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Hydrodynamic time correlation functions for a Lennard-Jones fluid

I. M. de Schepper* and E. G. D. Cohen
The Rockefeller University, 1230 York Avenue, New York, New York 10021

C. Bruin
Laboratory of Technical Physics, University of Technology, 2600 GA Delft, The Netherlands

J. C. van Rijs, W. Montfrooij, and L. A. de Graaf
Interuniversitair Reactor Instituut, 2629 JB Delft, The Netherlands

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Four time correlation functions of a Lennard-Jones (LJ) fluid at a reduced density of $n^*=n\sigma_{\mathrm{LJ}}^3=0.845$ and a reduced temperature of $T^*=k_BT/\varepsilon_{\mathrm{LJ}}=1.71$ have been determined numerically using molecular dynamics. They were computed as a function of wave number k for reduced wave numbers $0\leq k\sigma_{\mathrm{LJ}}<15$ and for reduced times $0\leq t/\tau_\sigma<2.6$, where τ_σ is an average collision time. From these four, all 25 correlation functions can be derived between three conserved and two nonconserved quantities: the number density, energy density, longitudinal velocity, momentum flux, and energy flux, respectively. They can be fitted consistently by five exponentials that correspond to the five eigenmodes of a 5×5 k-dependent, but not t-dependent, matrix based on the above-mentioned five quantities. Three of these eigenmodes are extensions of the usual hydrodynamic modes and suffice to describe the density-density correlation function alone. A comparison with previous work on Lennard-Jones, noble-gas, and hard-sphere fluids is made.

I. INTRODUCTION

In this paper molecular-dynamics (MD) results are reported for three microscopic correlation functions in a dense Lennard-Jones (LJ) fluid in equilibrium at a reduced temperature $T^*=k_BT/\varepsilon_{\mathrm{LJ}}=1.71$ and a reduced density $n^*=\sigma_{\mathrm{LJ}}^3=0.845$: the density-density $[F_{nn}(k,t)]$, the density-energy $[F_{ne}(k,t)]$, and the energy-energy $[F_{ee}(k,t)]$ time-correlation functions. Here k_B is Boltzmann's constant, σ_{LJ} is the LJ particle diameter, $\varepsilon_{\mathrm{LJ}}$ the LJ well depth, k a wave number, and t the time.

Apart from their intrinsic interest and their relevance for the corresponding noble-gas correlation functions, the knowledge of $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$ is also important for the following reasons.

(1) The three functions $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$ allow a unique determination of the three generalized transport coefficients:[1-3] the longitudinal viscosity $\phi(k,\omega)$, the thermal conductivity $\lambda(k,\omega)$, and the generalized ratio of specific heats $\gamma(k,\omega)$ as a function of k and the frequency ω. Although we could have determined these coefficients directly from MD simulations, using explicit theoretical expressions for them, such a direct numerical evaluation is considerably more complicated in practice than the indirect determination performed here, via $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$. This will be discussed in Sec. IV E.

(2) From the three independent functions $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$, the entire set of microscopic hydrodynamic time-correlation functions can be derived. Thus if one introduces, in addition to the microscopic density and energy fluctuations, the microscopic longitudinal velocity fluctuations labeled u, the temperature fluctuation T, the longitudinal stress-tensor fluctuation σ, and the longitudinal heat-flux fluctuation q, then the complete 5×5 correlation matrix $F_{jl}(k,t)$, with $j,l=n,u,e,\sigma,q$ or $j,l=n,u,T,\sigma,q$, can be obtained from $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$ alone. Here the microscopic temperature fluctuations T (Ref. 4) is a linear combination of n and e [cf. Eqs. (2.19)–(2.23)], and longitudinal refers to the direction parallel to a wave vector $\mathbf{k}$ with length $k=|\mathbf{k}|$.

For a fluid of hard spheres, Alley and Alder[3] determined the 3×3 matrix $F_{jl}(k,t)$ with $j,l=n,u,T$ for a number of densities from MD. They found at high densities that they could describe their MD data for $F_{jl}(k,t)$ in terms of the $F_{jl}(k,0)$ and a 3×3 matrix $\underline{H}^{(3)}(k)$ which depends upon k but not upon t. Since the elements of $\underline{H}^{(3)}(k)$ refer to the three hydrodynamic variables n, u, and T, such a description can be considered as a generalization of the hydrodynamic description and we will call this the hydrodynamic model for the fluid. In this description all nine correlation functions $F_{jl}(k,t)$, with $j,l=n,u,T$, are given by a sum of three exponentials related to the three eigenmodes, i.e., eigenvalues and eigenvectors, of the matrix $\underline{H}^{(3)}(k)$. These high-density MD results could be understood on the basis of the revised Enskog theory (RET) of a hard-sphere fluid.[5] However, at low and intermediate densities of the hard-sphere fluid the $F_{jl}(k,t)$ $(j,l=n,u,T)$ could not be satisfactorily described by a 3×3 k-dependent matrix. Instead a 5×5 matrix $\underline{H}^{(5)}(k)$ was needed. This matrix described not only the nine time-correlation functions mentioned previously, but in fact all 25 correlation functions between n,

u, T, σ and q.

The question arose then whether, also for the *dense* Lennard-Jones fluid considered here three exponentials would suffice to describe $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$ and consequently the nine $F_{jl}(j,t)$, with $j,l=n,u,T$ (or e), just as in the case of a dense hard-sphere fluid, or that perhaps a more elaborate description was necessary.

Before we address this question, we remark that, for the density-density correlation function $F(k,t)=F_{nn}(k,t)$ *alone,* many successful descriptions exist in the literature, using so-called k- and t-dependent memory kernels.[1,6–10] It was not clear to us, however, how such descriptions could be consistently applied to the three independent correlation functions considered in this paper. In particular, from the definition of the correlation functions it follows that their time dependence is given by the same time-evolution operator $\exp(tL)$, where L is the Liouville operator. It is not clear to what extent this restricts the assumptions one can make about the time dependence of the memory kernels.

In the absence of a solution to this problem, we proceeded in the simplest possible way by assuming, as was done by Alley and Alder for hard-sphere fluids, that all nine correlation functions $F_{jl}(k,t)$, with $j,l=n,u,e$, for the dense LJ fluid could be fitted by a sum of three exponentials, due to the three eigenmodes of a 3×3 matrix, with the condition that the hydrodynamic limit was correctly obtained for $k\rightarrow 0$. This turned out to be impossible and we proceeded to fit the data for the nine $F_{jl}(k,t)$, with $j,l=n,u,e$, and subsequently the 25 $F_{jl}(k,t)$, with $j,l=n,u,e,\sigma,q$, to five exponentials, related to the eigenmodes of a 5×5 matrix $\underline{H}^{(5)}(k)$. This matrix effectively replaces the Liouville operator L, as in the case of hard-sphere fluids at intermediate densities. Such a representation of our data was indeed possible and the results and an attempt at their interpretation are presented here.

We remark that we have actually computed not only $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$, but also the (dependent) longitudinal velocity autocorrelation function $F_{uu}(k,t)$ by an independent MD calculation. This is in the spirit of Rahman,[11] who calculated both $F_{nn}(k,t)$ and $F_{uu}(k,t)$ by MD to study the dynamic structure factor $S(k,\omega)$. He found that some details of the microscopic dynamics, relevant for $S(k,\omega)$, show up more clearly in $F_{uu}(k,t)$ than in $F_{nn}(k,t)$.[1,6,11,12] Here we use $F_{uu}(k,t)$ to increase the accuracy of the results for the $F_{jl}(k,t)$, with $j,l=n,u,e,\sigma,q$.

Thus, using the four correlation functions F_{nn}, F_{uu}, F_{ne}, and F_{ee}, we find that all 25 time-correlation functions $F_{jl}(k,t)$ between n, u, e, σ, and q can be described, in good approximation, for $0<k\sigma_{\text{LJ}}<15$, by the equations

$$\frac{\partial F_{jl}(k,t)}{\partial t}=-\sum_{i=1}^{5}H_{ji}(k)F_{il}(k,t)\quad (j,l=1,\ldots,5)\ . \tag{1.1}$$

Here $H_{jl}(k)$ is a (5×5) correlation matrix, which only depends on k but not on t. We have omitted the superscript 5 on the 5×5 matrix $\underline{H}(k)$. The subscripts $i,j=1,\ldots,5$ refer to n,u,e,σ,q, respectively.

As a consequence of Eq. (1.1), the $F_{jl}(k,t)$ can all be represented in terms of the five eigenmodes of the matrix $H_{ji}(k)$ as a sum of five exponentials. As before,[5] we call these modes the effective eigenmodes of the fluid. For small k, i.e., $k\sigma_{\text{LJ}}<1$, Eqs. (1.1) contain the linearized hydrodynamic equations for the nine hydrodynamic correlation functions between the three conserved quantities n, u, and e that were first discussed by Landau and Placzek in the context of the light scattering of a fluid,[1]

$$\frac{\partial}{\partial t}F_{jl}(k,t)=-\sum_{i=1}^{3}H_{ji}^{(h)}(k)F_{il}(k,t)\quad (j,l=1,2,3)\ . \tag{1.2}$$

Here the (3×3) hydrodynamic matrix $H_{ji}^{(h)}(k)$ can be expressed in terms of two thermodynamic quantities and two transport coefficients of the fluid. Its three eigenmodes are the three (longitudinal) hydrodynamic modes: one heat mode and two sound modes, the eigenvalues of which vanish for k going to zero. For these values of k the $F_{jl}(k,t)$ $(j,l=1,2,3)$ can be represented in terms of these three eigenmodes as a sum of three exponentials.

Although, according to Eq. (1.1), $F_{11}(k,t)=F(k,t)$ is in principle a sum of five exponentials, it can, for all k with $0\leq k\sigma_{\text{LJ}}<15$, be represented in practice by only three out of five exponentials. However, the character of the three modes that describe $F(k,t)$ changes continuously with k. For $k\sigma_{\text{LJ}}>1$ the three exponentials are the extensions of those in the hydrodynamic regime for $k\sigma_{\text{LJ}}<1$ and given by the three eigenmodes of $H_{jl}(k)$ that correspond to the three lowest eigenvalues of $H_{jl}(k)$. These three eigenmodes reduce for $k\sigma_{\text{LJ}}<1$ to those of $H_{jl}^{(h)}(k)$ and are called the three extended hydrodynamic modes. The other two (nonhydrodynamic) eigenmodes of $H_{jl}(k)$ are kinetic modes, the eigenvalues of which do not vanish for k going to zero. We emphasize that the three extended hydrodynamic modes can involve combinations of the two nonhydrodynamic quantities σ and q as well as of the three hydrodynamic quantities n, u, and e.

The description of $F(k,t)$ with three exponentials or, equivalently, of $S(k,\omega)$ with three Lorentzians, makes a comparison possible with other such descriptions discussed in the literature.[5,7,8,13–20] We will consider, in particular, the representation of $F(k,t)$ by three exponentials used by Copley and Lovesey[7,19] or, equivalently, by Kahol *et al.*[8] in their viscoelastic model.

In this model, the coupling of the microscopic quantities n, u, and σ with T and q is assumed to be negligible, as suggested originally by Ailawadi *et al.*[6] As a consequence, the generalized transport coefficients $\lambda(k,\omega)$ and $\gamma(k,\omega)$ are irrelevant for $S(k,\omega)$ and $S(k,\omega)$ is described by the longitudinal viscosity $\phi(k,\omega)$ and the frequency moments $\langle\omega^n\rangle=\int_{-\infty}^{+\infty}\omega^n S(k,\omega)d\omega$ of $S(k,\omega)$ with $n=0,2,4$ alone.

Assuming that $\phi(k,\omega)$ is Lorentzian, this model leads to a representation of $F(k,t)$ by three exponentials, where the corresponding eigenvectors are linear combinations of n, u, and σ only.[19] The present MD data for $F_{nn}(k,t)$, $F_{ne}(k,t)$, and $F_{ee}(k,t)$ are consistent with a Lorentzian-shaped $\phi(k,\omega)$. However, the contributions of $\lambda(k,\omega)$

and $\gamma(k,\omega)$ to $S(k,\omega)$ cannot be neglected, implying that the coupling of n, u, and σ with T and q is not weak enough in the Lennard-Jones fluid for the viscoelastic model to hold. This is in agreement with earlier estimates for $\lambda(k,\omega)$ and $\gamma(k,\omega)$ made by Sjödin and Sjölander[9] and by Bosse *et al.*[10]

The outline of this paper is as follows. The MD experiments are described in Sec. II, the results for the correlation functions are given in Sec. III, and a discussion is given in Sec. IV.

II. EXPERIMENT

A. Definitions

We consider a three-dimensional fluid of $N=864$ particles interacting through a cut-off Lennard-Jones potential $\phi(r,r_c)$ which vanishes for $r \geq r_c$, is continuous at $r=r_c$, and is given by

$$\phi(r,r_c)=4\varepsilon_{\mathrm{LJ}}[(\sigma_{\mathrm{LJ}}/r)^{12}-(\sigma_{\mathrm{LJ}}/r)^6 -(\sigma_{\mathrm{LJ}}/r_c)^{12}+(\sigma_{\mathrm{LJ}}/r_c)^6] \tag{2.1}$$

for $r \leq r_c$. Here we use $r_c=2.5\sigma_{\mathrm{LJ}}$, so that $\phi(r,r_c)$ is very close to the exact LJ potential $\phi(r,\infty)$.

The 25 corelation functions $F_{jl}(k,t)$ of interest are, for $k \neq 0$, given by

$$F_{jl}(k,t)=\langle a_j(\mathbf{k})^* e^{tL} a_l(\mathbf{k})\rangle \ , \tag{2.2}$$

where j or $l=1,\ldots,5$, $k=|\mathbf{k}|$, the asterisk denotes complex conjugation, and the brackets denote the canonical ensemble average at a reduced density $n^*=n\sigma_{\mathrm{LJ}}^3=0.845$ and a reduced temperature $T^*=k_BT/\varepsilon_{\mathrm{LJ}}=1.71$. The time-evolution operator $\exp(tL)$ replaces the position $\mathbf{r}_j$ and velocity $\mathbf{v}_j$ of an arbitrary particle j at $t=0$ by its position $\mathbf{r}_j(t)$ and velocity $\mathbf{v}_j(t)$, respectively, a time t later, and L is the Liouville operator given by

$$L=\sum_{i=1}^{N}\left[\mathbf{v}_i\cdot\frac{\partial}{\partial \mathbf{r}_i}-\frac{1}{m}\sum_{\substack{j=1\\ j\neq i}}^{N}\frac{\partial\phi(r_{ij},r_c)}{\partial \mathbf{r}_{ij}}\cdot\frac{\partial}{\partial \mathbf{v}_i}\right] , \tag{2.3}$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, $r_{ij}=|\mathbf{r}_{ij}|$, and m is the mass of a particle. The five wave-vector ($\mathbf{k}\neq 0$)-dependent microscopic quantities $a_j(\mathbf{k})$ in Eq. (2.2) are given by $(j=1,\ldots,5)$[4,7]

$$a_j(\mathbf{k})=\frac{1}{\sqrt{N}}\sum_{l=1}^{N}A_j^{(l)}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}_l} \ , \tag{2.4}$$

where l labels the N particles, and where

$$A_1^{(l)}(\mathbf{k})=1 \tag{2.5}$$

for the microscopic number density $(j=1)$,

$$A_2^{(l)}(\mathbf{k})=\mathbf{v}_l\cdot\mathbf{k}/k \tag{2.6}$$

for the microscopic longitudinal velocity $(j=2)$,

$$A_3^{(l)}(\mathbf{k})=\tfrac{1}{2}m\mathbf{v}_l^2+\tfrac{1}{2}\sum_{\substack{i=1\\ i\neq l}}^{N}\phi(r_{li},r_c) \tag{2.7}$$

for the microscopic energy density $(j=3)$,

$$A_4^{(l)}(\mathbf{k})=(\mathbf{v}_l\cdot\mathbf{k}/k)^2+\frac{i}{2mk^2}\sum_{\substack{i=1\\ i\neq l}}^{N}\mathbf{k}\cdot\frac{\partial\phi(r_{li},r_c)}{\partial \mathbf{r}_{li}} \times(e^{i\mathbf{k}\cdot\mathbf{r}_{li}}-1) \tag{2.8}$$

for the longitudinal momentum flux $(j=4)$, and

$$A_5^{(l)}(\mathbf{k})=\left[\tfrac{1}{2}m\mathbf{v}_l^2+\tfrac{1}{2}\sum_{\substack{i=1\\ i\neq l}}^{N}\phi(r_{li},r_c)\right]\mathbf{v}_l\cdot\mathbf{k}/k +\frac{i}{2k}\sum_{\substack{i=1\\ i\neq l}}^{N}\mathbf{v}_l\cdot\frac{\partial\phi(r_{li},r_c)}{\partial \mathbf{r}_{li}}(e^{i\mathbf{k}\cdot\mathbf{r}_{li}}-1) \tag{2.9}$$

for the longitudinal energy flux $(j=5)$.

These 25 correlation functions $F_{lj}(k,t)$ are symmetric in j and l, i.e.,

$$F_{jl}(k,t)=F_{lj}(k,t) \ , \tag{2.10}$$

and, using the fact that the velocity $\mathbf{v}_j(t)$ is the time derivative of the position $\mathbf{r}_j(t)$ of particle j at time t, they are related by $(l=1,\ldots,5)$

$$\begin{aligned} F_{2l}(k,t)&=\frac{i}{k}\frac{\partial}{\partial t}F_{1l}(k,t) \ , \\ F_{4l}(k,t)&=\frac{i}{k}\frac{\partial}{\partial t}F_{2l}(k,t) \ , \\ F_{5l}(k,t)&=\frac{i}{k}\frac{\partial}{\partial t}F_{3l}(k,t) \ , \end{aligned} \tag{2.11}$$

so that they can all be expressed in terms of $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ by at most fourfold time derivatives, or, if one includes $F_{22}(k,t)$ as well, to increase the accuracy, by at most threefold time derivatives. Equations (2.10) and (2.11) are obtained by using the conservation laws (A14) given in Appendix A and that L is an anti-Hermitian operator.

B. MD simulations

We determined the four correlation functions $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ in the following way. In our MD experiment we used periodic boundary conditions and we calculated $\mathbf{r}_j(t)$ and $\mathbf{v}_j(t)$ over a time range of $260\tau_\sigma$ with a time increment of $0.013\tau_\sigma$, where

$$\tau_\sigma=(m\sigma_{\mathrm{LJ}}^2/4k_BT)^{1/2}$$

is the average time a particle needs to traverse σ_{LJ} with thermal speed. Then, F_{11}, F_{22}, F_{13}, and F_{33} were obtained by time averaging 400 values of the quantities within angular brackets on the right-hand sides of Eq. (2.2) for 23 values of k and $0 \leq t \leq 2.6\tau_\sigma$. The errors in F_{11}, F_{22}, F_{13}, and F_{33} were estimated by repeating the simulation six times with different initial configurations. Thus over 9000 data points were obtained that will be analyzed below in terms of approximate eigenmodes of the operator L.

C. Initial values

Before this eigenmode analysis, we will discuss the initial values at $t=0$ of the 25 correlation functions $F_{jl}(k,t)$. These appear in the formal solution of Eq. (1.1),

$$F_{jl}(k,t)=[e^{-t\underline{H}(k)}\underline{V}(k)]_{jl} \ . \tag{2.12}$$

Here $\underline{H}(k)$ is the 5×5 time-evolution matrix, with elements $H_{jl}(k)$, introduced in Eq. (1.1) and $\underline{V}(k)$ is the 5×5 initial-value matrix, with elements $V_{jl}(k)$ given by the initial values of the $F_{jl}(k,t)$, i.e., by the equal time-correlation functions

$$V_{jl}(k)=F_{jl}(k,0)=\langle [a_j(\mathbf{k})]^* a_l(\mathbf{k})\rangle \ . \tag{2.13}$$

We determined the initial-value matrix $\underline{V}(k)$ from the MD results for $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ for $t=0$ as follows. Using the fact that $V_{jl}(k)$ is symmetric in j and l [cf. Eq. (2.10)] and that $V_{jl}(k)=0$ when j refers to a microscopic quantity which is even in the microscopic velocity (i.e., $j=1,3,4$) and l refers to a microscopic quantity which is odd (i.e., $l=2,5$) in the microscopic velocity, one has that $\underline{V}(k)$ is of the form

$$\underline{V}(k)=\begin{bmatrix} V_{11}(k) & 0 & V_{13}(k) & V_{14}(k) & 0 \\ 0 & V_{22}(k) & 0 & 0 & V_{25}(k) \\ V_{13}(k) & 0 & V_{33}(k) & V_{34}(k) & 0 \\ V_{14}(k) & 0 & V_{34}(k) & V_{44}(k) & 0 \\ 0 & V_{25}(k) & 0 & 0 & V_{55}(k) \end{bmatrix} . \tag{2.14}$$

The nine nonvanishing elements of $\underline{V}(k)$ can be expressed in terms of six independent functions, four of which are generalized k-dependent thermodynamic functions, known from the theory of critical phenomena.[2,21,23] Thus

$$\begin{aligned} &V_{11}(k)=S(k) \ , \\ &V_{22}(k)=V_{14}(k)=\frac{k_BT}{m} \ , \\ &V_{13}(k)=k_BT^2[h(k)S(k)-\alpha(k)] \ , \\ &V_{33}(k)=[\,k_BTc_p(k)+h(k)^2S(k) \\ &\qquad\qquad -2k_BT^2\alpha(k)h(k)] \ , \\ &V_{34}(k)=V_{25}(k)=\frac{k_BT}{m}h(k) \ , \\ &V_{44}(k)=-\frac{1}{k^2}\lim_{t\to 0}\frac{\partial^2}{\partial t^2}F_{22}(k,t) \ , \\ &V_{55}(k)=-\frac{1}{k^2}\lim_{t\to 0}\frac{\partial^2}{\partial t^2}F_{33}(k,t) \ . \end{aligned} \tag{2.15}$$

Here $S(k)=F_{11}(k,0)$ is the static structure factor,

$$h(k)=-\frac{m}{k_BT^2k^2}\lim_{t\to 0}\frac{\partial^2}{\partial t^2}F_{13}(k,t) \tag{2.16}$$

is the generalized enthalpy per particle, $\alpha(k)$ is the generalized thermal expansion coefficient, and $c_p(k)$ is the generalized specific heat at constant pressure per particle. For later we will need two more generalized thermodynamic quantities that are not independent of the preceding:

$$\begin{aligned} c_v(k)&=[V_{33}(k)-V_{13}^2(k)/V_{11}(k)]/k_BT^2 \\ &=c_p(k)-k_BT^2\alpha(k)^2/S(k) \end{aligned} \tag{2.17}$$

is the generalized specific heat at constant volume per particle and

$$\gamma(k)=c_p(k)/c_v(k) \tag{2.18}$$

is the generalized ratio of the specific heats.

D. Correlation matrix

As shown in Appendix A, the 5×5 correlation matrix $\underline{H}(k)$ in Eqs. (1.1) and (2.12) is asymmetric. It contains, in addition to three generalized k-dependent transport coefficients, the six independent functions of k that occur in $V(k)$, i.e., a total of nine functions of k. However, for the eigenvalues of $\underline{H}(k)$ only the three k-dependent transport coefficients and four independent combinations of the $V_{jl}(k)$, i.e., seven independent functions of k, are relevant. This reduction can be achieved by introducing five k-dependent orthonormal linear combinations $b_j(\mathbf{k})$ of the five microscopic quantities $a_j(\mathbf{k})$, i.e.,

$$b_j(\mathbf{k})=\sum_{l=1}^{5} U_{jl}(k)a_l(\mathbf{k}) \ , \tag{2.19}$$

which satisfy

$$\langle [b_j(\mathbf{k})]^* b_l(\mathbf{k})\rangle=\delta_{jl} \ . \tag{2.20}$$

The 5×5 transformation matrix $\underline{U}(k)$ with elements $U_{kl}(k)$ is related to $\underline{V}(k)$ by [cf. Eqs. (2.11), (2.19), and (2.20)]

$$\underline{U}^T(k)\underline{U}(k)=\underline{V}^{-1}(k) \ , \tag{2.21}$$

where the elements of the transposed matrix $\underline{U}^T(k)$ of $\underline{U}(k)$ are given by $U_{jl}^T(k)=U_{lj}(k)$. In the literature, various sets of orthonormal variables $b_j(\mathbf{k})$ have been studied.[2,4,21–23] Here we consider, in particular, the set obtained by a successive orthogonalization of n, u, e, σ, and q:

$$\underline{U}(k)=\begin{bmatrix} U_{11}(k) & 0 & 0 & 0 & 0 \\ 0 & U_{22}(k) & 0 & 0 & 0 \\ U_{31}(k) & 0 & U_{33}(k) & 0 & 0 \\ U_{41}(k) & 0 & U_{43}(k) & U_{44}(k) & 0 \\ 0 & U_{52}(k) & 0 & 0 & U_{55}(k) \end{bmatrix} , \tag{2.22}$$

where the matrix elements of $\underline{U}(k)$ are given by

$$
\begin{aligned}
&U_{11}(k)=1/\sqrt{S}(k)\ ,\\
&U_{22}(k)=(m/k_BT)^{1/2}\ ,\\
&U_{33}(k)=[k_BT^2c_v(k)]^{-1/2}\ ,\\
&U_{31}(k)=U_{33}(k)\left[\frac{k_BT^2\alpha(k)}{S(k)}-h(k)\right]\ ,\\
&U_{44}(k)=\left[V_{44}(k)-\left[\frac{k_BT}{m}\right]^2\frac{\gamma(k)}{S(k)}\right]^{-1/2}\ ,\\
&U_{43}(k)=-U_{44}(k)\frac{k_BT\alpha(k)}{mS(k)c_v(k)}\ ,\\
&U_{41}(k)=-U_{44}(k)\frac{k_BT[c_p(k)-\alpha(k)h(k)]}{mS(k)c_v(k)}\ ,\\
&U_{55}(k)=\left[V_{55}(k)-\frac{k_BT}{m}h(k)^2\right]^{-1/2}\ ,\\
&U_{52}(k)=-U_{55}(k)h(k)\ .
\end{aligned}
\tag{2.23}
$$

Then the $b_j(\mathbf{k})$ can be identified with the five orthonormal microscopic quantities: number density $(j=1)$, longitudinal velocity $(j=2)$, temperature $(j=3)$, longitudinal momentum flux $(j=4)$, and longitudinal heat flux $(j=5)$. Equations (2.12) for the $F_{jl}(k,t)$ can now be written in the form [cf. Eqs. (2.12) and (2.21)]

$$F_{jl}(k,t)=[\underline{U}^{-1}(k)e^{-t\overline{\underline{H}}(k)}(\underline{U}^T)^{-1}(k)]_{jl}\ , \tag{2.24}$$

where [cf. Eq. (2.21)]

$$\underline{U}^{-1}(k)=\underline{V}(k)\underline{U}^T(k) \tag{2.25}$$

and

$$\overline{\underline{H}}(k)=\underline{U}(k)\underline{H}(k)\underline{U}^{-1}(k)\ , \tag{2.26}$$

with (cf. Appendix A)

$$\overline{\underline{H}}(k)=\begin{bmatrix} 0 & if_{un}(k) & 0 & 0 & 0\\ if_{un}(k) & 0 & if_{uT}(k) & if_{u\sigma}(k) & 0\\ 0 & if_{uT}(k) & 0 & 0 & if_{Tq}(k)\\ 0 & if_{u\sigma}(k) & 0 & z_\sigma(k) & iz_{q\sigma}(k)\\ 0 & 0 & if_{Tq}(k) & iz_{q\sigma}(k) & z_q(k)\end{bmatrix}\ . \tag{2.27}$$

Here

$$
\begin{aligned}
&f_{un}(k)=\left[\frac{k_BT}{mS(k)}\right]^{1/2}k\ ,\\
&f_{uT}(k)=\left[\frac{k_BT[\gamma(k)-1]}{mS(k)}\right]^{1/2}k\ ,\\
&f_{u\sigma}(k)=\left[\frac{m^2S(k)V_{44}(k)-k_B^2T^2\gamma(k)}{mk_BTS(k)}\right]^{1/2}k\ ,\\
&f_{Tq}(k)=\left[\frac{mV_{55}(k)-k_BTh(k)^2}{mk_BT^2c_v(k)}\right]^{1/2}k
\end{aligned}
\tag{2.28}
$$

and explicit formal expressions for the three transport coefficients $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$ are given in Appendix A.

We refer to the four $f_{jl}(k)$ in $\overline{\underline{H}}(k)$ as "elastic forces," since when the dissipative forces, i.e., the three transport coefficients in $\overline{\underline{H}}(k)$, are set equal to zero, $\overline{\underline{H}}(k)$ is an anti-Hermitian matrix, whose eigenvalues are purely imaginary, so that the eigenmodes of $\exp[-t\overline{\underline{H}}(k)]$ are purely oscillatory in time and no dissipation occurs. With the three transport coefficients included, $\overline{\underline{H}}(k)$ is a symmetric (non-Hermitian) matrix with real and pairs of complex-conjugate eigenvalues, so that dissipation occurs. The behavior of the eigenmodes of $\overline{\underline{H}}(k)$ will be determined by the interplay of elastic and dissipative forces: when the former dominate the behavior will be oscillatory, when the latter dominate it will become overdamped.

We determined the correlation matrix $\underline{H}(k)$ of Eq. (1.1) from the MD $F_{jl}(k,t)$ using the eigenmodes of $\overline{\underline{H}}(k)$. These are defined by

$$\overline{\underline{H}}(k)\psi^{(i)}(k)=z_i(k)\psi^{(i)}(k)\quad(i=1,\dots,5)\ , \tag{2.29}$$

where $z_i(k)$ is an eigenvalue and $\psi^{(i)}(k)$ is the corresponding eigenvector, with components $\psi_l^{(i)}(k)$ $(l=1,\dots,5)$.

The eigenvectors satisfy, for all k, the orthonormality condition

$$\sum_{l=1}^{5}\psi_l^{(i)}(k)\psi_l^{(j)}(k)=\delta_{ij}\ , \tag{2.30}$$

so that the matrix elements of $\overline{\underline{H}}(k)$ are given by

$$\overline{H}_{jl}(k)=\sum_{i=1}^{5}z_i(k)\psi_j^{(i)}(k)\psi_l^{(i)}(k)\ , \tag{2.31}$$

and those of $e^{-t\overline{\underline{H}}(k)}$ by

$$[e^{-t\overline{\underline{H}}(k)}]_{jl}=\sum_{i=1}^{5}e^{-z_i(k)t}\psi_j^{(i)}(k)\psi_l^{(i)}(k)\ . \tag{2.32}$$

Then the $F_{jl}(k,t)$ can be expressed in terms of the eigenmodes of $\overline{\underline{H}}(k)$ as a sum of five exponentials [cf. Eqs. (2.22) and (2.32)],

$$F_{jl}(k,t)=\sum_{i=1}^{5}A_{jl}^{(i)}(k)e^{-z_i(k)t}\ , \tag{2.33}$$

with the amplitudes $A_{jl}^{(i)}(k)$ given by

$$A_{jl}^{(i)}(k)=\sum_{j',l'=1}^{5}U_{jj'}^{-1}(k)\psi_{j'}^{(i)}(k)\psi_{l'}^{(i)}(k)(U^T)_{l'l}^{-1}(k)\ . \tag{2.34}$$

From a weighted least-squares-fitting procedure on the basis of Eqs. (2.33) and (2.34) and using Eq. (2.28) for $f_{un}(k)$, $f_{uT}(k)$, $f_{u\sigma}(k)$, and $f_{Tq}(k)$, we determined the three transport coefficients $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$ in $\overline{\underline{H}}(k)$ as those that gave the best fit to the four MD correlation functions $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ for all times t. The matrix elements of $\overline{\underline{H}}(k)$ did not change significantly if, to increase the accuracy, we also used $f_{uT}(k)$, $f_{u\sigma}(k)$, and $f_{Tq}(k)$ as adjustable parameters in this fitting procedure. In this way the correlation ma-

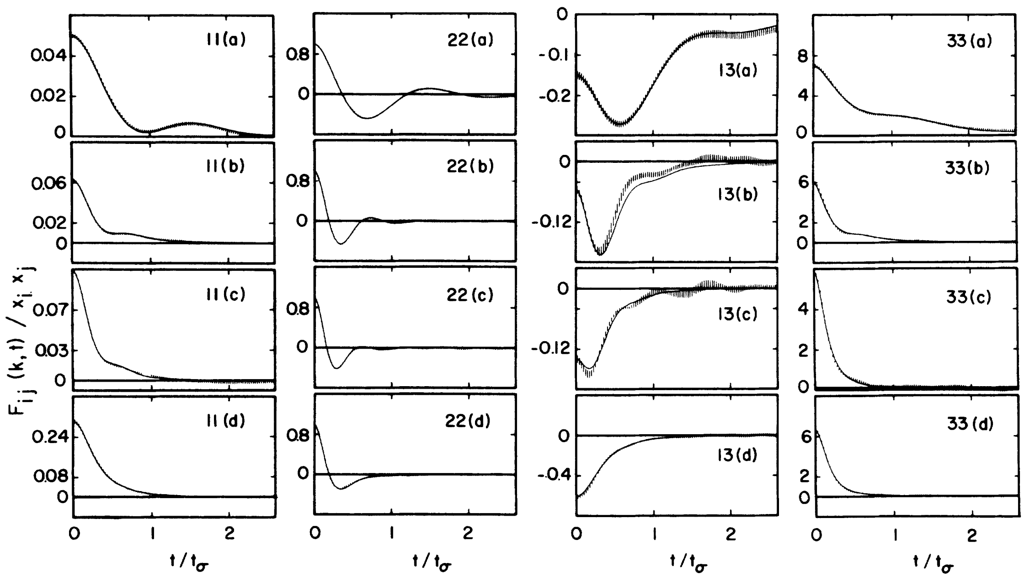

FIG. 1. MD results (vertical bars) for the reduced correlation functions $F_{jl}(k,t)/x_jx_l$ [cf. Eq. (2.2)] as functions of t/t_σ with $jl=11$, 22, 13, and 33 (as indicated) and $k\sigma_{\rm LJ}=1.24$ (a), 2.49 (b), 3.73 (c), and 4.98 (d) for a LJ fluid at $T^*=1.71$ and $n^*=0.845$, where $x_1=1$, $x_2=(k_BT/m)^{1/2}$, and $x_3=\varepsilon_{\rm LJ}$. Also shown are the best fits on the basis of Eq. (1.1) (solid curves).

trix $\underline{H}(k)$ in Eq. (1.1), which describes the time evolution of all 25 $F_{jl}(k,t)$ for all t, was obtained.

III. RESULTS

The MD results for $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$ at $k\sigma_{\rm LJ}=1.24$, 2.49, 3.73, and 4.98 are shown in Fig. 1 and at $k\sigma_{\rm LJ}=6.22$, 7.47, 8.71, and 9.95 in Fig. 2. We also show the best fits to the MD data with the five modes of $\underline{\bar{H}}(k)$, obtained from the least-squares-fitting procedure described in Sec. II D. We observe that the quality of the best fits is good, so that the 25 $F_{jl}(k,t)$ can indeed be described by Eq. (1.1).

The generalized thermodynamic quantities $S(k)$, $h(k)$, $\alpha(k)$, $c_v(k)$, and $\gamma(k)$ are shown in Figs. 3(a)–3(e), respectively, as functions of $k\sigma_{\rm LJ}$ and we plot [cf. Eq. (2.28)] the elastic forces $f_{un}(k)$ and $f_{u\sigma}(k)$ in Fig. 4(a) and $f_{uT}(k)$ and $f_{Tq}(k)$ in Fig. 4(b). In addition, the three transport

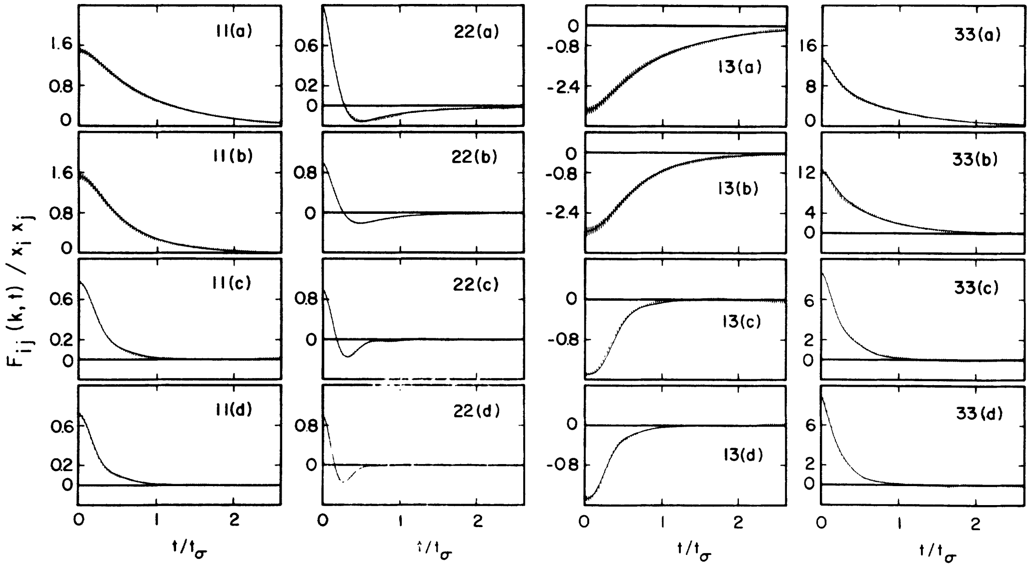

FIG. 2. MD results (vertical bars) for $F_{jl}(k,t)/x_jx_l$ as functions of t/t_σ with $jl=11$, 22, 13, and 33 and $k\sigma_{\rm LJ}=6.22$ (a), 7.47 (b), 8.71 (c), and 9.95 (d); the best fits (solid curves), as in Fig. 1.

coefficients $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$ are displayed in Fig. 4(c) as functions of $k\sigma_{\mathrm{LJ}}$. Thus all quantities which determine the initial value matrix $\underline{V}(k)$ [cf. Eq. (2.13)], the transformation matrix $\underline{U}(k)$ [cf. Eq. (2.22)], and the correlation matrix $\underline{\bar{H}}(k)$ [cf. Eq. (2.27)] are displayed in Figs. 3 and 4.

We shall now discuss the nature of the eigenmodes of $\underline{\bar{H}}(k)$ and their relevance for the correlation functions $F_{jl}(k,t)$, i.e., the dynamical processes relevant for the $F_{jl}(k,t)$. To that end, we consider first the behavior of the matrix $\underline{\bar{H}}(k)$ and its eigenmodes for small k, i.e., in the hydrodynamic regime.

A. Hydrodynamic modes

The matrix $\underline{\bar{H}}(k)$ has five eigenmodes, three of which reduce to the usual hydrodynamic modes for small k. In order to identify these three eigenmodes of $\underline{\bar{H}}(k)$ we first discuss the small-k behavior of the matrix $\underline{V}(k)$, which then allows us to obtain the small-k behavior of $\underline{\bar{H}}(k)$.

1. $\underline{V}(k)$

For $k \to 0$ all elements of the equal time-correlation matrix $\underline{V}(k)$ tend to finite limiting values that involve the bulk thermodynamic properties of the fluid [cf. Eqs. (2.15) and (2.16)],[22]

$$\begin{aligned}
&S(0)=nk_BT\kappa_T=-nk_BT(\partial V/\partial p)_T/V\ ,\\
&h(0)=h=(E+pV)/N\ ,\\
&\alpha(0)=\alpha=(\partial V/\partial T)_p/V\ ,\\
&c_v(0)=c_v=(\partial E/\partial T)_v/N\ ,\\
&c_p(0)=c_p=T(\partial S/\partial T)_p/N\ ,\\
&\gamma(0)=\gamma=c_p/c_v\ ,
\end{aligned} \tag{3.1}$$

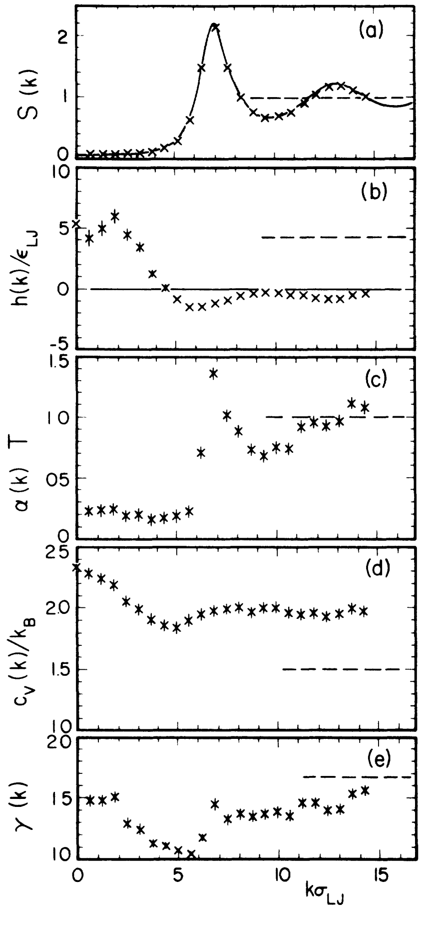

FIG. 3. (a) Static structure factor $S(k)$, (b) reduced enthalpy per particle $h(k)/\varepsilon_{\mathrm{LJ}}$, (c) reduced linear-expansion coefficient $\alpha(k)T$, (d) reduced specific heat per particle at constant volume $c_v(k)/k_B$, and (e) the ratio of specific heats $\gamma(k)=c_p(k)/c_v(k)$ as functions of $k\sigma_{\mathrm{LJ}}$ for a fluid at $T^*=1.71$ and $n^*=0.845$ (crosses). Also shown are the corresponding ideal-gas values (dashed curves) and in (a) the $S(k)$ of an equivalent fluid of hard spheres with diameter $\sigma=0.981\sigma_{\mathrm{LJ}}$, which fits the $S(k)$ of the LJ fluid best (solid curve).

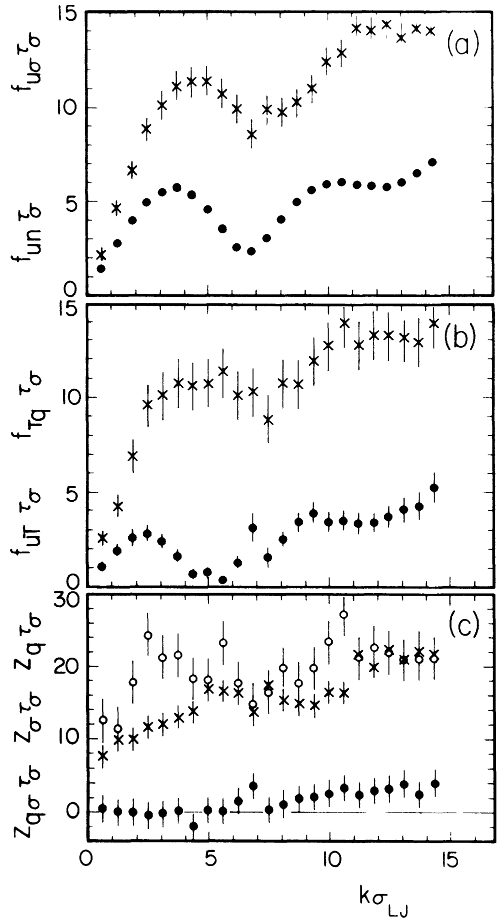

FIG. 4. Reduced matrix elements of the correlation matrix $\underline{\bar{H}}(k)$ [cf. Eq. (2.27)] for a LJ fluid at $T^*=1.71$ and $n^*=0.845$ as functions of $k\sigma_{\mathrm{LJ}}$. Shown are $f_{un}t_\sigma$ [closed circles in (a)], $f_{u\sigma}t_\sigma$ [crosses in (a)], $f_{uT}t_\sigma$ [closed circles in (b)], $f_{Tq}t_\sigma$ [crosses in (b)], $z_\sigma t_\sigma$ [crosses in (c)], $z_q t_\sigma$ [open circles in (c)], and $z_{q\sigma}t_\sigma$ [closed circles in (c)].

where κ_T is the isothermal compressibility, h is the enthalpy per particle, α is the volume expansion coefficient, c_v and c_p are the specific heat per particle at constant volume and pressure, respectively, γ is the ratio of specific heats, p is the pressure, V is the volume, and E and S are the total energy and entropy of the fluid, respectively. For the $k=0$ values of the two matrix elements $V_{44}(k)$ and $V_{55}(k)$, no expressions in terms of thermodynamic quantities exist.

2. $\underline{\underline{H}}(k)$

For $k \rightarrow 0$ the four elastic forces in $\underline{\underline{H}}(k)$ depend linearly on k, i.e., [cf. Eq. (2.28)],

$$\begin{aligned} f_{un}(k) &= \left[\frac{1}{\gamma}\right]^{1/2} ck + O(k^3) , \\ f_{uT}(k) &= \left[\frac{\gamma-1}{\gamma}\right]^{1/2} ck + O(k^3) , \end{aligned} \tag{3.2}$$

where $c = [k_B T\gamma/mS(0)]^{1/2}$ is the adiabatic speed of sound and

$$\begin{aligned} f_{u\sigma}(k) &= v_{u\sigma}k + O(k^3) , \\ f_{Tq}(k) &= v_{Tq}k + O(k^3) , \end{aligned} \tag{3.3}$$

with the velocities $v_{u\sigma}$ and v_{Tq} given by

$$\begin{aligned} v_{u\sigma} &= \left[\frac{m^2 S(0)V_{44}(0) - k_B^2 T^2 \gamma}{mk_B TS(0)}\right]^{1/2} , \\ v_{Tq} &= \left[\frac{mV_{55}(0) - k_B Th^2}{mk_B T^2 c_v}\right]^{1/2} . \end{aligned} \tag{3.4}$$

In addition to these elastic forces, there are three transport coefficients in $\underline{\underline{H}}(k)$, of which $z_{q\sigma}(k)$ tends to zero linearly in k,[2] while $z_\sigma(k)$ and $z_q(k)$ approach finite values, $z_\sigma(0)$ and $z_q(0)$, respectively. All of the quantities in Eqs. (3.1)–(3.4) as well as $z_\sigma(0)$ and $z_q(0)$ are determined from the MD results by extrapolation of the matrices $\underline{V}(k)$ and $\underline{\underline{H}}(k)$ computed at finite values of k, to $k=0$. They are given in Table I.

TABLE I. Static (thermodynamic) and dynamic (transport) properties of a LJ fluid at reduced density $n\sigma_{\mathrm{LJ}}^3 = 0.845$ and reduced temperature $T^* = 1.71$.

Static and dynamic properties	Experimental results
$S(0)$	0.048 ± 0.001
αT	0.25 ± 0.02
c_v/k_B	2.33 ± 0.02
γ	1.55 ± 0.10
$E/N\varepsilon_{\mathrm{LJ}}$	2.11 ± 0.02
$p\sigma_{\mathrm{LJ}}^3/\varepsilon_{\mathrm{LJ}}$	6.25 ± 0.06
$h/\varepsilon_{\mathrm{LJ}}$	5.28 ± 0.05
$c\tau_\sigma/\sigma_{\mathrm{LJ}}$	2.85 ± 0.05
$v_{u\sigma}\tau_\sigma/\sigma_{\mathrm{LJ}}$	3.7 ± 0.2
$v_{Tq}\tau_\sigma/\sigma_{\mathrm{LJ}}$	3.9 ± 0.2
$z_\sigma(0)\tau_\sigma$	8 ± 2
$z_q(0)\tau_\sigma$	11 ± 2
$D_T\tau_\sigma/\sigma_{\mathrm{LJ}}^2$	0.90 ± 0.15
$\phi\tau_\sigma/\sigma_{\mathrm{LJ}}^2$	1.7 ± 0.3
$\Gamma\tau_\sigma/\sigma_{\mathrm{LJ}}^2$	1.1 ± 0.2

3. *Eigenmodes*

The five eigenmodes of the 5×5 matrix $\underline{\underline{H}}(k)$ [cf. Eq. (2.29)] for $k \rightarrow 0$ are obtained by using standard perturbation theory around $\underline{\underline{H}}(0)$ with k as a small parameter. We omit the details of the derivative, since it is straightforward and we only quote the final results for the eigenvalues $z_i(k)$ and eigenvalues $\psi^{(i)}(k)$ of $\underline{\underline{H}}(k)$. There are three hydrodynamic modes, whose eigenvalues go to zero, and two kinetic modes, whose eigenvalues go to a nonzero value, when $k \rightarrow 0$. The three hydrodynamic modes are the following.

(a) A heat mode ($i=h$) with eigenvalue

$$z_h(k) = D_T k^2 + O(k^4) \tag{3.5}$$

and eigenvector

$$\psi^{(h)}(k) = ([(\gamma-1)/\gamma]^{1/2}, 0, -\gamma^{-1/2}, 0, 0) + O(k) , \tag{3.6}$$

where D_T is the thermal diffusivity,

$$D_T = \frac{v_{Tq}^2}{\gamma z_q(0)} = \frac{\lambda}{nmc_p} , \tag{3.7}$$

and λ is the thermal conductivity (see Appendix B).

(b) Two sound modes ($i=\pm$) with eigenvalues

$$z_\pm(k) = \pm i\omega_s(k) + z_s(k) , \tag{3.8}$$

where

$$\omega_s(k) = ck + O(k^3) \tag{3.9}$$

is the sound propagation and

$$z_s(k) = \Gamma k^2 + O(k^4) \tag{3.10}$$

is the sound damping and corresponding eigenvectors

$$\psi^{(\pm)}(k) = 2^{-1/2}(\gamma^{-1/2}, \pm 1, [(\gamma-1)/\gamma]^{1/2}, 0, 0) + O(k) . \tag{3.11}$$

In Eq. (3.10) Γ is the sound-damping coefficient,

$$\Gamma = \tfrac{1}{2}(\gamma-1)D_T + \tfrac{1}{2}\phi , \tag{3.12}$$

where

$$\phi = \frac{v_{u\sigma}^2}{z_\sigma(0)} = (\tfrac{4}{3}\eta + \zeta)/nm \tag{3.13}$$

is the longitudinal viscosity, where η and ζ are the shear and bulk viscosities, respectively (see Appendix B).

The two kinetic modes ($i=4,5$) are given by

$$\begin{aligned} z_4(k) &= z_\sigma(0) + O(k^2) , \\ \psi^{(4)}(k) &= (0,0,0,1,0) + O(k) \end{aligned} \tag{3.14}$$

and

$$z_5(k)=z_q(0)+O(k^2)\ ,$$
$$\psi^{(5)}(k)=(0,0,0,0,1)+O(k)\ , \tag{3.15}$$

which have no hydrodynamic analogous and give the rate of decay of the momentum and heat flux autocorrelation functions, respectively. We note that the values of D_T [cf. Eq. (3.7)], ϕ [cf. Eq. (3.13)], and Γ [cf. Eq. (3.12)] are given in Table I.

Thus all eigenvalues are real, except for the two sound modes for which the eigenvalues are each other's complex conjugate [cf. Eq. (3.8)]. We further remark that the three hydrodynamic heat- and sound-mode eigenfunctions have no kinetic components (i.e., $\psi_j^{(i)}(k)=0$ for $j=4$ or 5, $i=h$ [cf. Eq. (3.6)], and $i=\pm$ [cf. Eq. (3.11)]). As a consequence, the nine hydrodynamic correlation functions $F_{jl}(k,t)$ in Eq. (2.41), with j or $l=1,2,3$, are for $k\to 0$ determined by the heat and sound modes alone, i.e., for $k\to 0$,

$$F_{jl}(k,t)=\sum_{i=h,\pm} A_{jl}^{(i)}(k)e^{-z_i(k)t}\ , \tag{3.16}$$

and described by a sum of the same three exponentials that would occur if conventional hydrodynamics were used.

In particular, for the intermediate scattering function $F(k,t)=F_{11}(k,t)$, one has for the amplitudes $A_{11}^{(h)}(0)=S(0)(\gamma-1)/\gamma$ and $A_{11}^{(+)}(0)=A_{11}^{(-)}(0)=S(0)/(2\gamma)$ [cf. Eqs. (3.16), (2.15), (3.6), and (3.11)]. Thus the dynamic structure factor

$$S(k,\omega)=\frac{1}{\pi}\mathrm{Re}\sum_{i=h,\pm}\frac{A_{11}^{(i)}(k)}{i\omega+z_i(k)} \tag{3.17}$$

is given by the Landau-Placzek formula, containing a sum of three Lorentzians,[1] i.e., a central Rayleigh line due to the heat mode and two Brillouin lines centered around $\pm\omega_s(k)$ due to the two sound modes of the fluid.

This is in agreement with the MD results for $F_{11}(k,t)$, $F_{22}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$, which can indeed all be described by Eq. (3.16) for the smallest $k\sigma_{\mathrm{LJ}}$ value used, i.e., for $k\sigma_{\mathrm{LJ}}=0.62$. In fact, hydrodynamics is valid for $k\sigma_{\mathrm{LJ}}<1$. However, for $k\sigma_{\mathrm{LJ}}>1$, the hydrodynamic description fails and all five k-dependent eigenmodes of $\underline{\underline{H}}(k)$ need to be used [cf. Eq. (2.33)] to represent the MD results simultaneously (cf. Figs. 1 and 2).

B. Extended hydrodynamic and kinetic eigenmodes of $\underline{\underline{H}}(k)$

For values of $k\sigma_{\mathrm{LJ}}>1$, three of the five eigenmodes of $\underline{\underline{H}}_{ij}(k)$ are direct extensions of the heat and sound modes at small k, while two are extensions of the two kinetic modes at small k. We note that the three extended hydrodynamic modes are similar to the hydrodynamic modes in that the extended heat-mode eigenvalue $z_h(k)$ is real for all k [cf. Fig. 5(a)], while the extended sound-mode eigenvalues $z_\pm(k)$ are complex functions of $k\sigma_{\mathrm{LJ}}$, with $z_s(k)=\mathrm{Re}z_\pm(k)$ and $\omega_s(k)=|\mathrm{Im}z_\pm(k)|$ [cf. Figs. 5(b) and 5(c)].

The two extended kinetic modes, on the other hand, do not remain real for all k as they were for small k. In Fig. 6 we show the extension of the kinetic eigenvalues $z_4(k)$ and $z_5(k)$ from their (real) values for small k [cf. Eqs. (3.14) and (3.15)] to larger values of k. We observe in Fig. 6(a) that $z_4(k)$ and $z_5(k)$ are real up to $k\sigma_{\mathrm{LJ}}=3.5$ as well as in the regions $5.5<k\sigma_{\mathrm{LJ}}<6.0$ and $10.5<k\sigma_{\mathrm{LJ}}<11$. For the remaining values of $k\sigma_{\mathrm{LJ}}$, up to $k\sigma_{\mathrm{LJ}}=15$, they are complex and each other's complex conjugate.

We note that, although for $k\sigma_{\mathrm{LJ}}>1$ the MD results for all $F_{jl}(k,t)$ can only consistently be described by five exponentials, $F_{11}(k,t)$—or equivalently $S(k,\omega)$—alone can, within the accuracy of the MD results, still be described in terms of only three (extended) hydrodynamic eigenmodes of $\underline{\underline{H}}(k)$. This is consistent with earlier fits of

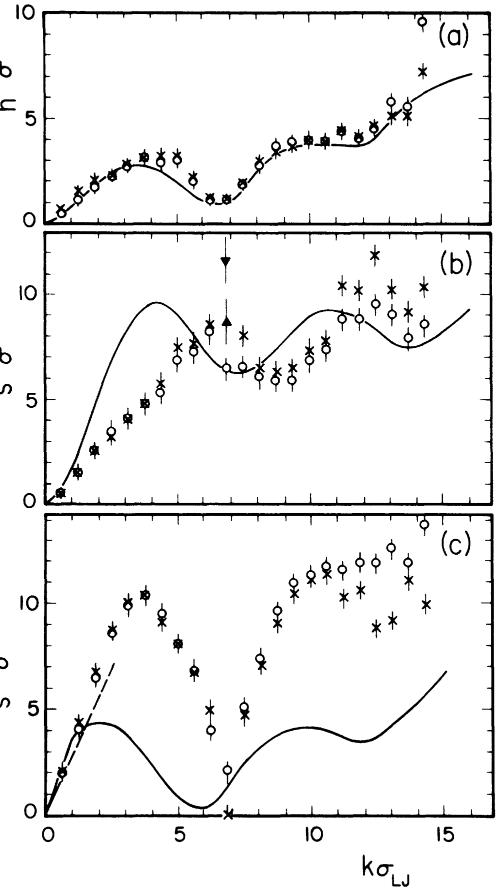

FIG. 5. Reduced-heat mode eigenvalue $z_h t_\sigma$, sound damping $z_s t_\sigma$, and sound dispersion $\omega_s t_\sigma$ [open circles in (a), (b), and (c), respectively] obtained from $\underline{\underline{H}}(k)$ for a LJ fluid at $T^*=1.71$ and $n^*=0.845$ as functions of $k\sigma_{\mathrm{LJ}}$. The $z_h t_\sigma$, $z_s t_\sigma$, and $\omega_s t_\sigma$ obtained from a least-squares-fitting procedure applied to $F_{11}(k,t)$ and $F_{22}(k,t)$ alone (cf. Ref. 12) are shown as crosses in (a), (b), and (c), respectively. Note that z_s is double valued [triangles in (b)] when $\omega_s=0$. The dashed curve in (c) is the hydrodynamic sound dispersion ckt_σ (cf. Table I). Also shown are the $z_h t_\sigma$, $z_s t_\sigma$, and $\omega_s t_\sigma$ calculated from the revised Enskog theory (cf. Ref. 5) for a fluid of hard spheres at $n\sigma^3=0.80$ [solid curves in (a), (b), and (c), respectively].

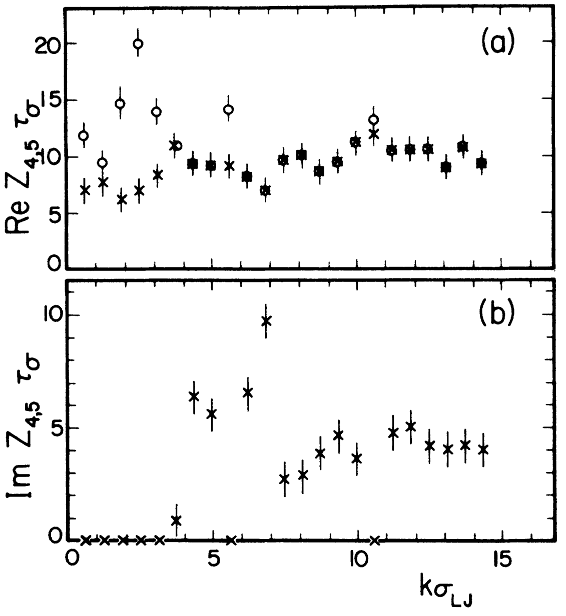

FIG. 6. Reduced eigenvalues $z_4 t_\sigma$ (crosses) and $z_5 t_\sigma$ (open circles) of $\underline{\bar{H}}(k)$ as functions of $k\sigma_{\mathrm{LJ}}$. The real parts are shown in (a) and the absolute values of the imaginary parts, which are equal, in (b).

$F_{11}(k,t)$ by three exponentials, as carried out for a LJ fluid^{12} and for liquid argon.^{14}

IV. DISCUSSION

We now discuss two earlier attempts to describe $S(k,\omega)$ by the three eigenmodes of a 3×3 matrix: the viscoelastic model^{6,7,8,19} and the hydrodynamic model.^{3,16} This is most conveniently and simply done on the basis of the five orthonormal microscopic quantities $b_j(\mathbf{k})$ introduced previously in Sec. II [cf. Eq. (2.19)], since the $b_j(\mathbf{k})$ contain for $j=3$ the microscopic temperature as an independent variable. Defining their correlation functions $G_{jl}(k,t)$ by

$$G_{jl}(k,t)=\langle [b_j(\mathbf{k})]^* e^{tL} b_l(\mathbf{k})\rangle , \tag{4.1}$$

the time evolution of the $G_{jl}(k,t)$ is given by the equations

$$\frac{\partial}{\partial t}G_{jl}(k,t)=-\sum_{i=1}^{5}\bar{H}_{jl}(k)G_{il}(k,t) , \tag{4.2}$$

so that $S(k,\omega)$ is given by

$$\begin{aligned} S(k,\omega)&=\frac{S(k)}{\pi}\mathrm{Re}\int_0^\infty dt\, e^{-i\omega t}G_{11}(k,t)\\ &=\frac{S(k)}{\pi}\mathrm{Re}[i\omega+\underline{\bar{H}}(k)]^{-1}_{11} . \end{aligned} \tag{4.3}$$

We first consider the viscoelastic theory.

A. Viscoelastic model

According to viscoelastic theory,^{6,7,8,19} the correlation functions $G_{jl}(k,t)$, with j or $l=1,2,4$, are for $k\sigma_{\mathrm{LJ}}>1$ in good approximation given by the functions $G^v_{jl}(k,t)$, which satisfy the viscoelastic equation

$$\frac{\partial}{\partial t}G^v_{jl}(k,t)=-\sum_{i=1,2,4}\bar{H}_{ji}(k)G^v_{il}(k,t) , \tag{4.4}$$

with j or $l=1,2,4$. Equation (4.4) follows from Eq. (4.2) when temperature fluctuations are neglected, i.e., when $\gamma(k)$ in $\underline{\bar{H}}(k)$ is replaced by 1. Then $f_{uT}(k)=0$ for all k [cf. Eq. (2.27)] and σ only couples with u, so that the cross transport coefficient $z_{q\sigma}(k)$ can be neglected. Then $\underline{\bar{H}}(k)$ separates into a 3×3 matrix with j or $l=1,2,4$ and a 2×2 matrix with j or $l=3,5$. Since for $S(k,\omega)$ only the 3×3 matrix is relevant, the viscoelastic prediction $S^v(k,\omega)$ for $S(k,\omega)$ reads [cf. Eqs. (2.27), (4.3), and (4.4)],

$$S^v(k,\omega)=\frac{S(k)}{\pi}\mathrm{Re}\frac{1}{i\omega+f_{un}(k)^2/[i\omega+k^2\phi^v(k,i\omega)]} , \tag{4.5}$$

where the generalized k- and ($z=i\omega$)-dependent longitudinal viscosity $\phi^v(k,i\omega)$ is given by

$$\phi^v(k,i\omega)=\frac{1}{k^2}\frac{f_{u\sigma}(k)^2}{i\omega+z_\sigma(k)} . \tag{4.6}$$

We note that $\lim_{k\to 0}\phi^v(k,0)=\phi$, with ϕ the longitudinal viscosity given by Eq. (3.13) [cf. Eq. (2.28)].

Thus $S^v(k,\omega)$ is given by a sum of three Lorentzians, which are determined by the three eigenmodes of the 3×3 matrix $\bar{H}_{ji}(k)$, with $j,i=1,2,4$, where the corresponding eigenfunctions are linear combinations of the density, velocity, and momentum flux.

Using our MD results for $f_{un}(k)$, $f_{u\sigma}(k)$, and $z_\sigma(k)$, $S^v(k,\omega)$ can be computed from Eqs. (4.5) and (4.6) and is shown in Fig. 7 as a function of $\omega\tau_\sigma$ for 16 values of $k\sigma_{\mathrm{LJ}}$. In the same figure the $S(k,\omega)$, derived from a best fit to the MD results from the $F_{jl}(k,t)$, is also shown as a function of $\omega\tau_\sigma$, where [cf. Eqs. (2.31) and (4.3)]

$$S(k,\omega)=\frac{S(k)}{\pi}\mathrm{Re}\sum_{i=1}^{5}\frac{[\psi_1^{(i)}(k)]^2}{i\omega+z_i(k)} . \tag{4.7}$$

We note that $S(k,\omega)$ is badly represented by $S^v(k,\omega)$ in the hydrodynamic regime, i.e., for $k\sigma_{\mathrm{LJ}}<1$. This is due to the fact that the viscoelastic equations [Eq. (4.4)] do not reduce to the usual hydrodynamic equations for $k\to 0^{7,19}$ since temperature fluctuations cannot be neglected then.

For $k\sigma_{\mathrm{LJ}}>1$, where the viscoelastic theory is assumed to be valid,^{7,19} we observe the following in Fig. 7. $S(k,\omega)$ is poorly described by $S^v(k,\omega)$ for $k\sigma_{\mathrm{LJ}}<5$ and $k\sigma_{\mathrm{LJ}}>7$ and very well described by $S^v(k,\omega)$ for $5<k\sigma_{\mathrm{LJ}}<7$. We note, however, that for $k\sigma_{\mathrm{LJ}}$ around 6, $S(k,\omega)$ is not only well represented by the viscoelastic theory but also by the hydrodynamic theory. The reason for this will be discussed in Sec. IV C.

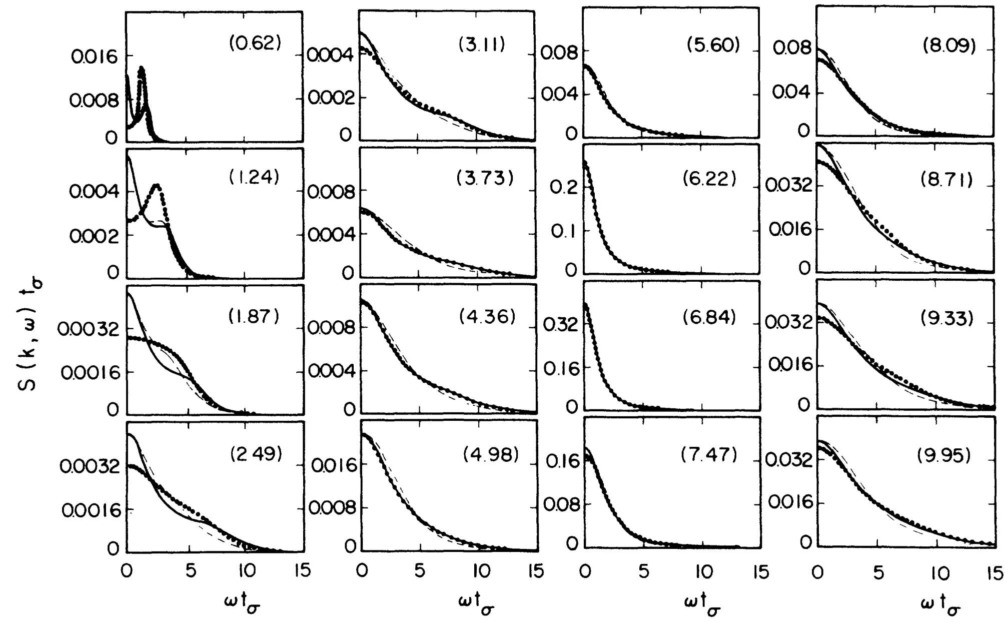

FIG. 7. Reduced dynamic structure factors $S(k,\omega)t_\sigma$ (solid curves) for a LJ fluid at $T^*=1.71$ and $n^*=0.845$ as functions of ωt_σ for 16 values of the reduced wave number $k\sigma_{\rm LJ}$, indicated by their values $(k\sigma_{\rm LJ})$ in each figure part. Also shown are the $S^v(k,\omega)t_\sigma$ [cf. Eq. (4.5)] (dotted curves) and the $S^h(k,\omega)t_\sigma$ [cf. Eq. (4.11)] (dashed curves). For $k\sigma_{\rm LJ}=5.60$, 6.22, 6.84, and 7.47 the three curves are indistinguishable.

B. Hydrodynamic model

To obtain the hydrodynamic interpretation of $S(k,\omega)$, we rewrite Eq. (4.2) for the 25 $G_{jl}(k,t)$ of the LJ fluid in Laplace language and eliminate all correlation functions with j or $l=4,5$. A similar procedure has been used to introduce the effective modes in a hard-sphere fluid.[5] The five equations (4.2) are then reduced to three equations,

$$z\tilde{G}_{jl}(k,z)=-\sum_{i=1}^{3}\underline{\bar{H}}^{(h)}_{ji}(k,z)\tilde{G}_{il}(k,z)+\delta_{jl}\ , \qquad (4.8)$$

where the $\tilde{G}_{jl}(k,z)$ are the Laplace transforms of the $G_{jl}(k,t)$ [cf. Eq. (A2)], with $j,l=1,2,3$, and where the generalized k- and z-dependent 3×3 hydrodynamic matrix $\underline{\bar{H}}^{(h)}$ is given by

$$\underline{\bar{H}}^{(h)}(k,z)=\begin{bmatrix} 0 & if_{un}(k) & 0 \\ if_{un}(k) & z_\phi(k,z) & if_{uT}(k)+i\Delta(k,z) \\ 0 & if_{uT}(k)+i\Delta(k,z) & z_T(k,z)\end{bmatrix}\ , \qquad (4.9)$$

where the generalized k- and z-dependent transport quantities $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$ in $\underline{\bar{H}}^{(h)}(k,z)$ given by

$$z_\phi(k,z)=\frac{f_{u\sigma}(k)^2}{z+z_\sigma(k)+z_{q\sigma}(k)^2/[z+z_q(k)]}\ , \qquad (4.10a)$$

$$z_T(k,z)=\frac{f_{Tq}(k)^2}{z+z_q(k)+z_{q\sigma}(k)^2/[z+z_\sigma(k)]}\ , \qquad (4.10b)$$

$$\Delta(k,z)=\frac{-f_{u\sigma}(k)f_{Tq}(k)z_{q\sigma}(k)}{[z+z_q(k)][z+z_\sigma(k)]+z_{q\sigma}(k)^2}\ , \qquad (4.10c)$$

respectively.

The hydrodynamic matrix $\underline{\bar{H}}^{(h)}(k,z)$ can also be expressed in terms of the generalized longitudinal viscosity $\phi(k,z)$ defined by

$$z_\phi(k,z)=k^2\phi(k,z)\ ,$$

the generalized thermal conductivity $\lambda(k,z)$ defined by

$$z_T(k,z)=k^2\lambda(k,z)/mnc_v(k)\ ,$$

and the generalized ratio of specific heats $\gamma(k,z)$ defined by[3]

$$\gamma(k,z)=1+mS(k)[f_{uT}(k)+\Delta(k,z)]^2/(k_BTk^2) .$$

In the hydrodynamic model one assumes that the z dependence of all three generalized transport coefficients $\phi(k,z)$, $\lambda(k,z)$, and $\gamma(k,z)$ is irrelevant, so that $\underline{\underline{H}}^{(h)}(k,z)\equiv\underline{\underline{H}}^{(h)}(k,z=0)=\underline{\underline{H}}^{(h)}(k)$. Then $S(k,\omega)$ is approximated by

$$S^h(k,\omega)=\frac{S(k)}{\pi}\text{Re}[i\omega+\underline{\underline{H}}^{(h)}(k)]_{11}^{-1} . \tag{4.11}$$

Thus $S^h(k,\omega)$ is given by a sum of three Lorentzians determined by the three eigenmodes of $\underline{\underline{H}}^{(h)}(k)$, where the corresponding eigenfunctions are linear combinations of the density, velocity, and temperature.

We show $S^h(k,\omega)$, using our MD results to determine $\underline{\underline{H}}^{(h)}(k)$ [cf. Eqs. (4.9) and (4.10)], in Fig. 7 as a function of $\omega\tau_\sigma$ for 16 values of $k\sigma_{\text{LJ}}$. We note that $S^h(k,\omega)$ agrees with $S(k,\omega)$ for $k\sigma_{\text{LJ}}<1$. This is due to the fact that $\underline{\underline{H}}(k)$ reduces for small k to the usual (Navier-Stokes) hydrodynamics matrix.[4] To see this, we note that $z_\phi(k,0)$, $z_T(k,0)$, and $\Delta(k,0)$ follow from the small-k behavior of the quantities on the right-hand side of Eq. (4.10): $f_{jl}(k)\sim z_{q\sigma}(k)\sim k$, $z_\sigma(k)\approx z_\sigma(0)$, and $z_q(k)\approx z_q(0)$, as discussed in Sec. III A. Thus, for small k, one has that $z_\phi(k,0)=\phi k^2$ [cf. Eqs. (4.10), (2.28), (3.3), and (3.13)], $z_T(k,0)=\gamma D_Tk^2$ [cf. Eqs. (4.10), (2.28), (3.3), and (3.7)], while $\Delta(k,0)\sim k^3$ can be neglected,[23] and $\underline{\underline{H}}^{(h)}(k)$ reduces to the usual hydrodynamic matrix.

As already mentioned in Sec. IV A, we see in Fig. 7 that $S^h(k,\omega)$ agrees with $S(k,\omega)$ for $5.6<k\sigma_{\text{LJ}}<7.5$. However, for $1<k\sigma_{\text{LJ}}<6$ and $k\sigma_{\text{LJ}}>7.5$, $S^h(k,\omega)$ represents $S(k,\omega)$ badly, which implies that momentum-flux and heat-flux fluctuations cannot be neglected for these values of k. Thus neither the viscoelastic nor the hydrodynamic model can describe $S(k,\omega)$ for the LJ fluid for all $k\sigma_{\text{LJ}}<15$.

C. Dominance of self-diffusion for $k\sigma\approx2\pi$

The reason that both viscoelastic theory and hydrodynamic theory represent $S(k,\omega)$ well around $k\sigma\approx6$ is that both contain the density fluctuation, which gives for $k\sigma\approx2\pi$ by far the most dominant contribution to $S(k,\omega)$. To see this, we eliminate in both theories all correlation functions in favor of the density correlation function G_{11} and neglect all time derivatives except that of G_{11}. In this way an equation is obtained for $G_{11}(k,t)$ alone which is of the form of a self-diffusion equation. For the viscoelastic model this equation reads [cf. Eq. (4.4)]

$$\frac{\partial}{\partial t}G_{11}^{v}(k,t)=-D_s^v(k)k^2G_{11}^{v}(k,t) , \tag{4.12a}$$

where $D_s^v(k)$ is a k-dependent self-diffusion coefficient given by

$$D_s^v(k)=\{f_{un}(k)/[kf_{u\sigma}(k)]\}^2z_\sigma(k) . \tag{4.12b}$$

In the hydrodynamic model this procedure, when applied to Eqs. (4.8) with $z=0$, leads to a similar equation,

$$\frac{\partial}{\partial t}G_{11}^{h}(k,t)=-D_s^h(k)k^2G_{11}^{h}(k,t) , \tag{4.13a}$$

with

$$D_s^h(k)=[f_{un}(k)/k]^2\{z_\phi(k,0)$$
$$+[f_{uT}(k)+\Delta(k,0)]^2/z_T(k,0)\}^{-1} .$$

We remark that Eqs. (4.13) would also result if the same procedure were applied to Eqs. (4.2).

In Fig. 8 the corresponding

$$S^\alpha(k,\omega)=(1/\pi)\text{Re}S(k)/[i\omega+D_s^\alpha(k)k^2] ,$$

with $\alpha=v$ and h, are computed with the $S(k,\omega)$ that is obtained from the best fit to the MD results and was already given in Fig. 7.

We see that for $k\sigma_{\text{LJ}}\approx2\pi$ both self-diffusion equations represent $S(k,\omega)$ very well. This implies, as has been noticed before for hard-sphere fluids,[24,25] that also for LJ fluids a self-diffusion process dominates the relaxation of density fluctuations when $k\sigma\approx6$, i.e., $k\sigma\approx2\pi$, where $S(k)$ has a sharp maximum.

We note that Eq. (4.12) as well as Eq. (4.13) each has one eigenmode, with eigenvalue $D_s^v(k)k^2$ or $D_s^h(k)k^2$, respectively, and eigenfunction 1, which represents the density. These eigenmodes effectively represent the dynamical processes in the fluid for k values around $k\sigma\approx2\pi$.

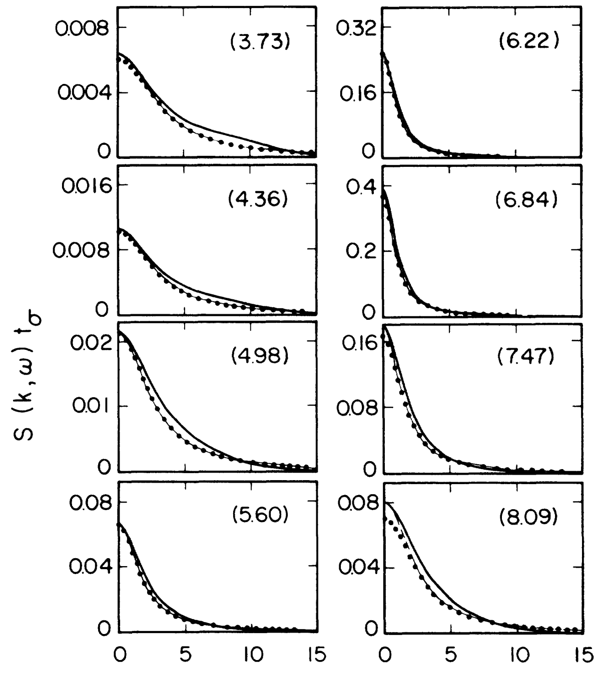

FIG. 8. Reduced dynamic structure factors $S(k,\omega)t_\sigma$ (solid curves) for a LJ fluid at $T^*=1.71$ and $n^*=0.845$ as functions of ωt_σ for eight values of $k\sigma_{\text{LJ}}$, as in Fig. 7. Also shown are the self-diffusion approximation to $S^v(k,\omega)t_\sigma$ [cf. Eq. (4.12)] (dotted curves) and the $S^h(k,\omega)t_\sigma$ [cf. Eq. (4.13)] (dashed curves). For $k\sigma_{\text{LJ}}=5.60-7.47$, the three curves are very close.

The question that arises is which of the five eigenmodes of the original G_{jl}, Eqs. (4.2), reduces to this self-diffusion eigenmode for k values around $k\sigma_{\rm LJ}=6$? As for hard spheres, this is the extended heat mode,[5,13,24,25] since $z_h(k)$ of Fig. 5(a) [or Eq. (2.29)] coincides with both $D_s^v(k)k^2$ and $D_s^h(k)k^2$ for the $k\sigma_{\rm LJ}$ values, $4 \le k\sigma_{\rm LJ} \le 8$, which contain $k\sigma_{\rm LJ}=2\pi$.

D. Comparison with a hard-sphere fluid

As already mentioned in the Introduction, Alley and Alder have shown[3] that for a hard-sphere fluid at a density comparable to that of our LJ fluid the hydrodynamic theory for $S(k,\omega)$, based on n, u, and T, is valid for all k, i.e., not only for $k\sigma_{hs}<1$ but for all $1<k\sigma_{hs}<15$. Thus for a dense hard-sphere fluid the z dependence of the 3×3 matrix $\underline{\underline{H}}^{(h)}(k,z)$ [cf. Eq. (4.9)] can be neglected and z can be replaced by $z=0$ for all k. The physical origin of this is the dominance of the instantaneous collisional transfer of momentum and energy in a hard-sphere fluid.[25] This would suggest that hard-sphere-like behavior, and consequently the hydrodynamic model, would be obtained for Lennard-Jones fluids at sufficiently high temperatures, because the steep repulsive part of the interaction potential (2.1) is similar to a hard-sphere repulsion. In terms of the eigenmodes of the fluids, this means that since the extended heat modes of the two fluids are very similar [cf. Fig. 5(a)], the extended sound modes of the LJ fluid, especially the sound dispersion, will become much less prominent [cf. Fig. 5(c)].

E. Remarks and open questions

We end with a number of remarks and open questions.

(1) From the three exponentials that fit $F(k,t)$—or equivalently, the three Lorentzians that describe $S(k,\omega)$—the three lowest-lying eigenvalues of the 5×5 correlation matrix $\underline{\underline{H}}(k)$ can be obtained. Therefore writing $F(k,t)$ in the form

$$F(k,t)=\sum_{i=h,\pm} A_i(k)\exp[-z_i(k)t] \; ,$$

three sum rules are satisfied,

$$\sum_{i=h,\pm} A_i(k)=S(k) \; ,$$

$$\sum_{i=h,\pm} A_i(k)z_i(k)=0 \; ,$$

$$\sum_{i=h,\pm} A_i(k)z_i(k)^2=-k^2/\beta m \; .$$

As a consequence of these sum rules the three exponentials that describe $F(k,t)$ are determined by the three independent functions $z_h(k)$, $\omega_s(k)=|\mathrm{Im}z_{\pm}(k)|$, and $z_s(k)=\mathrm{Re}z_{\pm}(k)$, since the amplitudes $A_i(k)$ are then functions of the $z_i(k)$. Also, the three Lorentzians that describe $S(k,\omega)$ have the correct frequency moments $\langle\omega^0\rangle=S(k)$ and $\langle\omega^2\rangle=k^2/\beta m$. Thus from the three-exponential fit to $F(k,t)$ [or then a three-Lorentzian fit to $S(k,\omega)$], together with the sum rules, one obtains $z_h(k)$, $\omega_s(k)$ and $z_s(k)$, i.e., the three lowest-lying eigenvalues of the 5×5 correlation matrix $\underline{\underline{H}}(k)$.

(2) In the Introduction we mentioned that the generalized transport coefficients $\phi(k,\omega)$, $\lambda(k,\omega)$, and $\gamma(k,\omega)$ can in principle be determined directly by MD simulations, but that it is easier to derive them from the $F_{11}(k,t)$, $F_{13}(k,t)$, and $F_{33}(k,t)$. This is so because these coefficients can be expressed in terms of three independent correlation functions that involve complicated projected currents rather than the simple hydrodynamic quantities considered here. This is discussed in more detail in Appendix C.

(3) It has been conjectured in the literature[9,26–28] that the coherent dynamic structure factor $S(k,\omega)$ approaches its Gaussian (ideal-gas) limit for $k=\infty$ via the incoherent dynamic structure factor $S_s(k,\omega)$, i.e., $S(k,\omega)\cong S_s(k,\omega)$ or, equivalently, $F(k,t)\cong F^s(k,t)$ for $k\sigma_{\rm LJ}\ge 10$.

It might be interesting to see whether not only $F(k,t)$ but all $F_{jl}(k,t)$ behave like the corresponding self-correlation functions $F_{jl}^s(k,t)$ for $k\sigma_{\rm LJ}\ge 10$. However, to do this one needs to determine all $F_{jl}^s(k,t)$ by independent MD calculations, which has not been done so far.

For the present LJ fluid we see in Fig. 3 that all generalized thermodynamic quantities and, in particular, $h(k)$ and $c_v(k)$ have not yet reached their corresponding ideal-gas values for the largest k values observed, i.e., for $k\sigma_{\rm LJ}=14.5$. This is consistent with neutron scattering results for $S(k,\omega)$ of liquid argon at 120 K, where ideal-gas-like behavior is observed only when $k\sigma_{\rm LJ}\ge 25$.[28]

(4) For $k\to\infty$, the description of the $F_{jl}(k,t)$ with five Lorentzians fails in principle, since then all $F_{jl}(k,t)$ are Gaussians, rather than a finite sum of exponentials. In practice, however, five (or even three) exponentials can mimic the Gaussian line shape very well. We expect therefore that the failure of the present description of the $F_{jl}(k,t)$ at large k can only be revealed by MD simulations of a higher accuracy than ours.

(5) It has been discussed in the literature that the $S(k,\omega)$ of liquid argon[29] and the $S_s(k,\omega)$ of hydrogen[30] and sodium[31,32] approach, for $k\to 0$, their corresponding hydrodynamic limits in a manner as that predicted by the mode-coupling theory. For $S(k,\omega)$ this implies that the sound dispersion $\omega_s(k)$ behaves, for small k, as $\omega_s(k)=ck+ak^{5/2}$, where a is a *positive* mode-coupling parameter which depends on the thermodynamic and transport properties of the fluid.[2,29] Indeed, for the present LJ fluid we see in Fig. 5(c) that $\omega_s(k)$ approaches its hydrodynamic limit ck from *above* when $k\to 0$. However, a quantitative comparison between the MD results for $\omega_s(k)$ and the mode-coupling theory could not be made since not all transport and thermodynamic properties, needed to determine the coefficient a, are known at present.

(6) Bosse *et al.*[10] have made an interesting attempt to use the mode-coupling theory not only for $k\approx 0$ but also for finite values of k. It would be worthwhile to investigate whether a similar theoretical mode-coupling calculation, using the five eigenmodes of $\underline{\underline{H}}(k)$ as "single modes," would lead to values of the generalized transport coefficients for our LJ fluid that are consistent with the

MD data. However, for such calculations the static three- and four-point equilibrium correlation functions are needed that are not available at present.

ACKNOWLEDGMENTS

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APPENDIX A

Here we derive Eq. (2.27) for the 5×5 correlation matrix $\underline{\underline{H}}(k)$ using the methods described in Refs. 2, 4, 6, and 21–23.

We start with the 25 correlation functions $G_{jl}(k,t)$ between the five orthonormal microscopic quantities $b_j(\mathbf{k})$ given by Eq. (2.19), i.e., with j or $l=1,\ldots,5$,

$$G_{jl}(k,t)=\langle [b_j(\mathbf{k})]^* e^{tL} b_l(\mathbf{k})\rangle \ , \tag{A1}$$

and their Laplace transforms

$$\tilde{G}_{jl}(k,z)=\int_0^\infty dt\, e^{-zt}G_{jl}(k,t) \ . \tag{A2}$$

Hence

$$\tilde{G}_{jl}(k,z)=\langle b_j(\mathbf{k}) \,|\, b_l(\mathbf{k},z)\rangle \ , \tag{A3}$$

where the bra-ket notation refers to the innerproduct $\langle f \,|\, g\rangle = \langle f^* g\rangle$ for any two functions f and g of microscopic variables and where

$$|\, b_l(\mathbf{k},z)\rangle = \frac{1}{z-L}\,|\, b_l(\mathbf{k})\rangle \ , \tag{A4}$$

so that

$$z\,|\, b_l(\mathbf{k},z)\rangle = L\,|\, b_l(\mathbf{k},z)\rangle + |\, b_l(\mathbf{k})\rangle \ . \tag{A5}$$

We introduce the projection operators P and $P_\perp = 1-P$ by

$$P=\sum_{j=1}^{5} |\, b_j(\mathbf{k})\rangle\langle b_j(\mathbf{k})\,| \ , \tag{A6}$$

so that, by applying P and $P_\perp$ to Eq. (A5),

$$zP\,|\, b_j(\mathbf{k},z)\rangle = PLP\,|\, b_j(\mathbf{k},z)\rangle + PLP_\perp\,|\, b_j(\mathbf{k},z)\rangle + |\, b_j(\mathbf{k})\rangle \tag{A7}$$

and

$$zP_\perp\,|\, b_j(\mathbf{k},z)\rangle = P_\perp LP\,|\, b_j(\mathbf{k},z)\rangle + \hat{L}\,|\, b_j(\mathbf{k},z)\rangle \ , \tag{A8}$$

where $\hat{L}=P_\perp L P_\perp$. In Eqs. (A7) and (A8) we eliminate $P_\perp \,|\, b_j(\mathbf{k},z)\rangle$, so that

$$zP\,|\, b_j(\mathbf{k},z)\rangle = PLP\,|\, b_j(\mathbf{k},z)\rangle + PLP_\perp \frac{1}{z-\hat{L}} P_\perp LP\,|\, b_j(\mathbf{k},z)\rangle + |\, b_j(\mathbf{k})\rangle \ . \tag{A9}$$

Then, using Eq. (A6) for P, one finds the exact kinetic equation

$$z\tilde{G}_{ij}(k,z) = -\sum_{l=1}^{5} \bar{H}_{il}(k,z)\tilde{G}_{lj}(k,z)+\delta_{ij} \ , \tag{A10}$$

where the symmetric k,z-dependent 5×5 correlation matrix $\bar{H}(k,z)$ is given by

$$\bar{H}_{ij}(k,z) = -L_{ij}(k) - U_{ij}(k,z) \ , \tag{A11}$$

with $L_{ij}(k)$, the symmetric Liouville matrix, given by

$$L_{ij}(k)=\langle b_i(\mathbf{k})\,|\, L \,|\, b_j(\mathbf{k})\rangle \tag{A12}$$

and $U_{ij}(k,z)$, the symmetric matrix of k,z-dependent transport coefficients, given by

$$U_{ij}(k,z)=\left\langle b_i(\mathbf{k}) \,\middle|\, LP_\perp \frac{1}{z-\hat{L}} P_\perp L \,\middle|\, b_j(\mathbf{k})\right\rangle \ . \tag{A13}$$

We use the conservation laws [cf. Eqs. (2.3)–(2.9)]

$$\begin{aligned} La_1(\mathbf{k}) &= -ika_2(\mathbf{k}) \ , \\ La_2(\mathbf{k}) &= -ika_4(\mathbf{k}) \ , \\ La_3(\mathbf{k}) &= -ika_5(\mathbf{k}) \ , \end{aligned} \tag{A14}$$

so that, with Eqs. (2.19) and (2.23),

$$\begin{aligned} Lb_1(\mathbf{k}) &= -if_{un}(k)b_2(\mathbf{k}) \ , \\ Lb_2(\mathbf{k}) &= -if_{un}(k)b_1(\mathbf{k}) - if_{uT}(k)b_3(\mathbf{k}) \\ &\quad - if_{u\sigma}(k)b_4(\mathbf{k}) \ , \\ Lb_3(\mathbf{k}) &= -if_{uT}(k)b_2(\mathbf{k}) - if_{Tq}(k)b_5(\mathbf{k}) \ , \end{aligned} \tag{A15}$$

where the $f_{jl}(k)$ are given by Eq. (2.28). Thus, for $j=1,2,3$,

$$P_\perp Lb_j(\mathbf{k})=0 \ , \tag{A16}$$

so that $U_{ij}(k,z)=0$ when i or $j=1,2,3$ [cf. Eq. (A13)]. Finally, we note that $L_{44}(k)=L_{55}(k)=0$ since L is odd, $b_4(\mathbf{k})$ is even, and $b_5(\mathbf{k})$ is odd in the microscopic velocities $\mathbf{v}_i$, respectively. Collecting the results yields

$$\underline{\underline{H}}(k,z)=\begin{bmatrix} 0 & if_{un}(k) & 0 & 0 & 0 \\ if_{un}(k) & 0 & if_{uT}(k) & if_{u\sigma}(k) & 0 \\ 0 & if_{uT}(k) & 0 & 0 & if_{Tq}(k) \\ 0 & if_{u\sigma}(k) & 0 & z_\sigma(k,z) & iz_{q\sigma}(k,z) \\ 0 & 0 & if_{Tq}(k) & iz_{q\sigma}(k,z) & z_q(k,z) \end{bmatrix} \ , \tag{A17}$$

where

$$\begin{aligned} z_\sigma(k,z)&=\int_0^\infty dt\, e^{-zt}J_\sigma(k,t)\ ,\\ z_q(k,z)&=\int_0^\infty dt\, e^{-zt}J_q(k,t)\ , \\ z_{q\sigma}(k,z)&=i\langle b_5(\mathbf{k})\,|\,L\ |\,b_4(\mathbf{k})\rangle+\int_0^\infty dt\, e^{-zt}J_{q\sigma}(k,t)\ , \end{aligned} \tag{A18}$$

where

$$\begin{aligned} J_\sigma(k,t)&=-\langle b_4(\mathbf{k})\,|\,LP_\perp e^{t\mathcal{L}}P_\perp L\ |\,b_4(\mathbf{k})\rangle\ ,\\ J_q(k,t)&=-\langle b_5(\mathbf{k})\,|\,LP_\perp e^{t\mathcal{L}}P_\perp L\ |\,b_5(\mathbf{k})\rangle\ ,\\ J_{q\sigma}(k,t)&=i\langle b_5(\mathbf{k})\,|\,LP_\perp e^{t\mathcal{L}}P_\perp L\ |\,b_4(\mathbf{k})\rangle\ . \end{aligned} \tag{A19}$$

When the time scale on which the time-correlation functions $J_\sigma(k,t)$, $J_q(k,t)$, and $J_{q\sigma}(k,t)$ decay to zero is shorter than the time scale on which the functions $G_{jl}(k,t)$ decay to zero, the z dependence of the transport coefficients $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$ in Eq. (A17) can be neglected. Then Eq. (2.34) for the 5×5 correlation matrix $\underline{\bar{H}}(k)=\underline{\bar{H}}(k,0)$ follows from Eq. (A17) for $\underline{\bar{H}}(k,z)$, with

$$\begin{aligned} z_\sigma(k)&=\int_0^\infty dt\, J_\sigma(k,t)\ ,\\ z_q(k)&=\int_0^\infty dt\, J_q(k,t)\ ,\\ z_{q\sigma}(k)&=i\langle b_5(\mathbf{k})\,|\,L\ |\,b_4(\mathbf{k})\rangle+\int_0^\infty dt\, J_{q\sigma}(k,t)\ , \end{aligned} \tag{A20}$$

which are real for all k.

By inverse Laplace transformation of Eq. (A10), with $\bar{H}_{il}(k,z)$ replaced by $\bar{H}_{il}(k)$, one obtains the coupled set of kinetic equations

$$\frac{\partial}{\partial t}G_{jl}(k,t)=-\sum_{i=1}^{5}\bar{H}_{ji}(k)G_{il}(k,t)\ , \tag{A21}$$

for the 25 $G_{jl}(k,t)$.

From this result and Eq. (2.19) one finds Eq. (1.1) for the 25 $F_{jl}(k,t)$ with the 5×5 correlation matrix $\underline{H}(k)$ given by [cf. Eq. (2.26)]

$$\underline{H}(k)=\underline{U}^{-1}(k)\underline{\bar{H}}(k)\underline{U}(k)\ . \tag{A22}$$

Thus

$$\underline{H}(k)=\begin{bmatrix} 0 & ik & 0 & 0 & 0\\ 0 & 0 & 0 & ik & 0\\ 0 & 0 & 0 & 0 & ik\\ H_{41}(k) & H_{42}(k) & H_{43}(k) & z_\sigma(k) & H_{45}(k)\\ H_{51}(k) & H_{52}(k) & H_{53}(k) & H_{54}(k) & z_q(k) \end{bmatrix}, \tag{A23}$$

with

$$\begin{aligned} H_{41}(k)&=\frac{k_BT}{mS(k)c_v(k)}[\alpha(k)h(k)-c_p(k)]z_\sigma(k)\ ,\\ H_{42}&=-ik\frac{m}{k_BT}\left[V_{44}(k)-\frac{k_B^2T^2\alpha(k)h(k)}{m^2S(k)c_v(k)}\right]\\ &\quad -ih(k)\frac{U_{55}(k)}{U_{44}(k)}z_{q\sigma}(k)\ ,\\ H_{43}(k)&=-\frac{k_BT\alpha(k)}{mS(k)c_v(k)}z_\sigma(k)\ ,\\ H_{45}(k)&=ik\frac{k_BT\alpha(k)}{mS(k)c_v(k)}+i\frac{U_{55}(k)}{U_{44}(k)}z_{q\sigma}(k)\ ,\\ H_{51}(k)&=ik\frac{k_BT^2\alpha(k)-S(k)h(k)}{k_BT^2S(k)c_v(k)U_{55}^2(k)}\\ &\quad +i\frac{k_BT[\alpha(k)h(k)-c_p(k)]U_{44}(k)}{mS(k)c_v(k)U_{55}(k)}z_{q\sigma}(k)\ ,\\ H_{52}(k)&=-h(k)z_q(k)\ ,\\ H_{53}(k)&=ik\frac{1}{k_BT^2c_v(k)U_{55}(k)^2}\\ &\quad -i\frac{k_BT\alpha(k)U_{44}(k)}{mS(k)c_v(k)U_{55}(k)}z_{q\sigma}(k)\ ,\\ H_{54}(k)&=ikh(k)+i\frac{U_{44}(k)}{U_{55}(k)}z_{q\sigma}(k)\ . \end{aligned} \tag{A24}$$

Thus the $H_{jl}(k)$ are expressed in terms of the three transport coefficients $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$; the four independent generalized thermodynamic parameters $S(k)$, $h(k)$, $\alpha(k)$, and $c_p(k)$; and the two quantities $U_{44}(k)$ [or $V_{44}(k)$] and $U_{55}(k)$.

APPENDIX B

Here we express the transport coefficients $z_\sigma(0)$ and $z_q(0)$, which are the nonvanishing elements of the 5×5 correlation matrix $\underline{\bar{H}}(k)$ when $k\to0$, in terms of the more familiar longitudinal viscosity ϕ [cf. Eq. (3.13)] and thermal conductivity λ [cf. Eq. (3.7)] of the fluid, respectively. This involves a transition from the projection operator P, introduced in Eq. (A6), to projection operator P', which will be introduced below. We proceed in two steps.

First we consider the 2×2 matrices of k and z dependent transport coefficients,

$$\underline{Z}^{(5)}(k,z)=\begin{bmatrix} z_\sigma(k,z) & iz_{q\sigma}(k,z)\\ iz_{q\sigma}(k,z) & z_q(k,z)\end{bmatrix}, \tag{B1}$$

which occurs in the 5×5 correlation matrix $\underline{\bar{H}}(k,z)$ [cf. Eq. (A17)] and

$$\underline{Z}^{(3)}(k,z)=\begin{bmatrix} z_\phi(k,z) & i\Delta(k,z)\\ i\Delta(k,z) & z_T(k,z)\end{bmatrix}, \tag{B2}$$

which occurs in the 3×3 generalized hydrodynamic matrix $\underline{\bar{H}}^{(h)}(k,z)$ [cf. Eq. (4.19)]. We first relate $\underline{Z}^{(5)}(k,z)$ to $\underline{Z}^{(3)}(k,z)$ for all k and z.

Expressions for the matrix elements $Z_{ij}^{(5)}(k,z)$ of $\underline{Z}^{(5)}(k,z)$ in terms of current-current time-correlation functions have been derived in Appendix A and the results are given in Eqs. (A18) and (A19). Expressions for the matrix elements $Z_{ij}^{(3)}(k,z)$ of $\underline{Z}^{(3)}(k,z)$ can be derived in a similar fashion as for $Z_{ij}^{(5)}(k,z)$. The result for i or $j=1,2$ is

$$Z_{ij}^{(3)}(k,z)=-\langle [b_{i+1}(\mathbf{k})]^* L P'_{\perp}\frac{1}{z-\hat{L}'}P'_{\perp}L b_{j+1}(\mathbf{k})\rangle \ , \tag{B3}$$

or, in terms of current-current time-correlation functions,

$$Z_{ij}^{(3)}(k,z)=f_i(k)f_j(k)\int_0^\infty dt\, e^{-zt}\langle [b_{i+3}(\mathbf{k})]^* \times e^{tL'}b_{j+3}(\mathbf{k})\rangle \ . \tag{B4}$$

Here $f_1(k)=f_{u\sigma}(k)$, $f_2(k)=f_{Tq}(k)$, and $P'_{\perp}=1-P'$ with

$$P'=\sum_{i=1}^{3}|b_i(\mathbf{k})\rangle\langle b_i(\mathbf{k})| \ , \tag{B5}$$

$\hat{L}'=P'_{\perp}LP'_{\perp}$, and where we used the conservation laws for $j=1,2$ [cf. Eqs. (A15) and (B5)],

$$P'_{\perp}Lb_{j+1}(\mathbf{k})=-if_j(k)b_{j+3}(\mathbf{k}) \ . \tag{B6}$$

Using Eq. (B6) in Eq. (B3) and applying to Eq. (B3) operator identities of the form

$$\frac{1}{z-\hat{L}'}=\frac{1}{z}+\frac{1}{z}\hat{L}'\frac{1}{z-\hat{L}'} \tag{B7}$$

and

$$\frac{1}{z-\hat{L}'}=\frac{1}{z-L}+\frac{1}{z-\hat{L}}(\hat{L}'-\hat{L})\frac{1}{z-\hat{L}'} \ , \tag{B8}$$

one obtains straightforwardly the relation (i or $j=1,2$):

$$zZ_{ij}^{(3)}(k,z)=f_i^2(k)\delta_{ij} -\sum_{l=1}^{2}\frac{f_i(k)}{f_l(k)}Z_{il}^{(5)}(k,z)Z_{lj}^{(3)}(k,z) \ . \tag{B9}$$

Using this equation one can express the matrix elements $Z_{ij}^{(3)}(k,z)$ in terms of those of $Z_{ij}^{(5)}(k,z)$ and in terms of the $f_i(k)$. The results are given by Eqs. (4.10), when $z_\sigma(k)$, $z_q(k)$, and $z_{q\sigma}(k)$ on the right-hand side of this equation are replaced by $z_\sigma(k,z)$, $z_q(k,z)$, and $z_{q\sigma}(k,z)$, respectively.

Next, we consider the hydrodynamic regime where $k\to 0$ and where the $Z_{ij}(k,z)$ may effectively be replaced by $Z_{ij}(k,0)$. It follows then from Eqs. (B4) and (3.3) that $Z_{11}^{(3)}(k,0)=z_\phi(k,0)=\phi k^2$, with

$$\phi=v_{u\sigma}^2\lim_{k\to 0}\int_0^\infty dt\langle [b_4(\mathbf{k})]^* e^{tL}b_4(\mathbf{k})\rangle \ , \tag{B10}$$

and that $Z_{22}^{(3)}(k,0)=z_T(k,0)=\lambda k^2/mnc_v$, with

$$\lambda=mnc_v v_{Tq}^2\lim_{k\to 0}\int_0^\infty dt\langle [b_5(\mathbf{k})]^* e^{tL}b_5(\mathbf{k})\rangle \ . \tag{B11}$$

We remark on these results in the following.

(i) For $k\to 0$, the time-evolution operator $\exp(t\hat{L}')$ in Eq. (B4) may be replaced by $\exp(tL)$ [cf. Eqs. (B10) and (B11)]. This is because $b_4(\mathbf{k})$ and $b_5(\mathbf{k})$ are (nonconserved) quantities orthogonal to the (conserved) quantities $b_1(\mathbf{k})$, $b_2(\mathbf{k})$, and $b_3(\mathbf{k})$, which are exact (zero) eigenfunctions of L and $\hat{L}'$, so that $\exp(t\hat{L}')=\exp(tL)$. From this result and Eqs. (2.19) and (2.23), one shows straightforwardly that the expression (B10) for ϕ and (B11) for λ are the same as the usual expressions for the longitudinal viscosity ϕ and heat conductivity λ, respectively, given in the literature.[21-23]

(2) While in Eq. (B2) for $\underline{Z}^{(3)}(k,z)$, $z_\phi(k,0)$, and $z_T(k,0)$ vanish proportionally to k^2 when $k\to 0$; $\Delta(k,0)$ vanishes proportionally to k^3, since

$$\lim_{k\to 0}\int_0^\infty dt\langle [b_5(\mathbf{k})]^* e^{tL}b_4(\mathbf{k})\rangle=0 \ ,$$

due to the different tensorial character of the momentum and heat fluxes, respectively.[2] As a consequence of this and Eqs. (3.3) and (4.10), the transport coefficient $z_{q\sigma}(k)=z_{q\sigma}(k,0)$ in $\underline{Z}^{(5)}(k,0)$ vanishes proportionally to k, while $z_\sigma(k)=z_\sigma(k,0)$ and $z_q(k)=z_q(k,0)$ approach $z_\sigma(0)$ and $z_q(0)$, respectively, when $k\to 0$. This then leads directly, with Eqs. (3.3) and (4.10), to Eqs. (3.13), $z_\sigma(0)=v_{u\sigma}^2/\phi$, and (3.7), $z_q(0)=mnc_v v_{Tq}^2/\lambda$, which is the desired result.

APPENDIX C

The three generalized transport coefficients $\phi(k,\omega)$, $\lambda(k,\omega)$, and $\gamma(k,\omega)$ or, equivalently, $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$, that occur in Eq. (4.9) for $\underline{\bar{H}}^{(h)}(k,z)$ can be expressed directly in terms of the current-current correlation functions $Y_{ij}(k,t)$ as

$$\begin{aligned} z_\phi(k,z)&=\int_0^\infty dt\, e^{-zt}Y_{11}(k,t) \ ,\\ z_T(k,z)&=\int_0^\infty dt\, e^{-zt}Y_{22}(k,t) \ ,\\ i\Delta(k,z)&=\int_0^\infty dt\, e^{-zt}Y_{12}(k,t) \ , \end{aligned} \tag{C1}$$

where $(i,j=1,2)$

$$Y_{ij}(k,t)=\langle [J_i(\mathbf{k})]^* e^{t\hat{L}'}J_j(\mathbf{k})\rangle \tag{C2}$$

and $J_i(\mathbf{k})$ is the projected current $(i=1,2)$,

$$J_i(\mathbf{k})=P'_{\perp}Lb_{i+1}(\mathbf{k}) \ , \tag{C3}$$

as follows from Eqs. (B2) and (B3) in Appendix B. The $Y_{ij}(k,t)$ satisfy the equation $(i,j=1,2)$

$$Y_{ij}(k,t)=\bar{Y}_{ij}(k,t)+\sum_{l=1}^{2}\int_0^t dt'\bar{X}_{il}(k,t')Y_{lj}(k,t-t') \ , \tag{C4}$$

where

$$\bar{Y}_{ij}(k,t)=\langle [J_i(\mathbf{k})]^* e^{tL}J_j(\mathbf{k})\rangle \tag{C5}$$

and

$$\bar{X}_{ij}(k,t)=\langle [J_i(\mathbf{k})]^* e^{tL}b_{j+1}(\mathbf{k})\rangle \ , \tag{C6}$$

which can be derived using methods similar to those used in Appendix B. In principle, the $Y_{ij}(k,t)$ can then be obtained from MD results for $\overline{Y}_{ij}(k,t)$ and $\overline{X}_{ij}(k,t)$ using Eq. (C4). Thus such a MD calculation of $z_\phi(k,z)$, $z_T(k,z)$, and $\Delta(k,z)$ involves the six functions $\overline{Y}_{ij}(k,t)$ and $\overline{X}_{ij}(k,t)$, and is therefore more complicated (albeit more accurate) than the method used in this paper, based on $F_{nn}(k,t)$, $F_{en}(k,t)$, and $F_{ee}(k,t)$ alone.

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[*] Permanent address: Interuniversitair Reactor Instituut, Mekelweg 15, 2629 JB Delft, The Netherlands.

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