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Mode-coupling theory of simple classical liquids

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A microscopic theory for the dynamics of simple classical liquids is formulated with the longitudinal and transverse current-fluctuation spectra expressed in terms of relaxation kernels. The kernels are approximated by two-mode decay integrals coupling longitudinal and transverse excitations that result in a closed set of nonlinear equations which can be solved numerically. The only input required is the pair potential and the static two- and three-particle correlation functions. The theory gives correctly the zeroth, second, and fourth moments for the dynamical structure factor, the zeroth and second moments of the longitudinal and transverse current correlation functions, the free-particle limit, a proper hydrodynamical limit, and reflects the long-time anomalies of the dynamical transport coefficients.

I. INTRODUCTION

Neutron-scattering experiments[1-6] and computer simulation studies[5,7-13] have produced a wealth of interesting information on the dynamical behavior of simple classical liquids. During recent years various theoretical attempts have been made to explain the available data on the velocity autocorrelation function and on the density- and current-fluctuation spectra. Basically, one can distinguish two lines of approach in the theoretical work: generalized kinetic equations and generalized hydrodynamics.

Kinetic equations give a description of the liquid in terms of phase-space distribution functions. One aims at a generalization of Boltzmann's equation. To account for the strong correlations in liquids the Vlasov self-consistent interaction was extended reducing it approximately to the dynamical self-diffusion function.[14-19] Boltzmann's equation has also been extended by including retardation effects and spatial nonlocalities of the collision operator.[20-22] The studies mentioned yield good results for the neutron scattering function. However, all of them have used phenomenological input data. Moreover, those theories do not contain the long-time singularities of transport coefficients. Thus, they do not reflect all qualitative aspects of the liquid dynamics. The kinetic equation approach has been especially successful for the hard-sphere liquid model,[23] but so far the relevance of those calculations for realistic interactions is not quite clear.

Generalized hydrodynamics is formulated most effectively within the formalism developed by Zwanzig[24] and Mori.[25] One derives generalized Langevin equations for a finite set of variables such as density and currents. The relaxation kernels in these equations describe the coupling to those modes not considered explicitly. Usually, the kernels are approximated phenomenologically.[11,12,26] In this way the experiments are parametrized rather successfully in a systematic fashion (compare the review article by Copley and Lovesey[6]).

In order to get rid of phenomenological approximations a theory for the liquid dynamics has been proposed[27] based on the evaluation of the memory kernels in Mori's continued fraction expansion by a generalization of Kawasaki's mode-coupling approximation.[28] A first-principles evaluation of the current correlations according to this method[27] yielded reasonable quantitative agreement with experiment for liquid argon at intermediate wave numbers. However in the original work on liquid argon some crude approximations were introduced for the sake of calculational simplicity which spoiled the results for small and for large wave numbers.

In this paper we will present an improved version of the mode-coupling approach to liquid dynamics, which we have applied to compute fluctuation spectra of liquid argon[29] and liquid rubidium.[29] The quantities we want to calculate are the longitudinal and transverse current correlation functions. The transverse function describes shear excitations in liquids; in particular, it determines the dynamical shear viscosity. The longitudinal function describes density fluctuation excitations; in particular it determines the propagation and damping of first and zeroth sound. The longitudinal excitation spectrum is proportional to the Van Hove function which determines the neutron-scattering cross section. The following theory also yields a microscopic derivation for the shear viscosity and for the sound damping constant.

The paper is organized as follows: in Sec. II the underlying definitions, abbreviations, and standard formulas are given; they do not present new results, but we include them to make the paper self-contained. Sections III and IV contain the Mori representation for the current correlation functions, the connection with sum rules, and dynamical transport coefficients. We discuss our concept of considering fluctuations of the second-time derivatives of the currents as the basic quantities of liquid dynamics.

In Sec. V the mode-coupling approximation is formulated and motivated. The idea consists of interpreting the relaxation spectra as mode decay probabilities and approximating the decay by the simplest channels: decays into pairs of current excitations. It is important that an excitation (either longitudinal or transverse) can decay into a pair of two longitudinal modes as well as into a pair consisting of one longitudinal and one transverse mode. In this sense longitudinal and transverse excitations are coupled in liquids—a feature not reflected in previous theories.[30] The theory takes care of vertex renormalizations as well as of long time anomalies.

The decay vertex is expressed in terms of equal time two- and three-particle correlation functions and of the interaction potential (Sec. VI). Sections VII–X contain the technical details for an efficient evaluation of the decay integrals.

The theory in its present form suffers from two defects. First, since there is no good information about the three-particle correlation function, we used Kirkwood's superposition approximation in Sec. VI with a modification necessary for small Fourier components. Second, energy fluctuations are not considered. In principle, one could include energy currents. The evaluation of the corresponding decay integral would not introduce major problems. The corresponding decay vertex, however, would be rather complicated containing, e.g., unknown four-particle correlations. However neglecting decay channels which involve energy fluctuations for the damping of current excitations cannot be compared with the effect[31] of too small a basis set upon truncation of a continued fraction. Since no experimental results are known for the energy-fluctuation spectrum outside the hydrodynamical regime, the calculation did not seem very rewarding.

II. FORMAL FRAMEWORK

Let us consider a simple classical fluid of N particles of mass m enclosed in a volume V. Dynamical variables describing the system depend on positions $\vec{r}_i$ and momenta $\vec{p}_i$ ($i=1,\ldots,N$) of the particles only. In the following we will investigate correlations of the three Cartesian components of the particle current density:

$$A_\alpha = j_\alpha(\vec{q}) = \sum_i \frac{(\vec{p}_i)_\alpha}{m}\, e^{-i\vec{q}\cdot\vec{r}_i}, \quad \alpha = 1, 2, 3 \tag{1a}$$

and of the particle density

$$A_4 = \rho(\vec{q}) = \sum_i e^{-i\vec{q}\cdot\vec{r}_i}\,. \tag{1b}$$

We therefore consider the 4×4 matrix of correlation functions

$$\phi(\vec{q};t) = C_0(\vec{q})^{-1} C(\vec{q};t) \tag{2}$$

corresponding to the basic variables defined above with the abbreviations ($\mu,\nu = 1,\ldots,4$)

$$C_{\mu\nu}(\vec{q};t) = \langle \delta A_\mu^*(t)\,\delta A_\nu \rangle \tag{3a}$$

and

$$C_0(\vec{q}) = C(\vec{q};t=0)\,. \tag{3b}$$

The angular brackets in Eq. (3a) indicate a thermal average at temperature T, and δA is the fluctuation $A - \langle A\rangle$. The normalization matrix (3b) for a classical fluid has a very simple structure. It is diagonal and one finds that equal-time current correlations

$$(1/N)\langle j_\alpha^*(\vec{q})\, j_\beta(\vec{q})\rangle = \delta_{\alpha\beta} v_{\mathrm{th}}^2 \tag{4a}$$

do not depend on the wave vector, whereas density correlations do:

$$1/N \langle \delta\rho^*(\vec{q})\,\delta\rho(\vec{q})\rangle = S(q)\,. \tag{4b}$$

Here and in the following subscripts α, β denote cartesian components and $v_{\mathrm{th}} = (k_B T/m)^{1/2}$ stands for the thermal velocity, with Boltzmann's constant k_B. The structure factor $S(q)$ is related to the pair correlation function $g(r)$ via Fourier transform

$$S(q) = 1 + n\int d^3r\, e^{-i\vec{q}\cdot\vec{r}}[g(r) - 1]\,, \tag{5}$$

where $n = N/V$ is the equilibrium number density. In evaluating the time-dependent correlation functions (3a) we find it most convenient to make use of the formalism developed by Zwanzig[24] and Mori.[25] Introducing the scalar product for classical variables A and B,

$$(A\,|\,B) = \langle \delta A^* \delta B\rangle/(k_B T)\,, \tag{6}$$

the correlation functions of Eq. (3a) appear as matrix elements of the unitary time-evolution operator

$$C_{\mu\nu}(\vec{q};t) = k_B T (A_\mu | e^{-it\mathcal{L}} | A_\nu) . \tag{7}$$

The (Hermitian) Liouville operator $\mathcal{L}$ of the system is defined by the equation of motion for any dynamical variable A:

$$\dot{A}(t) = i\mathcal{L}A(t) \rightarrow A(t) = e^{it\mathcal{L}}A(t=0) . \tag{8a}$$

For a classical system of particles the explicit form of $\mathcal{L}$ is determined from Newton's equations of motion:

$$\partial_t \vec{r}_i = (1/m)\vec{p}_i ,$$

$$\partial_t \vec{p}_i = -\sum_j{}' \frac{\partial}{\partial \vec{r}_i} v(r_{ij}) , \tag{8b}$$

with (8c)

$$r_{ij} = |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j| .$$

Here $v(r)$ is the central symmetric pair potential acting between the particles, and the prime on the sum in Eq. (8c) indicates that particles i and j must be different. We will exploit internal symmetries of the system whenever possible: Translational invariance ensures that matrices of type (7) are diagonal in the wave number. Time inversion $\vec{r}_i(t) \rightarrow \vec{r}_i(-t)$; $\vec{p}_i(t) \rightarrow -\vec{p}_i(-t)$ causes $j_\alpha(\vec{q})$ and $\mathcal{L}^2 j_\alpha(\vec{q})$ to have odd parity and $\rho(\vec{q})$ to have even parity. With the scalar product (6), variables of opposite parity like A and $\mathcal{L}A$ are orthogonal, since averages are invariant under time inversion. Rotational invariance of averages implies that second-rank tensors like the current correlations

$$C_{\alpha\beta}(\vec{q};t) = \frac{q_\alpha q_\beta}{q^2} C_L(q;t) + \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{q^2}\right) C_T(q;t) \tag{9a}$$

are determined by two scalar functions, the longitudinal and transversal parts $C_L(q;t)$ and $C_T(q;t)$, which depend only on the modulus q of the vector $\vec{q}$. Henceforth, we will assume

$$\vec{q} = (0, 0, q) , \tag{9b}$$

so that the 3×3 matrix (9a) is diagonal. Rotational invariance also forbids correlations between transverse currents and the density, i.e., $C_{4\alpha} = C_{\alpha 4} = 0$ for $\alpha = 1, 2$. The particle-conservation law

$$\mathcal{L}\rho(\vec{q}) = -\vec{q} \cdot \vec{j}(\vec{q}) \tag{10}$$

gives rise to simple relations between correlations of the density and the longitudinal current. In the following we shall adopt a dispersion relation representation of correlation functions.[32] Consider the Laplace transform of Eq. (2) defined by

$$\phi(\vec{q};z) = \pm i \int_{-\infty}^{+\infty} dt\, \Theta(\pm t) e^{itz} \phi(\vec{q};t) \quad \text{for } \mathrm{Im}\, z \gtrless 0 \tag{11a}$$

$$= \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \, \frac{\phi''(\vec{q};\omega)}{\omega - z} , \tag{11b}$$

where $\Theta(t)$ denotes the unit step function. The spectral function $\phi''(\vec{q};\omega)$, which is the discontinuity of $\phi(\vec{q};z)$ on the real axis

$$\phi(\vec{q};\omega \pm i0) = \phi'(\vec{q};\omega) \pm i\phi''(\vec{q};\omega) , \tag{12a}$$

is given by

$$\phi''(\vec{q};\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} dt\, e^{it\omega} \phi(\vec{q};t) \; .$$

$$= \frac{1}{2i} [\phi(\vec{q};\omega + i0) - \phi(\vec{q};\omega - i0)] . \tag{12b}$$

From the Cauchy integral (11b) one has, moreover,

$$\phi'(\vec{q};\omega) = \mathrm{PP} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \, \frac{\phi''(\vec{q};\omega')}{\omega' - \omega} , \tag{12c}$$

where PP indicates a principal-value integral. $\phi(\vec{q};z)$ will now be expressed in terms of characteristic frequencies and relaxation kernels. Explicit expressions for the latter quantities are generated most easily using Eqs. (6) and (7). Starting from

$$\phi_{\mu\nu}(\vec{q};t) = \sum_\lambda (A|A)^{-1}_{\mu\lambda} (A_\lambda | e^{-it\mathcal{L}} | A_\nu) , \tag{13}$$

we have, according to (11a) and applying an obvious matrix notation,

$$\phi(\vec{q};z) = (A|A)^{-1} \left(A \left| \frac{1}{\mathcal{L} - z} \right| A \right)$$

$$= [\tilde{\omega}(\vec{q}) - z - \tilde{m}(\vec{q};z)]^{-1} . \tag{14a}$$

In Eq. (14a) a well-known identity[24,25,33] for resolvent matrix elements was used to cast $\phi(\vec{q};z)$ into the Dyson-equation form with the matrix

$$\tilde{\omega}(\vec{q}) = (A|A)^{-1}(A|\mathcal{L}|A) \tag{14b}$$

and the relaxation kernel

$$\tilde{m}(\vec{q};z) = (A|A)^{-1} \left(A \left| \mathcal{L}\mathcal{Q} \frac{1}{\mathcal{Q}\mathcal{L}\mathcal{Q} - z} \mathcal{Q}\mathcal{L} \right| A \right) . \tag{14c}$$

Here

$$\mathcal{Q} = 1 - \mathcal{P} \quad \text{with } \mathcal{P} = |A)(A|A)^{-1}(A| \tag{14d}$$

projects orthogonal to the space spanned by the A_ν ($\nu = 1, \ldots, 4$). Note that $\tilde{m}(q;z)$, like $\phi(\vec{q};z)$, is analytic off the real axis and falls off at least as fast as $1/z$ for large z, so it has a spectral representation like Eq. (11b) giving rise to a Kramers-Kronig dispersion relation analogous to Eq. (12c). Tong and Desai[34] showed that the representation of

Eq. (14) is equivalent to results obtained in terms of dispersion functions.[32] The only nonvanishing elements of matrix (14b) are

$$\tilde{\omega}_{34}(\vec{q}) = \frac{(j_3(\vec{q})|\mathcal{L}|\rho(\vec{q}))}{(j_3(\vec{q})|j_3(\vec{q}))} = -q\,, \tag{15a}$$

$$\tilde{\omega}_{43}(\vec{q}) = \frac{(\rho(\vec{q})|\mathcal{L}|j_3(\vec{q}))}{(\rho(\vec{q})|\rho(\vec{q}))} = -\frac{\Omega_0^2(q)}{q}\,. \tag{15b}$$

The characteristic frequency $\Omega_0(q)$ is defined by

$$\Omega_0^2(q) = \frac{(\rho(\vec{q})|\mathcal{L}^2|\rho(\vec{q}))}{(\rho(\vec{q})|\rho(\vec{q}))} = \frac{v_{\mathrm{th}}^2 q^2}{S(q)}\,. \tag{16}$$

The relaxation kernel is given by correlation functions of the generalized fluctuating forces

$$\tilde{A}_\nu = \mathcal{Q}\mathcal{L}A_\nu = \mathcal{L}A_\nu - \sum_\mu A_\mu \tilde{\omega}_{\mu\nu}\,. \tag{17}$$

$\tilde{\mathcal{L}} = \mathcal{Q}\mathcal{L}\mathcal{Q}$ is the fluctuation Liouville operator.[24,25,33] One can treat the resolvent matrix in (14c) in the same way as in (14a), obtaining a representation for $\tilde{m}(\vec{q};z)$ as a fraction. Iteration of this procedure would yield Mori's continued fraction for $\phi(\vec{q};z)$. Rotational invariance and the vanishing fourth component $\tilde{A}_4 = 0$ imply a diagonal matrix $\tilde{m}(\vec{q};z)$ which will be denoted as

$$\tilde{m}_{11}(q;z) = \tilde{m}_{22}(q;z) = q^2 D_T(q;z)\,, \tag{18}$$

$$\tilde{m}_{33}(q;z) = q^2 D_L(q;z)\,. \tag{19}$$

The relaxation matrix $\varphi(\vec{q};z)$ [Eq. (14a)] thus decouples into a diagonal 2×2 block of transverse functions and into a full 2×2 block of longitudinal functions. Transverse current correlation functions therefore have a much simpler structure than their longitudinal counterparts due to the coupling of density and longitudinal current in the latter.

III. TRANSVERSE CURRENT CORRELATION FUNCTION

From Eqs. (14) and (18) one finds for the transverse current correlation function

$$\phi_T(q;z) = (-1)/[z + q^2 D_T(q;z)]\,. \tag{20}$$

The generalized diffusion coefficient $D_T(q;z)$ is defined by

$$D_T(q;z) = \frac{m}{q^2 N}\left(\tau_1(\vec{q})\left|\frac{1}{\tilde{\mathcal{L}} - z}\right|\tau_1(\vec{q})\right), \tag{21}$$

which is a correlation function of the q-dependent transverse stress $\tau_1(\vec{q})/q = \sigma_T(\vec{q})$, where

$$\tau_\alpha(\vec{q}) = \mathcal{L}j_\alpha(\vec{q})\,. \tag{22}$$

Both spectra $\phi_T''(q,\omega)$ and $D_T''(q,\omega)$ are positive and even in ω. In the limit of small momenta $\rho(\vec{q})$ and $\vec{j}(\vec{q})$ reduce to conserved quantities from which $\lim_{q\to 0}\tilde{\mathcal{L}} = \mathcal{L}$ follows. Assuming regularity of $D_T(q;z)$ for $q \to 0$ one gets the Kubo formula

$$\lim_{q\to 0} D_T(q;z) = D_T(z) = \frac{m}{N}\left(\sigma_T\left|\frac{1}{\mathcal{L} - z}\right|\sigma_T\right)\,. \tag{23}$$

Here $\sigma_T = \lim_{q\to 0}\sigma_T(\vec{q})$ is a transverse component of the ordinary stress. The spectral function $D_T''(\omega)$ of $D_T(z)$ is the Fourier transform of the stress correlation function. Taking also the zero-frequency limit the real part $D_T'(\omega \to 0)$ vanishes and the imaginary part approaches a constant, conventionally denoted by $\eta/(mn)$:

$$\lim_{\omega\to 0} D_T(\omega \pm i0) = \pm i \lim_{\omega\to 0} D_T''(\omega) = \pm i\eta/(mn)\,. \tag{24a}$$

So, for small q and ω, one arrives at the approximation

$$\phi_T(q;z) \approx \frac{(-1)}{z \pm i q^2 \eta/(mn)} \quad \text{for } \mathrm{Im} z \gtrless 0\,. \tag{24b}$$

This is the hydrodynamic limit of the transverse-correlation function. In this limit the damping of the diffusive shear excitations, responsible for the width of the transverse current relaxation function (24b), is given by the shear viscosity η.

The relaxation functions $\phi_T(q,t)$ and $D_T(q,t)$ can be determined by computer experiments simulating classical fluids.[12] Outside the hydrodynamic regime $D_T(q,z)$ can no longer be approximated by a constant. For higher wave vectors and frequencies it has a pronounced dependence on both. Let us therefore introduce a representation of $q^2 D_T(q;z)$ in terms of its relaxation kernel. Rewriting Eq. (21) in analogy to Eqs. (14) leads to

$$q^2 D_T(q;z) = -\Omega_T^2(q)/[z + M_T(q;z)]\,. \tag{25}$$

The square of the characteristic frequency $\Omega_T(q)$,

$$\Omega_T^2(q) = \frac{(j_1(\vec{q})|\mathcal{L}^2|j_1(\vec{q}))}{(j_1(\vec{q})|j_1(\vec{q}))}$$

$$= v_{\mathrm{th}}^2 q^2 + \frac{n}{m}\int d^3r\,(1 - e^{iqr_3})g(r)\,\partial_1^2 v(r)\,, \tag{26}$$

normalizes the spectrum $q^2 D_T''(q;\omega)$. The relaxation kernel is

$$M_T(q;z) = \frac{m}{N\Omega_T^2(q)}\left(\tau_1(\vec{q})\left|\mathcal{L}\mathcal{Q}\frac{1}{\hat{\mathcal{L}} - z}\mathcal{Q}\mathcal{L}\right|\tau_1(\vec{q})\right)\,. \tag{27}$$

The Liouville operator $\hat{\mathcal{L}} = \hat{\mathcal{Q}}\mathcal{L}\hat{\mathcal{Q}}$ is reduced by the projector

$$\hat{\mathcal{Q}} = \tilde{\mathcal{Q}}\mathcal{Q} = \mathcal{Q}\tilde{\mathcal{Q}} = 1 - \mathcal{P} - \tilde{\mathcal{P}} \tag{28}$$

to a space perpendicular to the variables A_ν [Eq. (1)] and $\tilde{A}_\nu$ [Eq. (17)]. Note that

$$\hat{\mathcal{Q}}\mathcal{L}\mathcal{Q}\tau_1(\vec{q}) = \mathcal{Q}\mathcal{L}\tau_1(\vec{q}) = [\mathcal{L}^2 - \Omega_T^2(q)]\,j_1(\vec{q})\,.$$

The spectrum $M_T''(q,\omega)$, which is positive and even in ω, plays the central role in our theory. According to the general properties of correlation functions listed in Eqs. (12) the real part is determined via

$$M'_T(q,\omega)=\frac{2\omega}{\pi}\,\mathrm{PP}\int_0^\infty d\omega'\,\frac{M''_T(q,\omega')}{\omega'^2-\omega^2}\,, \tag{29}$$

and $D''_T(q,\omega)$ is given bv

$$D''_T(q,\omega)=\frac{\Omega_T^2(q)}{q^2}\,\frac{M''_T(q,\omega)}{[\omega+M'_T(q,\omega)]^2+[M''_T(q,\omega)]^2}\,. \tag{30}$$

Combining Eqs. (20) and (25) we finally arrive at

$$\phi_T(q;z)=-\frac{z+M_T(q;z)}{z^2-\Omega_T^2(q)+zM_T(q;z)}\,, \tag{31a}$$

$$\phi''_T(q;\omega)=\frac{\Omega_T^2(q)M''_T(q,\omega)}{[\omega^2-\Omega_T^2(q)+\omega M'_T(q,\omega)]^2+[\omega M''_T(q,\omega)]^2}\,. \tag{31b}$$

This exact result expresses the transverse-current correlation in terms of $\Omega_T^2(q)$, Eq. (26), and the relaxation kernel, Eq. (27). The above representation guarantees the correct zeroth and second moment of the spectral distribution of transverse current fluctuations. Our subsequent approximation for $M_T(q,z)$ does not destroy that property.

We consider the relaxation kernel $M_T(q;z)$ to be the basic quantity for microscopic approximations rather than the generalized viscosity, since the latter is unsuited for approximations in two limiting regimes of a fluid. In the weak coupling limit, i.e., in the low-density limit of a fluid or for the model of small interactions, the absence of an effective relaxation mechanism leads to a divergence of $D_T(q;z)$. This result is well known from kinetic gas theory. On the other hand, a straightforward perturbation expansion for $M_T(q;z)$ yields a value for η compatible with the Boltzmann equation result.[35] Thus the singular behavior of $D_T(q;z)$ in one limit of physical interest gives a first hint that it is better to focus on the relaxation kernel $M_T(q;z)$ for approximations. An investigation of the strong coupling limit suggests the same: high-density liquids have short-range correlations similar to a solid. One therefore would prefer a theory for liquid dynamics that also allows a simple identification of possible phononlike excitations. Indeed, Eq. (31) is the standard way used to discuss phonons in lattice dynamics. $\Omega_T(q)$ represents the ideal phonon dispersion and $M_T(q;z)$ is the polarization operator. In particular $M''_T(q;\omega)$ describes phonon damping due to imperfections and anharmonic effects. A small $M_T(q;z)$ yields sharp phonons; according to Eq. (25) this limit implies a strongly varying $D_T(q;z)$ making it inaccessible to simple approximations.

IV. LONGITUDINAL CURRENT CORRELATION FUNCTION

Like its transverse counterpart the longitudinal current density is a conserved variable. Moreover, it is coupled to the density via particle conservation (10). It is this coupling to another conserved variable which allows for an oscillatory propagation of fluctuations relaxing towards equilibrium. Formally this leads to the more complicated structure of longitudinal correlations due to the appearance of the nondiagonal elements (15). From Eqs. (14), (15), and (19) one finds for the longitudinal current relaxation function

$$\phi_L(q;z)=\frac{-z}{z^2-\Omega_0^2(q)+zq^2D_L(q;z)}\,, \tag{32}$$

and for the density relaxation function

$$\phi_{\rho\rho}(q;z)=\frac{(-1)}{z-\Omega_0^2(q)/[z+q^2D_L(q;z)]}\,. \tag{33}$$

Obviously density correlations and current correlations are related by

$$\phi_{\rho\rho}(q;z)=-\frac{1}{z}+\frac{\Omega_0^2(q)}{z^2}\,\phi_L(q;z)\,, \tag{34a}$$

$$\phi''_{\rho\rho}(q;\omega)=\frac{\Omega_0^2(q)}{\omega^2}\,\phi''_L(q;\omega)=\frac{\pi S(q;\omega)}{S(q)}\,, \tag{34b}$$

reflecting the continuity Eq. (10). It is important that this conservation law and the information on static density correlations contained in $\Omega_0^2(q)$ [Eq. (16)] be incorporated explicitly into a theory for the current spectra as it is done here. In the second part of Eq. (34b), the relationship with the classical Van Hove scattering function[6] is indicated for convenience. The generalized longitudinal damping function

$$D_L(q;z)=\frac{m}{q^2N}\left(\mathfrak{Q}\tau_3(\vec{q})\left|\frac{1}{\tilde{\mathfrak{L}}-z}\right|\mathfrak{Q}\tau_3(\vec{q})\right) \tag{35}$$

correlates generalized longitudinal stresses $\sigma_L(\vec{q})$,

$$\sigma_L(\vec{q})=\frac{\mathfrak{Q}\tau_3(\vec{q})}{q}=\frac{\tau_3(\vec{q})}{q}+\rho(\vec{q})\,\frac{\Omega_0^2(q)}{q^2}\,. \tag{36}$$

Note that $\tau_3(\vec{q})$ has an overlap with the density. In the small-q limit $\tilde{\mathfrak{L}}$ may again be replaced by $\mathfrak{L}$ leading to

$$\lim_{q\to 0}D_L(q;z)=D_L(z)=\frac{m}{N}\left(\sigma_L\left|\frac{1}{\mathfrak{L}-z}\right|\sigma_L\right), \tag{37a}$$

which is a correlation function of $\sigma_L=\lim_{q\to 0}\sigma_L(\vec{q})$. Assuming $D_L(q;z)$ to be regular in the hydrodynamic regime one approximates it by the zero-frequency limit D_L of (37a),

$$\lim_{\omega\to 0}D_L(\omega\pm i0)=\pm i\lim_{\omega\to 0}D''_L(\omega)=\pm iD_L\,, \tag{37b}$$

to obtain the standard hydrodynamic form

$$\phi_L(q;z) \approx -\frac{z}{z^2 - c_{\text{th}}^2 q^2 \pm izq^2 D_L}\,, \quad \operatorname{Im} z \gtrless 0\,, \tag{38}$$

where c_{th} denotes the isothermal sound velocity

$$c_{\text{th}}^2 = \lim_{q\to 0} \frac{\Omega_0^2(q)}{q^2} = \frac{v_{\text{th}}^2}{S(q=0)}\,. \tag{39}$$

Actually the generalized sound damping function $D_L(q;z)$ is not regular since the longitudinal current couples to energy-density fluctuations. Because of the nonzero overlap of $\tau_3(\vec{q})$ with the energy density, $D_L(q;z)$ [Eq. (35)] exhibits hydrodynamic singularities due to energy fluctuations. It is not difficult in principle to extend the set of basic variables to take account of this effect.[32] In such a scheme the correct adiabatic sound velocity would enter instead of the isothermal one appearing in Eq. (38). In our numerical work, however, we have ignored heat fluctuations and so we do not include them here either. Experimentally D_L is determined from sound damping measurements. Neutron-scattering supplies information on $\phi''_{\rho\rho}(q,\omega)$, and computer simulations yield $D_L(t)$ as well.[12]

The correlation function (32) has a form similar to the phonon propagator in lattice dynamics. From the point of view of analogy to solid state physics it would be tempting to consider $D_L(q;z)$ as a candidate for simple approximations. However, in the weakly coupled gas limit $D_L(q;z)$ diverges in the same way as $D_T(q;z)$. So we prefer here also to use a representation in terms of the relaxation kernel generated by Mori's formalism

$$q^2 D_L(q;z) = -\Delta^2(q)/[z + M_L(q;z)]\,. \tag{40}$$

The positive quantity $\Delta^2(q)$ normalizing the spectrum $q^2 D''_L(q,\omega)$ is given by

$$\Delta^2(q) = \frac{(j_3(\vec{q})|\mathfrak{L}\mathfrak{Q}\mathfrak{L}|j_3(\vec{q}))}{(j_3(\vec{q})|j_3(\vec{q}))} = \Omega_L^2(q) - \Omega_0^2(q)\,, \tag{41a}$$

where $\Omega_L(q)$ is a characteristic longitudinal frequency

$$\Omega_L^2(q) = \frac{(j_3(\vec{q})|\mathfrak{L}^2|j_3(\vec{q}))}{(j_3(\vec{q})|j_3(\vec{q}))} = 3v_{\text{th}}^2 q^2 + \frac{n}{m}\int d^3r\,(1 - e^{iqr_3})g(r)\,\partial_3^2 v(r)\,. \tag{41b}$$

For a discussion of the characteristic frequencies $\Omega_0(q)$, $\Omega_L(q)$, and $\Omega_T(q)$ see e.g., Ref. 6. The relaxation kernel $M_L(q;z)$ has the following structure:

$$M_L(q;z) = \frac{1}{\Delta^2(q)}\frac{m}{N} \times \left(\tau_3(\vec{q})\middle|\mathfrak{L}\mathfrak{Q}\frac{1}{\hat{\mathfrak{L}} - z}\mathfrak{Q}\mathfrak{L}\middle|\tau_3(\vec{q})\right). \tag{42}$$

Here again the Liouville operator $\hat{\mathfrak{L}} = \hat{\mathfrak{Q}}\mathfrak{L}\hat{\mathfrak{Q}}$ is reduced by the projector $\hat{\mathfrak{Q}} = \mathfrak{Q}\tilde{\mathfrak{Q}}$ (28) to a space orthogonal to A_ν [Eq. (1)] and $\tilde{A}_\nu$ [Eq. (17)]. Note that

$$\hat{\mathfrak{Q}}\mathfrak{L}\mathfrak{Q}\tau_3(\vec{q}) = \mathfrak{Q}\mathfrak{L}\tau_3(\vec{q}) = [\mathfrak{L}^2 - \Omega_L^2(q)]\,j_3(\vec{q})\,. \tag{43}$$

Formulas (29) and (30) hold with an obvious change of notation. The longitudinal current relaxation function expressed in terms of $M_L(q;z)$ is, however, slightly more complicated than its transverse counterpart (31),

$$\phi_L(q;z) = -\frac{z + M_L(q;z)}{z^2 - \Omega_L^2(q) + [z^2 - \Omega_0^2(q)]M_L(q;z)/z}\,, \tag{44a}$$

$$\phi''_L(q,\omega) = [\Omega_L^2(q) - \Omega_0^2(q)]M''_L(q,\omega) \times\left[\left(\omega^2 - \Omega_L^2(q) + (\omega^2 - \Omega_0^2(q))\frac{M'_L(q,\omega)}{\omega}\right)^2 + \left((\omega^2 - \Omega_0^2(q))\frac{M''_L(q,\omega)}{\omega}\right)^2\right]^{-1}. \tag{44b}$$

This form ensures the correct zeroth and second moment of the spectral distribution of longitudinal current fluctuations, i.e., the second and fourth moment of the density-fluctuation spectrum (34). In addition to that the above representation gives static density correlations, since Eqs. (44) guarantee also the correct zeroth moment of the dynamical structure factor.

V. MODE-COUPLING APPROXIMATION

Within the preceding exact formalism the calculation of current correlation functions has been reduced to an evaluation of the resolvent matrix element

$$N_{\alpha\beta}(\vec{q};z) = \left(\tau_\alpha(\vec{q})\middle|\mathfrak{L}\mathfrak{Q}\frac{1}{\hat{\mathfrak{Q}}\mathfrak{L}\hat{\mathfrak{Q}} - z}\mathfrak{Q}\mathfrak{L}\middle|\tau_\beta(\vec{q})\right)\frac{m}{N}\,, \tag{45}$$

with $\mathfrak{Q}$ projecting orthogonal to the variables A_ν [Eq. (1)] and $\hat{\mathfrak{Q}} = \mathfrak{Q}\tilde{\mathfrak{Q}}$ eliminating in addition the variables $\tilde{A}_\nu$ [Eq. (17)]. The two independent functions $N_{11}(q;z) = N_{22}(q;z)$ and $N_{33}(q;z)$ determine the transversal relaxation kernel $M_T(q;z)$ [Eq. (27)] and the longitudinal kernel $M_L(q;z)$ [Eq. (42)], respectively.

Our approximation for them consists in the following: In an expansion of the resolvent operator $(\hat{\mathfrak{Q}}\mathfrak{L}\hat{\mathfrak{Q}} - z)^{-1}$ with respect to a complete set of variables we retain only matrix elements between the most simple variables consisting of products of the basic variables A_ν. Due to invariance with respect to time inversion only combinations of currents with density fluctuations

$$B_{\vec{k}}^{\alpha}(\vec{q}) = \mathfrak{Q}\,j_\alpha(\vec{k})\,\delta\rho(\vec{q} - \vec{k})/N\,, \tag{46}$$

have nonzero overlap with $\mathcal{Q}\mathcal{L}\tau_\alpha(\vec{q})$. So we approximate

$$\mathcal{Q}\,\frac{1}{\hat{\mathcal{Q}}\mathcal{L}\hat{\mathcal{Q}}-z}\,\mathcal{Q}\approx\mathcal{Q}\mathcal{P}_2\,\frac{1}{\hat{\mathcal{Q}}\mathcal{L}\hat{\mathcal{Q}}-z}\,\mathcal{P}_2\mathcal{Q}\,, \tag{47a}$$

with $\mathcal{P}_2$ denoting the projector onto the two-mode variables [Eq. (46)],

$$\mathcal{P}_2=\sum_{\alpha,\beta}\sum_{\vec{k},\vec{p}}|B^\alpha_{\vec{k}}(\vec{q}))[(B|B)^{-1}]^{\alpha\beta}_{\vec{k}\vec{p}}(B^\beta_{\vec{p}}(\vec{q})|\;. \tag{47b}$$

In the long-wavelength limit, Eq. (47a) is still exact. This can be seen as follows: $\mathcal{L}\tau_\alpha(\vec{q})$ is given by a sum over two-mode variables $j_\beta(\vec{k})\rho(\vec{q}-\vec{k})$ plus a free streaming term $\mathcal{L}_0^2 j_\alpha(\vec{q})$ which vanishes like q^2,

$$\begin{aligned}\mathcal{L}\tau_\alpha(\vec{q})&=\mathcal{L}^2 j_\alpha(\vec{q})\\ &=\frac{1}{m}\sum_\beta\sum_{i,j}{}'\,V_{\alpha\beta}(\vec{q};\vec{r}_{ij})\,\frac{(\vec{p}_i)_\beta}{m}\,e^{-i\vec{q}\cdot\vec{r}_i}\\ &\quad+\frac{1}{m}\sum_i\left(\frac{\vec{q}\cdot\vec{p}_i}{m}\right)^2\frac{(\vec{p}_i)_\alpha}{m}\,e^{-i\vec{q}\cdot\vec{r}_i}\\ &=\frac{n}{m}\sum_\beta\frac{1}{N}\sum_{\vec{k}}V_{\alpha\beta}(\vec{q};\vec{q}-\vec{k})\,j_\beta(\vec{k})\rho(\vec{q}-\vec{k})\\ &\quad+\mathcal{L}_0^2 j_\alpha(\vec{q})\,.\end{aligned} \tag{48b}$$

So $\mathcal{Q}\mathcal{L}^2 j_\alpha(\vec{q})$ is a linear combination of $B^\beta_{\vec{k}}(\vec{q})$ in that limit. Here

$$\begin{aligned}V_{\alpha\beta}(\vec{q};\vec{r})=[&(1-e^{i\vec{q}\cdot\vec{r}})\,\nabla_\alpha\nabla_\beta\\ &-i(\delta_{\alpha\beta}\vec{q}\cdot\vec{\nabla}+2\nabla_\alpha q_\beta)]v(r)\,,\end{aligned} \tag{48c}$$

and

$$V_{\alpha\beta}(\vec{q};\vec{\kappa})=\int d^3r\,e^{-i\vec{\kappa}\cdot\vec{r}}\,V_{\alpha\beta}(\vec{q};\vec{r})$$

is its Fourier transform. In evaluating the resolvent matrix elements

$$\Psi^{\alpha\beta}_{\vec{k}\vec{p}}(\vec{q};z)=\left(B^\alpha_{\vec{k}}(\vec{q})\left|\frac{1}{\hat{\mathcal{L}}-z}\right|B^\beta_{\vec{p}}(\vec{q})\right)\,, \tag{49}$$

which enter in Eq. (47a), we assume the two modes to propagate independently, i.e., in addition to Eq. (47a), we approximate

$$\begin{aligned}&\langle\{j_\alpha(\vec{k})\delta\rho(\vec{q}-\vec{k})\}^*_{t,\hat{\mathcal{Q}}}\,j_\beta(\vec{p})\delta\rho(\vec{q}-\vec{p})\rangle\\ &\quad\cong\langle j_\alpha(\vec{k},t)^*j_\beta(\vec{p})\rangle\,\langle\delta\rho(\vec{q}-\vec{k},t)^*\delta\rho(\vec{q}-\vec{p})\rangle\\ &\qquad+\langle j_\alpha(\vec{k},\vec{t})^*\delta\rho(\vec{q}-\vec{p})\rangle\,\langle\delta\rho(\vec{q}-\vec{k},t)^*j_\beta(\vec{p})\rangle\,.\end{aligned} \tag{50}$$

Equation (50) implies that factorizing correlations approximately takes care of the projectors $\hat{\mathcal{Q}}$ as well. The spectral function of (49), $\psi^{\alpha\beta}_{\vec{k},\vec{p}}(\vec{q};\omega)''$, is given by the Fourier transform of Eq. (50),

$$\begin{aligned}\Psi^{\alpha\beta}_{\vec{k}\vec{p}}(\vec{q};\omega)''mnv_{\mathrm{th}}=\delta_{\vec{k},\vec{p}}\kappa^2\bigg[&\frac{k_\alpha k_\beta}{k^2}\,F_1(k,\kappa;\omega)\\ &+\left(\delta_{\alpha\beta}-\frac{k_\alpha k_\beta}{k^2}\right)F_2(k,\kappa;\omega)\bigg]\\ &+\delta_{\vec{\kappa},\vec{p}}k_\alpha\kappa_\beta F_3(k,\kappa;\omega)\end{aligned} \tag{51a}$$

in terms of convolutions of current spectra

$$\begin{aligned}F_{1,2}(k,\kappa;\omega)&=nv_{\mathrm{th}}^3\int_{-\infty}^{+\infty}\frac{d\epsilon}{\pi}\,\phi''_{L,T}(k,\omega-\epsilon)\\ &\qquad\times\phi''_L(\kappa,\epsilon)\,\frac{1}{\epsilon^2}\,,\\ F_3(k,\kappa;\omega)&=nv_{\mathrm{th}}^3\int_{-\infty}^{+\infty}\frac{d\epsilon}{\pi}\,\phi''_L(k,\omega-\epsilon)\\ &\qquad\times\phi''_L(\kappa,\epsilon)\,\frac{1}{\epsilon(\omega-\epsilon)}\,,\end{aligned} \tag{51b}$$

where $\vec{\kappa}=\vec{q}-\vec{k}$. The functions $F_i(k,\kappa;\omega)$ are dimensionless. The normalization matrix for the two-mode variables thus reads

$$\begin{aligned}(B^\alpha_{\vec{k}}(\vec{q})|B^\beta_{\vec{p}}(\vec{q}))&=\int_{\infty}^{\infty}\frac{d\omega}{\pi}\,\Psi^{\alpha\beta}_{\vec{k}\vec{p}}(\vec{q};\omega)''\\ &=\frac{\delta_{\alpha\beta}\delta_{\vec{k}\vec{p}}\,S(\kappa)}{m}\,.\end{aligned} \tag{51c}$$

Furthermore, we have to evaluate the vertex function $\varphi^\alpha_\gamma(\vec{q};\vec{k})$ given by the overlap of $\mathcal{Q}\mathcal{L}\tau_\alpha(\vec{q})$ with the two mode variables $B^\gamma_{\vec{k}}(\vec{q})$ "divided" by the normalization matrix (51c),

$$\varphi^\alpha_\gamma(\vec{q};\vec{k})=(\mathcal{Q}\mathcal{L}\tau_\alpha(\vec{q})|B^\gamma_{\vec{k}}(\vec{q}))m/S(\kappa)\,. \tag{52}$$

One finds that free-particle contributions to the vertex in Eq. (52) vanish, and we finally have

$$\varphi^\alpha_\gamma(\vec{q};\vec{k})=\frac{n}{m}\int d^3r\,e^{-i\vec{\kappa}\cdot\vec{r}}\,V_{\alpha\gamma}(\vec{q};\vec{r})G_{\vec{\kappa}}(\vec{r})\,, \tag{53a}$$

with

$$\begin{aligned}G_{\vec{\kappa}}(\vec{r})=\bigg(g(r)+n\int d^3r'\,&e^{-i\vec{\kappa}\cdot(\vec{r}'-\vec{r})}\\ &\times[g(\vec{r}';\vec{r})-g(r')g(r)]\bigg)\bigg/S(\kappa)\,.\end{aligned} \tag{53b}$$

The vertex is thus given in terms of potential derivatives (48c) multiplied by pair-correlation functions (5),

$$n^2g(r)=\frac{1}{V}\sum_{i,j}{}'\,\langle\delta(\vec{r}-\vec{r}_{ij})\rangle\,, \tag{54a}$$

and triple correlations

$$n^3g(\vec{r};\vec{r}')=\frac{1}{V}\sum_{i,j,l}{}'\,\langle\delta(\vec{r}-\vec{r}_{il})\delta(\vec{r}'-\vec{r}_{jl})\rangle\,. \tag{54b}$$

The summation includes only particle triples with pairwise distinct positions. Combining the preceding results we find the following two-mode contribution $N^{(2)}_{\alpha\beta}(\vec{q};z)$ to (45):

$$N^{(2)}_{\alpha\beta}(\vec{q};z)=\frac{m}{N}\sum_{\vec{k},\vec{p}}\sum_{\gamma\delta}\varphi^{\alpha}_{\gamma}(\vec{q};\vec{k})\times\Psi^{\gamma\delta}_{\vec{k}\vec{p}}(\vec{q};z)\varphi^{\beta}_{\delta}(\vec{q};\vec{p})^{*}. \tag{55a}$$

The spectral function reads

$$N^{(2)}_{\alpha\beta}(\vec{q};\omega)''=\frac{1}{v_{\text{th}}n^{2}}\int\frac{d^{3}k}{(2\pi)^{3}}\times\sum_{i=1}^{3}f^{i}_{\alpha\beta}(\vec{q};\vec{k})\kappa^{2}F_{i}(k,\kappa;\omega), \tag{55b}$$

where $F_i(k,\kappa;\omega)$ are the convolution integrals (51b) and

$$f^{1}_{\alpha\beta}(\vec{q};\vec{k})=\sum_{\gamma,\delta}\varphi^{\alpha}_{\gamma}(\vec{q};\vec{k})\frac{k_{\gamma}k_{\delta}}{k^{2}}\varphi^{\beta}_{\delta}(\vec{q};\vec{k})^{*}, \tag{55c}$$

$$f^{2}_{\alpha\beta}(\vec{q};\vec{k})=\sum_{\gamma,\delta}\varphi^{\alpha}_{\gamma}(\vec{q};\vec{k})\left(\delta_{\gamma\delta}-\frac{k_{\gamma}k_{\delta}}{k^{2}}\right)\varphi^{\beta}_{\delta}(\vec{q};\vec{k})^{*}, \tag{55d}$$

$$f^{3}_{\alpha\beta}(\vec{q};\vec{k})=\sum_{\gamma,\delta}\varphi^{\alpha}_{\gamma}(\vec{q};\vec{k})\frac{k_{\gamma}\kappa_{\delta}}{\kappa^{2}}\varphi^{\beta}_{\delta}(\vec{q};\vec{\kappa})^{*}. \tag{55e}$$

We have replaced $(1/N)\sum_{\vec{k}}\cdots$ in (55b) by $(1/n)\int[d^{3}k/(2\pi)^{3}]\cdots$.

Mode-coupling approximations have been used earlier by Kawasaki[28] in the discussion of dynamical critical phenomena. Since one is interested in asymptotic expansions only, further arguments in favor of the approximations can be given[28,36] in that case. Mode coupling approximations are known to yield the correct power laws for the long-time singularities of $D_T(t)$ and $D_L(t)$.[37] Hence the present theory takes care of these singularities also. Within the phonon theory of solids, approximation (50) is used to calculate the polarization operator in leading order. The factorization (50) is also correct in the weakly coupled gas limit; in this case one is in addition allowed to work out the functions F in Eqs. (50b) for the noninteracting system.[35]

The physical content of the preceding formulas is obvious. $N''_{\alpha\beta}(\vec{q};\omega)$ is the function describing the current excitation damping. According to Eq. (55) this damping is approximately determined by the decay of a current into pairs of current excitations. The decay rate is given by $N''_{\alpha\beta}(\vec{q};\omega)$, which is a generalized Golden Rule expression for the transition probabilities including kinematical restrictions due to momentum and energy conservation. The vertex $\varphi^{\alpha}_{\beta}(\vec{q};\vec{k})$ in Eq. (53a) is given in terms of the potential and the two- and three-particle correlations. These functions occur in such a way, that they screen the strong repulsive parts of the interaction. Crucial features of the preceding formalism are the handling of the long-time singularities by the factorization (50) and the screening of short-time hard-core singularities by static correlation functions in the vertex (53).

Since the two-mode variables $B^{\alpha}_{\vec{k}}(\vec{q})$ (46) have no overlap with the free streaming term in (48), the latter is projected out in (52) by our approximation (47). The vertex $\varphi^{\alpha}_{\gamma}(\vec{q};\vec{k})$ [Eq. (53a)] and hence $N^{(2)}_{\alpha\beta}(\vec{q};z)$ [Eq. (55)] vanishes for vanishing interaction potential. Approximation (47) was shown to be exact in the limit $q\to 0$ since only the mode-coupling term in Eq. (48b) survives. For large q, however, the free-particle motion represented by the second term in (48b) becomes relevant. To keep these free-streaming contributions to $N_{\alpha\beta}(\vec{q};z)$ (45) one has to include single-particle functions of the type

$$\sum_{i}e^{-i\vec{q}\cdot\vec{r}_{i}}(\vec{p}_{i})_{\alpha}(\vec{p}_{i})_{\beta}$$

as intermediate "states" in an expansion of the resolvent in (45) also. Since these contributions to N become relevant for large q we approximate them by the value $N^{(0)}_{\alpha\beta}(q;z)$ of the noninteracting system. Technically one evaluates $\Phi^{(0)}_{L,T}(q;z)$ in terms of error functions. After determining $\Omega^{(0)}_{0}(q)$ and $\Omega^{(0)}_{L,T}(q)$ for the ideal gas one uses Eqs. (31a) and (44a) to obtain $N^{(0)}_{L,T}(q;z)$. The present theory thus uses the formula

$$N_{\alpha\beta}(\vec{q};z)\cong N^{(2)}_{\alpha\beta}(\vec{q};z)+N^{(0)}_{\alpha\beta}(\vec{q};z), \tag{55f}$$

which is exact in the limit of the noninteracting system. This splitting is also exact for time $t=0$. Thus Eq. (55f) assumes that property to hold for all times.

Since the relaxation kernels $N_{L,T}(q;z)$ have been expressed in terms of the current correlation functions according to Eqs. (51b)–(55), a closed set of nonlinear integral equations has been derived to calculate $\phi_{L,T}(q;z)$. There are no problems in solving these equations by straightforward iteration: the nth approximation for the current correlations via Eqs. (51b)–(55) determines the $(n+1)$th approximation for the relaxation kernels $M_L(q;z)=N_L(q;z)/\Delta^2(q)$, $M_T(q;z)=N_T(q;z)/\Omega^2_T(q)$. These in turn yield via Eqs. (29), (31), and (44) the $(n+1)$th approximation for the spectra of current correlation functions. Practical calculations have been carried out for liquid argon[29] and liquid rubidium[29] on an IBM 360/91 computer. One iteration step requires about 2 min computer time, and, starting with a reasonable zeroth-order guess for the $\phi''_{T,L}(q;\omega)$, about three iteration steps are necessary to get the solution stable within 1%.

VI. DECAY VERTEX

In Sec. V the vertex was shown to be determined by the interparticle potential $v(r)$, the pair-correlation function $g(r)$, and the triple-correlation function $g(\vec{r};\vec{r}\,')$. For realistic liquids the potential $v(r)$ exhibits a strong repulsive core and a weak attractive tail. For liquid argon and liquid rubidium, $v(r)$ is sufficiently well known. The reliability of an effective interionic potential for our purpose in the case of rubidium is discussed in Refs. 6 and 13. Also the structure factor $S(k)$ has been measured in x-ray and neutron-scattering experiments. Regarding the third ingredient of our vertex there is unfortunately still a lack of detailed information on the triple correlations $g(\vec{r};\vec{r}\,')$. Therefore we used the Kirkwood superposition approximation

$$g(\vec{r};\vec{r}\,') \approx g(r)g(r')g(|\vec{r}-\vec{r}\,'|)\,, \tag{56a}$$

which does not destroy the effective shielding of the divergent bare potential for hard-core distances in (53).

This approximation however cannot reproduce the correct small κ behavior of the numerator in Eq. (53b). Since $S(\kappa)$ becomes very small, this entails too large a vertex for values of κ less than 1 Å^{-1}. We corrected this unpleasant feature of our vertex, caused by the deficiencies of the Kirkwood approximation, by replacing $1/S(\kappa)$ by unity in Eq. (53b), i.e.,

$$G_{\vec{\kappa}}(\vec{r}) \cong g(r)F_{\vec{\kappa}}(\vec{r})\,, \tag{56b}$$

$$F_{\vec{\kappa}}(\vec{r}) = 1 + n\int d^3r'\, e^{i\vec{\kappa}\cdot\vec{r}\,'} g(|\vec{r}-\vec{r}\,'|)[g(r')-1]\,. \tag{56c}$$

We have also investigated the effect of a lower cutoff for the κ integrals at about 1 Å^{-1} in Eq. (55b). There was no remarkable difference of the results compared to those obtained with Eqs. (56). According to (48c), the vertex (53a) contains derivatives of the potential

$$\vec{\nabla}v(r) = v'(r)\vec{r}/r\,,$$

$$\nabla_\alpha\nabla_\beta v(r) = \frac{r_\alpha r_\beta}{r^2}\,v''(r) + \left(\delta_{\alpha\beta} - \frac{r_\alpha r_\beta}{r^2}\right)\frac{v'(r)}{r}\,,$$

multiplied by the weight factor $g(r)$. Since the pair-distribution function $g(r)$ shows a peak, where $v''(r)$ is big and $v'(r)$ is small, we neglect the first derivatives in (53a) and use the approximation[6,16]

$$4\pi(n/m)r^2 g(r)v''(r) \approx 3\Omega_E^2\,\delta(r-r_0)\,. \tag{57a}$$

Here the Einstein frequency of the fluid is given by

$$\Omega_E^2 = \frac{1}{3}\,\frac{n}{m}\int d^3r\, g(r)\Delta v(r)\,, \tag{57b}$$

and the parameter r_0 is determined by a fit to $\Omega_{T,L}(q)$ [Eqs. (26) and (41b)]. Thus we approximate $V_{\alpha\beta}(\vec{q};\vec{r})$ [Eq. (48c)] in Eq. (53a) by

$$V_{\alpha\beta}(\vec{q};\vec{r})g(r) \cong \frac{3}{4\pi}\,\frac{m}{n}\,\Omega_E^2\,\frac{r_\alpha r_\beta}{r^2}\,\frac{1}{r^2} \times\delta(r-r_0)(1-e^{i\vec{q}\cdot\vec{r}})\,. \tag{57c}$$

We checked the validity of (57c) by carrying out the integrals (53a) numerically for some representative values of q. The results for the relaxation kernels are not influenced significantly. Note, however, that approximation (57) is appropriate for the dense liquids because of the peaked pair correlation $g(r)$, but is not allowed in gases. Our final result for the vertex is

$$\varphi^\alpha_\beta(\vec{q};\vec{k}) = \frac{3}{4\pi}\,\Omega_E^2\int d^3r\, e^{-i\vec{\kappa}\cdot\vec{r}}\,\frac{r_\alpha r_\beta}{r^2}\,\frac{1}{r^2}\,\delta(r-r_0) \times(1-e^{i\vec{q}\cdot\vec{r}})F_{\vec{\kappa}}(\vec{r})\,, \tag{58}$$

where $\vec{\kappa} = \vec{q}-\vec{k}$.

VII. VERTEX FOR $q\neq 0$–DETAILS

We list some formulas necessary for a tabulation of the vertex (58), which is a symmetric 3×3 matrix. Its elements are real, which is easily demonstrated using the property $F^*_{\vec{\kappa}}(\vec{r}) = F_{\vec{\kappa}}(-\vec{r})$ of the scalar function

$$\begin{aligned}F_{\vec{\kappa}}(\vec{r}) &\equiv f(\kappa, r, x)\\ &= 1 + 2\pi n\\ &\quad\times\int_0^\infty dr'\, r'^2[g(r')-1]\\ &\quad\quad\times\int_{-1}^{+1} dx'\, e^{i\kappa x r' x'} g(R)\\ &\quad\quad\quad\times J_0(\kappa(1-x^2)^{1/2} r'(1-x'^2)^{1/2})\,,\end{aligned} \tag{59a}$$

$$x = \cos(\vec{\kappa},\vec{r})\,. \tag{59b}$$

Here $R = (r^2 + r'^2 - 2rr'x')^{1/2}$, and the azimuthal angle integration has been carried out in Eq. (56c) leading to the Bessel function J_0. Since the remaining integrals in Eqs. (59) contain the pair-correlation function, they have to be done numerically.

For further evaluation of the vertex we must decide on a basis $\{\vec{e}_1, \vec{e}_2, \vec{e}_3\}$ for the representation of the matrix φ^α_β, and we must choose a coordinate system $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$ in which to carry out the $\vec{r}$ integration of Eq. (58). The matrix $\varphi^\alpha_\beta(\vec{q},\vec{k})$ can then be written

$$\begin{aligned}\varphi^\alpha_\beta &= \langle e_\alpha|B|e_\beta\rangle\\ &= \sum_{\gamma,\delta}(\vec{e}_\alpha\cdot\vec{a}_\gamma)B^{(a)}_{\gamma\delta}(\vec{a}_\delta\cdot\vec{e}_\beta)\,,\end{aligned} \tag{60a}$$

where the index a refers to the $\vec{a}$ basis. The $\vec{r}$ integration is done most efficiently in a coordinate system with basis vectors

$$\vec{a}_3=\frac{\vec{\kappa}}{\kappa}\,,\quad \vec{a}_2=\frac{\vec{\kappa}\times\vec{k}}{|\vec{\kappa}\times\vec{k}|}\,,\quad \vec{a}_1=\vec{a}_2\times\vec{a}_3\,, \tag{60b}$$

i.e., with the z-axis pointing into the direction of $\vec{\kappa}=\vec{q}-\vec{k}$ and $\vec{q}$ in the x-z plane. Then the azimuthal angle integration in addition to the integral over the magnitude of $\vec{r}$ can be carried out in Eq. (58). Denoting

$$y=\cos(\vec{q};\vec{\kappa})=(q^2+\kappa^2-k^2)/2q\kappa\,, \tag{61a}$$

we get from Eqs. (58) and (59b):

$$B^{(a)}_{\gamma\delta}(q,k,\kappa)=\tfrac{3}{2}\Omega_E^2\int_{-1}^{+1}dx\,e^{-i\kappa r_0 x}f(\kappa,r_0,x)\times b^{(a)}_{\gamma\delta}(q,k,\kappa;r_0,x)\,. \tag{61b}$$

The integral must be computed numerically using a table of $f(\kappa,r_0,x)$ produced from Eq. (59) and the functions

$$b^{(a)}_{\gamma\delta}(q,k,\kappa;r,x)=\int_0^{2\pi}\frac{d\varphi}{2\pi}\left((1-e^{i\vec{q}\cdot\vec{r}})\frac{r_\gamma r_\delta}{r^2}\right)_a=\begin{pmatrix}(1-x^2)C_2 & 0 & x(1-x^2)^{1/2}C_1\\ 0 & (1-x^2)(C_0-C_2) & 0\\ x(1-x^2)^{1/2}C_1 & 0 & x^2C_0\end{pmatrix}_a\,. \tag{61c}$$

The $b^{(a)}_{\gamma\delta}$ were arranged in a matrix with the index a denoting the basis (60b), and we introduced the abbreviations

$$\begin{aligned}C_0&=\int_0^{2\pi}\frac{d\varphi}{2\pi}(1-e^{i\vec{q}\cdot\vec{r}})=1-e^{i\zeta}J_0(z)\,,\\ C_1&=\int_0^{2\pi}\frac{d\varphi}{2\pi}(1-e^{i\vec{q}\cdot\vec{r}})\cos\varphi=-ie^{i\zeta}J_1(z)\,,\\ C_2&=\int_0^{2\pi}\frac{d\varphi}{2\pi}(1-e^{i\vec{q}\cdot\vec{r}})\cos^2\varphi\\ &=\tfrac{1}{2}-e^{i\zeta}\left(J_0(z)-\frac{J_1(z)}{z}\right)\,,\end{aligned} \tag{62a}$$

where

$$\vec{q}\cdot\vec{r}=qr[xy+\cos\varphi(1-x^2)^{1/2}(1-y^2)^{1/2}]$$

and

$$\zeta=qrxy,\quad z=qr(1-x^2)^{1/2}(1-y^2)^{1/2}\,. \tag{62b}$$

In the decay integrals (55) it is more convenient to use a representation of the vertex matrix with respect to the basis $\{\vec{e}_\alpha(\vec{k})\}$

$$\vec{e}_3=\frac{\vec{q}}{q}\,,\quad \vec{e}_2=\vec{a}_2=\frac{\vec{q}\times\vec{k}}{|\vec{q}\times\vec{k}|}\,,\quad \vec{e}_1=\vec{e}_2\times\vec{e}_3\,. \tag{63a}$$

From Eq. (60a), the transformation matrix is

$$\vec{e}_\alpha\cdot\vec{a}_\gamma=\begin{pmatrix}y & 0 & -(1-y^2)^{1/2}\\ 0 & 1 & 0\\ (1-y^2)^{1/2} & 0 & y\end{pmatrix}\,, \tag{63b}$$

and one then finds

$$\varphi_{\alpha\beta}(q,k,\kappa)=\begin{pmatrix}[y^2B_{11}-2y(1-y^2)^{1/2}B_{13}+(1-y^2)B_{33}] & 0 & [y(1-y^2)^{1/2}(B_{11}-B_{33})+(2y^2-1)B_{13}]\\ 0 & B_{22} & 0\\ [y(1-y^2)^{1/2}(B_{11}-B_{33})+(2y^2-1)B_{13}] & 0 & [(1-y^2)B_{11}+2y(1-y^2)^{1/2}B_{13}+y^2B_{33}]\end{pmatrix}_e\,, \tag{63c}$$

where $B_{\gamma\delta}$ abbreviates $B^{(a)}_{\gamma\delta}(q,k,\kappa)$ given in Eqs. (61).

VIII. DECAY INTEGRALS (55) FOR $q\neq0$—DETAILS

Here we want to write the two-mode contribution $N^{(2)}_{\alpha\beta}(\vec{q};\omega)''$ in a more-detailed form accessible for a numerical treatment. In order to evaluate the longitudinal and transverse part we must, according to Eqs. (55), determine

$$f^{(i)}_L(q,k,\kappa)=\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}f^i_{\alpha\beta}(\vec{q};\vec{k})\,, \tag{64a}$$

$$f^{(i)}_T(q,k,\kappa)=\frac{1}{2}\sum_{\alpha,\beta}\left(\delta_{\alpha\beta}-\frac{q_\alpha q_\beta}{q^2}\right)f^i_{\alpha\beta}(\vec{q};\vec{k}) \tag{64b}$$

for $i=1,2,3$. This is achieved by simple matrix algebra using the representation of the vertex (63c) with respect to the basis (63a) in which

$$\vec{q}=q(0,0,1)_e,\quad \vec{k}=k((1-u^2)^{1/2},0,u)_e\,, \tag{65a}$$

with

$$u=\cos(\vec{q};\vec{k})=(q^2+k^2-\kappa^2)/(2q\kappa)\,. \tag{65b}$$

One finds

$$f_L^{(1)}=[(1-u^2)^{1/2}\varphi_{13}+u\varphi_{33}]^2\,, \tag{66a}$$

$$f_T^{(1)}=\tfrac{1}{2}[(1-u^2)^{1/2}\varphi_{11}+u\varphi_{13}]^2\,, \tag{66b}$$

$$f_L^{(2)}=[u\varphi_{13}-(1-u^2)^{1/2}\varphi_{33}]^2\,, \tag{66c}$$

$$f_T^{(2)}=\tfrac{1}{2}\{\varphi_{22}^2+[u\varphi_{11}-(1-u^2)^{1/2}\varphi_{13}]^2\}\,. \tag{66d}$$

In the above formulas all matrix elements $\varphi_{\alpha\beta}$ depend on the same argument combination $\varphi_{\alpha\beta}(q,k,\kappa)$. The third component $f_{L,T}^{(3)}(q,k,\kappa)$ requires more attention since according to (55e) also the

$$\varphi_\delta^\beta(\vec{q};\vec{\kappa})=\tilde{\varphi}_{\beta\delta}(q,\kappa,k)=t_\beta\varphi_{\beta\delta}(q;\kappa,k)t_\delta$$

enters with $t_\alpha=\vec{e}_\alpha(\vec{k})\cdot\vec{e}_\alpha(\vec{\kappa})$. A straightforward calculation yields

$$\begin{aligned}f_L^{(3)}&(q,k,\kappa)\\ &=[(1-u^2)^{1/2}\varphi_{13}(q,k,\kappa)+u\varphi_{33}(q,k,\kappa)]\\ &\quad\times(k/\kappa)[-(1-y^2)^{1/2}\tilde{\varphi}_{13}(q,\kappa,k)+y\tilde{\varphi}_{33}(q,\kappa,k)]\,,\end{aligned} \tag{66e}$$

$$\begin{aligned}f_T^{(3)}&(q,k,\kappa)\\ &=\tfrac{1}{2}[(1-u^2)^{1/2}\varphi_{11}(q,k,\kappa)+u\varphi_{33}(q,k,\kappa)]\\ &\quad\times(k/\kappa)[-(1-y^2)^{1/2}\tilde{\varphi}_{11}(q,\kappa,k)+y\tilde{\varphi}_{13}(q,\kappa,k)]\,.\end{aligned} \tag{66f}$$

We note that the vertex functions $f_{L,T}^{(i)}$ depend only on scalar variables q,k,κ, which enables us to carry out one angle integration in Eq. (55b). The remaining integral over a polar angle can be transformed into one over κ using relation (65b).

We thus find

$$\begin{aligned}N_{L,T}^{(2)}&(q;\omega)''\\ &=\frac{1}{v_{\text{th}}(2\pi n)^2}\sum_{i=1}^{3}\int_0^\infty dk\int_{|q-k|}^{q+k}d\kappa\,\frac{k\kappa^3}{q}f_{L,T}^{(i)}(q,k,\kappa)\\ &\qquad\times F_i(k,\kappa;\omega)\,.\end{aligned} \tag{67}$$

IX. VERTEX FOR $q=0$–DETAILS

In the zero wave-number limit the function $D_T(z)$ [Eqs. (23) and (25)] and $D_L(z)$ [Eqs. (37a) and (40)] require knowledge of

$$\hat{\varphi}_{\alpha\beta}(k,u)=\lim_{q\to 0}\frac{\varphi_{\alpha\beta}(q,k,\kappa)}{q}\,. \tag{68}$$

This will be given by Eq. (63c), with the matrix elements $B_{\gamma\delta}$ replaced by

$$\hat{B}_{\gamma\delta}(k,u)=\lim_{q\to 0}B_{\gamma\delta}(q,k,\kappa)/q\,.$$

Performing that limit one finds from Eqs. (62),

$$\begin{aligned}\hat{C}_0&=-ir_0xy\,,\\ \hat{C}_1&=-\tfrac{1}{2}ir_0(1-x^2)^{1/2}(1-y^2)^{1/2}\,,\\ \hat{C}_2&=\tfrac{1}{2}C_0\,.\end{aligned} \tag{69}$$

Since $y=-u$ for $q=0$ all elements $\hat{B}_{\gamma\delta}$ can be expressed in terms of u and two integrals ($\nu=1,2$)

$$\begin{aligned}A_\nu(k)=i\tfrac{3}{2}\Omega_E^2r_0\frac{1}{2}\int_{-1}^{+1}&dx\,x^{(2\nu-1)}\\ &\times e^{-ikr_0x}f(k,r_0,x)\,.\end{aligned} \tag{70}$$

Both are real and vanish linearly for small k. The final result is

$$\hat{\varphi}_{\alpha\beta}(k;u)=\begin{pmatrix}u[(3u^2-2)A_1+(4-5u^2)A_2] & 0 & +(1-u^2)^{1/2}[(1-3u^2)A_1+(5u^2-1)A_2]\\ 0 & u[A_1-A_2] & 0\\ (1-u^2)^{1/2}[(1-3u^2)A_1+(5u^2-1)A_2] & 0 & u[(3-3u^2)A_1+(5u^2-3)A_2]\end{pmatrix}_e\,. \tag{71}$$

X. DECAY INTEGRALS FOR $q=0$–DETAILS

In the long-wavelength limit one has to evaluate

$$\begin{aligned}\lim_{q\to 0}\frac{N_{L,T}^{(2)}(q;\omega)''}{q^2}&=\frac{1}{v_{\text{th}}(2\pi n)^2}\\ &\quad\times\sum_{i=1}^{3}\int_0^\infty dk\,k^4F_i(k,k;\omega)\\ &\quad\times\int_{-1}^{+1}du\,\hat{f}_{L,T}^{(i)}(k;u)\,,\end{aligned} \tag{72a}$$

with

$$\hat{f}_{L,T}^{(i)}(k;u)=\lim_{q\to 0}\frac{f_{L,T}^{(i)}(q;k,\kappa)}{q^2}\,. \tag{72b}$$

Here we changed the integral over κ [Eq. (67)], into an integral over $u=\cos(\vec{q};\vec{k})$. For $i=1,2$, $\hat{f}_{L,T}^{(i)}(k;u)$ is given by Eqs. (66a)–(66d) with $\varphi_{\alpha\beta}(q,k,\kappa)$ replaced by $\hat{\varphi}_{\alpha\beta}(k;u)$ [Eq. (71)]. For $i=3$, application of

$$\lim_{q\to 0}\frac{\varphi_{\alpha\beta}(q,k,\kappa)}{q}=-\lim_{q\to 0}\frac{\tilde{\varphi}_{\alpha\beta}(q,\kappa,k)}{q} \tag{73a}$$

in Eqs. (66e) and (66f) leads to

$$\hat{f}_{L,T}^{(3)}(k;u)=\hat{f}_{L,T}^{(1)}(k;u)\,. \tag{73b}$$

Relation (73a) is most easily demonstrated in its equivalent form

$$\lim_{q\to 0}\frac{\varphi_\beta^\alpha(\vec{q};\vec{k})}{q}=-\lim_{q\to 0}\frac{\varphi_\beta^\alpha(\vec{q};\vec{q}-\vec{k})}{q}$$

in Eq. (58) with the help of $F_{-\vec{k}}(\vec{r})=F_{\vec{k}}(-\vec{r})$. The integral over u can be performed and leads to the final result for the decay integrals:

$$\lim_{q\to 0}\frac{N^{(2)}_{L,T}(q;\omega)''}{q^2}=\frac{1}{v_{\text{th}}(2\pi n)^2}\times\int_0^\infty dk\,k^4[\tilde{f}^{(1)}_{L,T}(k)L(k;\omega)+\tilde{f}^{(2)}_{L,T}(k)T(k;\omega)],\tag{74a}$$

with

$$L(k;\omega)=F_1(k,k;\omega)+F_3(k,k;\omega)=nv_{\text{th}}^3\omega\int_{-\infty}^{+\infty}\frac{d\epsilon}{\pi}\,\phi''_L(k;\omega-\epsilon)\phi''_L(k;\epsilon)\times\frac{1}{\epsilon^2(\omega-\epsilon)},\tag{74b}$$

$$T(k;\omega)=F_2(k,k;\omega)=nv_{\text{th}}^3\int_{-\infty}^{+\infty}\frac{d\epsilon}{\pi}\,\phi''_T(k;\omega-\epsilon)\phi''_L(k;\epsilon)\frac{1}{\epsilon^2},\tag{74c}$$

describing the $q=0$ decay into two longitudinal or one longitudinal and one transverse excitation, respectively. The decay strength is determined by

$$\tilde{f}^{(i)}_{L,T}(k)=\int_{-1}^{+1}du\,\hat{f}^{(i)}_{L,T}(k;u),\tag{75a}$$

with

$$\tilde{f}^{(1)}_L(k)=\tfrac{2}{15}[2A_1^2(k)+3A_2^2(k)-2A_1(k)A_2(k)],\tag{75b}$$

$$\tilde{f}^{(1)}_T(k)=\tfrac{1}{30}[A_1(k)-3A_2(k)]^2,\tag{75c}$$

$$\tilde{f}^{(2)}_L(k)=\tfrac{4}{15}[A_1(k)-A_2(k)]^2,\tag{75d}$$

$$\tilde{f}^{(2)}_T(k)=\tfrac{1}{5}[A_1(k)-A_2(k)]^2.\tag{75e}$$

From Eqs. (74) and (75) we can derive a simple expression for the quotient ζ/η of a liquid. Following Refs. 32 and 33, we obtain the shear viscosity

$$\eta=mn\lim_{\omega\to 0}\lim_{q\to 0}\frac{\omega^2}{q^2}\,\phi''_T(q;\omega)=\frac{mn(c_T^2)^2}{N_T}\tag{76a}$$

from Eqs. (31b), (27), (45), and the bulk viscosity ζ,

$$\zeta+\tfrac{4}{3}\eta=mn\lim_{\omega\to 0}\lim_{q\to 0}\frac{\omega^2}{q^2}\,\phi''_L(q;\omega)=\frac{mn(c_L^2-c_{\text{th}}^2)^2}{N_L}\tag{76b}$$

from Eqs. (44b), (42), and (45) with

$$N_{T,L}=\lim_{\omega\to 0}\lim_{q\to 0}\frac{N^{(2)}_{T,L}(q;\omega)''}{q^2}\tag{76c}$$

and

$$c_{L,T}=\lim_{q\to 0}\frac{\Omega_{L,T}(q)}{q}.\tag{76d}$$

The isothermal sound velocity c_{th} is defined in Eq. (39). Since $\lim_{\omega\to 0}L(k;\omega)=0$, we see from (74a), (75d), and (75e) that

$$N_T/N_L=\tfrac{3}{4},\tag{77}$$

within the mode-coupling approximation discussed in this paper. Combining Eqs. (76a), (76b), and (77) this means

$$\frac{\zeta}{\eta}=\frac{N_T}{N_L}\left(\frac{c_L^2-c_{\text{th}}^2}{c_T^2}\right)^2-\frac{4}{3}=\frac{3}{4}\left(\frac{c_L^2-c_{\text{th}}^2}{c_T^2}\right)^2-\frac{4}{3}.\tag{78}$$

It is not hard to convince oneself that result (78) does not depend on the solely technical approximations (56) and (57), but rather is a consequence of the two-mode approximation described in Sec. VI.

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