G}_{25}(k,z)\widetilde{G}_{33}(k,z) - iz\widetilde{G}_{13}(k,z)\widetilde{G}_{35}(k,z)}{f_{un}(k)^2\widetilde{G}_{22}(k,z)\widetilde{G}_{33}(k,z) + z^2\widetilde{G}_{13}(k,z)^2}. \quad \text{(D6)}$$

The above relation can be exploited to eliminate $\widetilde{G}_{13}(k,z)$, so that, replacing the value of $\Delta(k,z)$ into Eqs. (D3) and (D4), it turns out that only six intermediate- to low-order functions $\widetilde{G}_{ij}(k,z)$ [constructed by nine $F_{ij}(k,t)$ cf's, only three of them independent] are required to obtain $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$. Hence,

$$\frac{z\widetilde{G}_{13}(k,z)}{f_{un}(k)} = i\frac{N_{13}(k,z)}{D_{13}(k,z)} \quad \text{(D7)}$$

and

$$\frac{\Delta(k,z)}{f_{u\sigma}(k) f_{Tq}(k)} = \frac{\widetilde{G}_{22}(k,z)\widetilde{G}_{34}(k,z)\widetilde{G}_{35}(k,z) - \widetilde{G}_{33}(k,z)\widetilde{G}_{24}(k,z)\widetilde{G}_{25}(k,z)}{\widetilde{G}_{22}(k,z)\widetilde{G}_{33}(k,z)D_{13}(k,z)^2 - N_{13}(k,z)^2}. \quad \text{(D8)}$$

In Eqs. (D7) and (D8), we have defined

$$\begin{aligned} N_{13}(k,z) = {} & f_{Tq}(k)\widetilde{G}_{33}(k,z)\widetilde{G}_{25}(k,z) \\ & - f_{u\sigma}(k)\widetilde{G}_{22}(k,z)\widetilde{G}_{34}(k,z) \end{aligned} \quad \text{(D9)}$$

and

$$D_{13}(k,z) \equiv f_{Tq}(k)\widetilde{G}_{35}(k,z) - f_{u\sigma}(k)\widetilde{G}_{24}(k,z). \quad \text{(D10)}$$

Moreover, Eq. (D6) shows that the first term of Eq. (D3) is sufficient to describe the dependence of the longitudinal component ($m = 4$) of the stress tensor. In fact, Eq. (D6) does not depend explicitly on this component, so that $\Delta(k,z)$ and the second term of Eq. (D3) do not depend on the stress tensor. In conclusion, to generalize the longitudinal component (zz) of the stress tensor with another component such as xx or yy, as in the case of a generalized definition of bulk viscosity, only the first term of Eq. (D3) is necessary. It is also possible to obtain the three generalized quantities (as detailed in Ref. [13]) only employing intermediate and higher order functions. We have

$$\frac{z_\phi(k,z)}{f_{u\sigma}(k)^2} = \frac{\widetilde{G}_{44}(k,z)D_{35}(k,z) + i f_{Tq}(k)\widetilde{G}_{45}(k,z)\widetilde{G}_{34}(k,z)}{D_J(k,z)}, \tag{D11}$$

$$\frac{z_T(k,z)}{f_{Tq}(k)^2} = \frac{\widetilde{G}_{55}(k,z)D_{24}(k,z) + i f_{u\sigma}(k)\widetilde{G}_{45}(k,z)\widetilde{G}_{25}(k,z)}{D_J(k,z)}, \tag{D12}$$

$$\frac{\Delta(k,z)}{f_{u\sigma}(k) f_{Tq}(k)} = \frac{f_{Tq}(k)\widetilde{G}_{34}(k,z)\widetilde{G}_{55}(k,z) - i\ \widetilde{G}_{45}(k,z)D_{35}(k,z)}{D_J(k,z)}, \tag{D13}$$

$$\frac{\Delta(k,z)}{f_{u\sigma}(k) f_{Tq}(k)} = \frac{f_{u\sigma}(k)\widetilde{G}_{25}(k,z)\widetilde{G}_{44}(k,z) - i\ \widetilde{G}_{45}(k,z)D_{24}(k,z)}{D_J(k,z)}, \tag{D14}$$

where

$$D_J(k,z) = D_{35}(k,z)D_{24}(k,z) - f_{u\sigma}(k) f_{Tq}(k)\widetilde{G}_{34}(k,z)\widetilde{G}_{25}(k,z), \tag{D15}$$

$$D_{24}(k,z) = 1 - i f_{u\sigma}(k)\widetilde{G}_{24}(k,z), \tag{D16}$$

$$D_{35}(k,z) = 1 - i f_{Tq}(k)\widetilde{G}_{35}(k,z). \tag{D17}$$

Equations (D3) and (D14) being equal implies

$$\widetilde{G}_{45}(k,z) = \frac{f_{Tq}(k)\widetilde{G}_{34}(k,z)\widetilde{G}_{55}(k,z) - f_{u\sigma}(k)\widetilde{G}_{25}(k,z)\widetilde{G}_{44}(k,z)}{f_{Tq}(k)\widetilde{G}_{35}(k,z) - f_{u\sigma}(k)\widetilde{G}_{24}(k,z)} \tag{D18}$$

so that Eqs. (D3) and (D14) become

$$i\Delta(k,z)\left[\frac{\widetilde{G}_{35}(k,z)}{f_{u\sigma}(k)} - \frac{\widetilde{G}_{24}(k,z)}{f_{Tq}(k)}\right]D_J(k,z) = f_{Tq}(k)\widetilde{G}_{34}(k,z)\widetilde{G}_{55}(k,z)D_{24}(k,z) - f_{u\sigma}(k)\widetilde{G}_{25}(k,z)\widetilde{G}_{44}(k,z)D_{35}(k,z) \tag{D19}$$

and the cf's required to calculate the three parameters $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$ are just six $\widetilde{G}_{ij}(k,z)$ [constructed by eleven $F_{ij}(k,t)$ cf's, only three of them independent]. It is worth noting that the simpler definitions are more convenient at low frequency, while the latter definitions are more accurate at high frequency. The second intermediate definitions (D3)–(D7) have the great advantage of allowing an easy generalization of bulk viscosity. Finally, we will calculate the three coefficients $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ by means of the three higher-order functions $\widetilde{G}_{44}(k,z)$, $\widetilde{G}_{45}(k,z)$, and $\widetilde{G}_{55}(k,z)$, as opposed to the calculation of $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$ by means of the three lower-order functions $\widetilde{G}_{11}(k,z)$ [or $\widetilde{G}_{22}(k,z)$], $\widetilde{G}_{13}(k,z)$, and $\widetilde{G}_{33}(k,z)$. The latter three functions are, as that of the lower frequency order, independent and sufficient to invert the calculation. Unlike what was shown in Sec. II D, the results for $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ are much simpler than that for $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$. In fact, we obtain

$$z + z_\sigma(k,z) = \frac{\widetilde{G}_{55}(k,z)}{D_{45}(k,z)} - \frac{z\ f_{u\sigma}(k)^2}{z^2 + f_{un}(k)^2 + f_{uT}(k)^2}, \tag{D20}$$

$$z + z_q(k,z) = \frac{\widetilde{G}_{44}(k,z)}{D_{45}(k,z)} - \frac{[z^2 + f_{un}(k)^2]\ f_{Tq}(k)^2}{z[z^2 + f_{un}(k)^2 + f_{uT}(k)^2]}, \tag{D21}$$

$$z_{q\sigma}(k,z) = \frac{i\widetilde{G}_{45}(k,z)}{D_{45}(k,z)} + \frac{f_{u\sigma}(k)\ f_{Tq}(k)\ f_{uT}(k)}{z^2 + f_{un}(k)^2 + f_{uT}(k)^2}, \tag{D22}$$

with

$$D_{45}(k,z) = \widetilde{G}_{55}(k,z)\widetilde{G}_{44}(k,z) - \widetilde{G}_{45}(k,z)^2. \tag{D23}$$

Note that in Eqs. (D20) and (D21), the terms on the rhs are purely imaginary, and as a consequence the real part of $z_\sigma(k,z)$ and $z_q(k,z)$ is obtained by only the first corresponding term. This simplification is compensated by a more complicated calculation of $\widetilde{G}_{44}(k,z)$,$\widetilde{G}_{55}(k,z)$, and $\widetilde{G}_{45}(k,z)$, in fact, $b_4 = U_{41}a_1 + U_{43}a_3 + U_{44}a_4$ and $b_5 = U_{52}a_2 + U_{55}a_5$ [see Eqs. (2.12)] and, as a consequence, twelve instead of three $F_{ij}(k,t)$ cf's are necessary for this calculation, even if only three are independent. Moreover, if $\widetilde{G}_{45}(k,z)^2 \ll \widetilde{G}_{55}(k,z)\widetilde{G}_{44}(k,z)$, we obtain $z'_\sigma(k,z) \simeq 1/\widetilde{G}_{44}(k,z)$ and $z'_q(k,z) \simeq 1/\widetilde{G}_{55}(k,z)$. Finally, from Eq. (D2) we may remark that for $\omega \to 0$, the right term is always positive, but the first term is not zero, even if both $\widetilde{G}_{45}(k,z)$ and $\widetilde{G}_{55}(k,z)$, unlike $\widetilde{G}_{44}(k,z)$, go to zero [see Eqs. (C10)–(C13)]. This is a consequence of the ratio $\widetilde{G}_{45}(k,z)\ /\widetilde{G}_{55}(k,z)$, which is not zero in the same limit.

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