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Light scattering by longitudinal acoustic modes in supercooled molecular liquids II: microscopic derivation of the phenomenological equations

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Abstract. The constitutive equations for the orientational dynamics of a liquid formed of linear molecules are derived microscopically. The resulting generalised Langevin equations coincide with the phenomenological approach of Dreyfus *et al.* [1]. Formally exact expressions are given for the phenomenological coefficients and various constraints are shown to be consequences of this microscopic approach.

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1 Introduction

Light-scattering has proven to be an important tool for investigating condensed matter physics. In the field of supercooled liquids, the structural relaxation covers many decades either in the time, or in the frequency domain, the latter being accessible by *e.g.*, Fabry-Perot techniques. The measured spectra, see *e.g.* [2], reflect the slowing down of the structural relaxation upon lowering the temperature and exhibit the nontrivial power-laws and stretching effects found by other techniques, such as dielectric spectroscopy for instance. The most direct measure of the hindered motion due to the cage effect can be observed by depolarised light-scattering in the back-scattering geometry. For depolarised light-scattering performed at other scattering angles, one observes an admixture of the transverse current motion to the pure back-scattering signal. Similarly, for polarised scattering, one obtains a contribution from density fluctuations which result in the Brillouin resonance [3].

The subtlety of light-scattering lies in disentangling the dependence on frequency shift, ω, and wave-vector transfer, q, as well as on incident and outgoing polarisations. Since the wave-vector transfer, q, is small for light-scattering, a generalised hydrodynamics approach is suitable. There, the spectra are described in terms of a number of frequency-dependent memory kernels, *e.g.* viscosities. These kernels have sometimes been written on the basis of heuristic arguments. This is the case, for instance of [1], in which different previous attempts are also described and discussed. A more fundamental approach consists in deriving them from a microscopic theory through, say, a Zwanzig-Mori technique. The first such attempt was made by Andersen and Pecora [4], who, in fact, made a purely formal use of the technique, the memory kernels being eventually approximated by instantaneous interactions (Markov approximation). Much more recently, the technique was used in its full generality in [5]. Using only general symmetry considerations, [5] showed that the description of the light scattering spectra involved ten frequency-dependent functions. This large number was the price to be paid in order not to miss any effect that leads to a fluctuation of the dielectric tensor $\delta\epsilon_{ij}(\mathbf{q},t)$. In the present paper, we shall follow an intermediate route; we shall derive, for a selected set of dynamical variables, the precise form of their equations of motion, and of the corresponding relaxation kernels. Our results are valid whatever the temperature but are restricted to the case of molecular supercooled liquids formed of symmetric top molecules. Their application to the light scattering problem requires a precise form of $\delta\epsilon_{ij}(\mathbf{r},t)$; following equation (12) of Part I of this series of papers, we shall *assume* $\delta\epsilon_{ij}(\mathbf{q},t)$ to depend only on two variables of the problem, namely the density and the orientation fluctuations. Then the light-scattering problem is reduced to calculating the density-density, orientation-orientation as well as mixed correlation functions which are expressed with the help of appropriate memory kernels.

As a further simplification, we shall ignore temperature fluctuations, *i.e.* the hydrodynamic poles associated

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with energy conservation. This restriction is probably justified for Brillouin scattering experiments, since, for the scattering vectors involved, the Rayleigh line lies at so low a frequency that it is inaccessible to the usual frequency domain methods. Furthermore, for liquids, the ratio of the isobaric heat capacity to the isochoric one is close to unity and, correspondingly, the total weight of the Brillouin lines is much larger than the weight contained in the Rayleigh line; similarly, the isothermal sound velocity is close to the adiabatic one. The situation is different for time-based methods like impulsive thermal stimulated Brillouin scattering [6–8] where the heat diffusion contribution can be observed as a late stage of the relaxation signal, but this aspect of the problem will not be dealt with here.

The goal of this paper is twofold. The first is to give a microscopic derivation of the constitutive equations for the density and orientation fluctuations used in [1,3,9], and to derive some new results from this microscopic approach[1]. The second is to compare the results one can obtain from the three microscopic approaches [4,5] and the present paper, which differ in the variables taken into account and/or in the scattering model.

Consequently, this paper is organized as follows. The phenomenological equations of [9,1] are microscopically derived in Section 2. In particular, we show that the four memory functions which enter into those equations, namely the bulk viscosity, $\eta_b(t)$, the center-of-mass shear viscosity, $\eta_s(t)$, the rotational friction $\Gamma'(t)$, and the rotation-translation coupling, $\mu(t)$, can be expressed in terms of the dynamical variables of the problem, and of a reduced time evolution $R'(t)$ which does not contain the hydrodynamics poles of the problem. Similarly, the rotation-translation coupling constant, Λ', and the molecular libration frequency, ω_0, which are the other ingredients of these equations of motion, will be expressed in terms of equal time thermal averages of some variables of the problem. We make use of these microscopic expressions of the memory functions in Section 3 to derive necessary conditions on the imaginary part of their Laplace transform, and on some contributions of them. These conditions will be such that the light scattering spectra will be always positive whatever the values of the coefficients linearly coupling the density and orientation fluctuations to $\delta\epsilon_{ij}(\mathbf{q},t)$. Section 4 makes use of the same expressions of the memory functions to relate, through a Green-Kubo formalism, the correlation functions of some variables to specific combinations of the Laplace transforms of these memory functions. In particular, we shall show that $\eta_b(t)$ can be expressed as such a correlation function. The same will be true for $\eta_T(t)$, the memory function which takes into account all the retardation effects related to the propagation of the transverse phonons; this is not *a priori* obvious because $\eta_T(\omega)$ will turn out to depend in a complex way on the Laplace transforms of several memory functions defined above, as well as on Λ' and ω_0. Section 5 will compare the expressions for the light scattering intensities that can be obtained using the three sets of variables and of dielectric fluctuation models already mentioned. We shall show that the set proposed in [4] leads to awkward forms of the relaxation kernels when they are not restricted to a Markov approximation, but used for a molecular supercooled liquid. Conversely, as expected, the results obtained in Part I are a restriction of those of [5] corresponding to definite simplifying assumptions. A brief summary and some comments conclude the paper.

2 A Zwanzig-Mori derivation of the dynamical equations

We consider a dense liquid of N linear molecules of mass m at temperature T enclosed in a volume V. Statistical correlations of phase space variables in terms of the Kubo scalar product [11], $(A(t)|B) = \langle \delta A(t)^* \delta B\rangle$, $\delta A = A - \langle A\rangle$, provide the simplest information on the system's dynamics with $\langle . \rangle$ denoting canonical averaging. The thermodynamic limit, $N \to \infty$, with fixed particle density, $n = N/V$, is implied throughout. The time evolution of the observables is driven by the Liouvillian $\mathcal{L}$: $\partial_t A = \mathrm{i}\mathcal{L}A = \{H, A\}$, where H denotes the Hamilton function and $\{\,,\,\}$ the Poisson bracket. We consider the dynamics of the fluctuating molecular orientation tensor, written directly in the reciprocal space:

$$Q_{ij}(\mathbf{q}) = N^{-1/2} \sum_{\alpha=1}^{N} \left(\hat{u}_{\alpha i}\hat{u}_{\alpha j} - \frac{1}{3}\delta_{ij} \right) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha}\,, \qquad (1)$$

where the degrees of freedom of the α-th molecule are specified by a unit vector, $\hat{\mathbf{u}}_\alpha$, for the orientation and by the position of its center-of-mass, $\mathbf{R}_\alpha$. The spatial modulation of a fluctuation is characterized by its wave vector, $\mathbf{q}$, and Latin indices denote Cartesian components. The 9 components of $Q_{ij}(\mathbf{q})$ are not independent, since the orientation tensor is symmetric and traceless, reducing the number of independent components to 5. The normalisation is chosen such that the correlation functions are intensive.

Furthermore, we consider the fluctuations in the mass density:

$$\rho(\mathbf{q}) = mN^{-1/2} \sum_{\alpha=1}^{N} \exp\left(\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha\right), \qquad (2)$$

and the Cartesian components of the mass current:

$$J_i(\mathbf{q}) = N^{-1/2} \sum_{\alpha=1}^{N} P_{\alpha i} \exp\left(\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha\right)\,, \qquad (3)$$

where $\mathbf{P}_\alpha$ denotes the momentum of the αth molecule. (Equivalently, one could use the particle density $n(\mathbf{q}) = \rho(\mathbf{q})/m$ and the velocity $v_i(\mathbf{q}) = J_i(\mathbf{q})/\rho_m$, where $\rho_m = mn$ is the mean mass density.)

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[1] A very brief study along similar lines was previously reported in [10].

2.1 Static averages

The static correlation functions need to be evaluated to lowest order in q only. Since the Hamilton function respects rotational invariance, all static averages in the liquid phase have to remain unchanged under any rotation of the system: this implies that, *e.g.* correlators between, say, any second rank traceless tensor and any scalar will vanish in the long-wavelength limit (see, *e.g.* equation (7)).

The static average of the density can be expressed as:

$$(\rho(\mathbf{q})|\rho(\mathbf{q})) = m^2v^2/c^2 + \mathcal{O}(q^2)\,, \tag{4}$$

where c is, here, the isothermal sound velocity [2] defined in terms of the long-wavelength limit of the static structure factor *via* $c^2 = v^2/S(q \to 0)$, while $v = \sqrt{k_BT/m}$ denotes the thermal velocity. As usual, the current correlations read:

$$(J_i(\mathbf{q})|J_k(\mathbf{q})) = \delta_{ik}m^2v^2\,. \tag{5}$$

To lowest order in q, the equal-time correlators of the tensor variables read:

$$(Q_{ij}(\mathbf{q})|Q_{kl}(\mathbf{q})) = S^2\varDelta_{ij,kl} + \mathcal{O}(q^2)\,, \tag{6a}$$

where:

$$\varDelta_{ij,kl} = \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl}\right) \tag{6b}$$

is a fourth-rank tensor, the structure of which is governed by rotational symmetry. The long-wavelength limit of the 9×9 correlators in equation (6a) is thus determined by a single number, S^2, denoting the long-wavelength limit of the corresponding generalised structure factor, a quantity which is, as in equation (4), proportional in leading order to k_BT.

Due to rotational symmetry, the overlap of the tensor variables with the density vanishes in the long-wavelength limit according to:

$$(Q_{ij}(\mathbf{q})|\rho(\mathbf{q})) = \mathcal{O}(q^2). \tag{7}$$

We shall also need to consider the tensor currents, $\dot{Q}_{ij}(\mathbf{q}) = \mathrm{i}\mathcal{L}Q_{ij}(\mathbf{q})$, which are normalised by:

$$(\dot{Q}_{ij}(\mathbf{q})|\dot{Q}_{kl}(\mathbf{q})) = \varOmega^2\varDelta_{ij,kl} \tag{8}$$

with the characteristic frequency scale $\varOmega$; we show, in Appendix A, equation (A.11), that $\varOmega = \sqrt{2k_BT/5I}$, where I is the moment of inertia of the molecule for a rotation around an axis perpendicular to the molecule symmetry axis and passing through its center of mass. The ratio of the static averages of the orientation and the orientational current, $\omega_0 = \varOmega/S$, will determine the axial libration frequency, a frequency characteristic of the short-time expansion for the orientation correlation function (see Eq. (30c)). Hence, there is a close analogy between the set of equations (6a) and (8) and the set of density plus momentum current correlators whose ratio determines the isothermal sound velocity c characteristic of the initial decay of the density correlators; c and ω_0 are, to leading order, independent of temperature.

The correlation function between the mass current and the tensor current components has now to be considered; it is strictly equal to zero, whatever is $\mathbf{q}$:

$$(\dot{Q}_{ij}(\mathbf{q})|J_k(\mathbf{q})) = 0\,. \tag{9}$$

This is due to the fact that we put the point of reference of each molecule, $\mathbf{R}_\alpha$, at its center-of-mass, (see Appendix A for a thorough discussion of this property). The remaining static averages between the four distinguished variables $\rho(\mathbf{q}), J_i(\mathbf{q}), Q_{ij}(\mathbf{q})$ and $\dot{Q}_{ij}(\mathbf{q})$ vanish due to time reversal symmetry.

2.2 Constitutive equations

The mass conservation law relates the density to the momentum current:

$$\partial_t\rho(\mathbf{q},t) = \mathrm{i}q_kJ_k(\mathbf{q},t)\,. \tag{10}$$

Similarly, the conservation of momentum yields:

$$\partial_tJ_k(\mathbf{q},t) = \mathrm{i}q_l\varPi_{kl}(\mathbf{q},t)\,, \tag{11}$$

where $\varPi_{kl}(\mathbf{q},t)$ denotes the fluctuating momentum current tensor. At last, we can write the trivial identity:

$$\partial_t^2Q_{ij}(\mathbf{q},t) = \ddot{Q}_{ij}(\mathbf{q},t)\,, \tag{12}$$

which defines $\ddot{Q}_{ij}(\mathbf{q},t)$ as an orientational tensor force. In order to close the system, we need constitutive equations for the momentum current tensor, $\varPi_{kl}(\mathbf{q},t)$ and the orientational tensor force. This will be achieved here through generalised Langevin equations which will introduce appropriate memory kernels. Let us first introduce the projection operator, P:

$$\begin{aligned} P = {} & |Q_{kl}(\mathbf{q}))\frac{1}{2S^2}(Q_{kl}(\mathbf{q})| \\ & +|\dot{Q}_{kl}(\mathbf{q}))\frac{1}{2\varOmega^2}(\dot{Q}_{kl}(\mathbf{q})| + |\rho(\mathbf{q}))\frac{c^2}{m^2v^2}(\rho(\mathbf{q})| \\ & +|J_k(\mathbf{q}))\frac{1}{m^2v^2}(J_k(\mathbf{q})| + \mathcal{O}(q^2)\,, \end{aligned} \tag{13}$$

where the sum over repeated indices is implied. P is a projection operator because, once the symmetric character of $Q_{ij}(\mathbf{q})$ and $\dot{Q}_{ij}(\mathbf{q})$ has been taken into account, one can check that indeed $P^2 = P$. P projects onto the subspace spanned by density, mass current and the symmetric traceless parts of the orientation and the corresponding current.

The time evolution operator, $R(t) = \exp(\mathrm{i}\mathcal{L}t)$, can be exactly reformulated as

$$R(t) = R(t)P + \int_0^t R(s)P\mathrm{i}\mathcal{L}R'(t-s)\mathrm{d}s + R'(t), \tag{14}$$

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[2] See Section 4.2 for a careful discussion on the isothermal/adiabatic property.

with the reduced operator $R'(t) = Q\exp(\mathrm{i}Q\mathcal{L}Qt)Q$, where $Q = 1 - P$, and a short proof of equation (14) is given in Appendix B. The benefit of this procedure lies in the following. The time evolution operator, $R(t)$, possesses, in addition to a non-hydrodynamic part, long-lived hydrodynamic modes that are due to conservation laws. This leads to resonances in the spectra, *viz.* the Fourier transforms of the time correlation functions of all the distinguished variables for small but nonzero wave vectors. Conversely, the reduced time evolution operator, $R'(t)$, devoids the hydrodynamic singularities and correlation functions with $R'(t)$ are regular in the long-wavelength limit. The problem of handling the slow relaxation due to hydrodynamic conservation laws is treated explicitly in the low-dimensional subspace of the distinguished variables. On the contrary, the slow structural relaxation will be dealt with the help of correlation functions of $R'(t)$, the second term of the r.h.s. of equation (14), which will appear in the form of memory kernels. In the spirit of generalised hydrodynamics, the long-wavelength properties are described properly by keeping the wave-vector dependences introduced explicitly by the conservation laws, while the memory kernels can be evaluated in their long-wavelength limit.

Before deriving the constitutive equations from equation (14) for the missing quantities, $\Pi_{ij}(\mathbf{q},t)$ and $\dot{Q}_{ij}(\mathbf{q},t)$, some comments on the structure of the resulting equations in the long-wavelength limit are in order. First, from time reversal symmetry, the instantaneous coupling (first term of the r.h.s. of Eq. (14)) will be non-zero only for variables of identical time-parity. Since both the momentum current and the orientational force have even time parity, this instantaneous part will consist of density and orientation only. Second, rotational symmetry implies that the coupling of irreducible tensors of different ranks is suppressed in the long-wavelength limit by appropriate powers of the wave number. The dynamical correlators enjoy the same property, since the time evolution does not change the rank of a tensor. We shall keep only the lowest nontrivial terms in this small-wave-number expansion, as was already hinted at by keeping only the lowest order of the static averages in the preceding section.

Finally, in the second term of the r.h.s. of equation (14), one can let $\mathrm{i}\mathcal{L}$ operate on the 'bra' part of the projector, P; for instance:

$$\begin{aligned}|\rho(\mathbf{q}))\frac{c^2}{m^2v^2}(\rho(\mathbf{q})|\mathrm{i}\mathcal{L} &= -|\rho(\mathbf{q}))\frac{c^2}{m^2v^2}(\dot{\rho}(\mathbf{q})| \\ &= |\rho(\mathbf{q}))\frac{c^2}{m^2v^2}\mathrm{i}q_k(J_k(\mathbf{q})|\,; \qquad (15\text{a})\end{aligned}$$

because $R'(t-s)$ contains, on its l.h.s, a $Q = 1 - P$ factor, the contribution of $J_k(\mathbf{q})$, and similarly of $\dot{Q}_{kl}(\mathbf{q})$, are eliminated from this second term and one obtains:

$$\begin{aligned}P\mathrm{i}\mathcal{L}R'(t-s) &= -|\dot{Q}_{kl}(\mathbf{q}))\frac{1}{2\Omega^2}(\ddot{Q}_{kl}(\mathbf{q})|R'(t-s) \\ &\quad + |J_k(\mathbf{q}))\frac{\mathrm{i}q_l}{mk_BT}(\Pi_{kl}(\mathbf{q})|R'(t-s). \qquad (15\text{b})\end{aligned}$$

Let's first handle the momentum current tensor which we decompose into:

$$\Pi_{ij}(\mathbf{q},t) = \delta_{ij}p(\mathbf{q},t) + \pi_{ij}(\mathbf{q},t)\,. \qquad (16\text{a})$$

Here:

$$p(\mathbf{q},t) = [\Pi_{xx}(\mathbf{q},t) + \Pi_{yy}(\mathbf{q},t) + \Pi_{zz}(\mathbf{q},t)]/3 \qquad (16\text{b})$$

denotes the fluctuating pressure so that $\pi_{ij}(\mathbf{q},t)$ is a traceless symmetric second rank tensor. Multiplying equation (14) from the right by $p(\mathbf{q})$ yields the desired Langevin equation for the pressure fluctuation:

$$\begin{aligned}p(\mathbf{q},t) = R(t)Pp(\mathbf{q}) &+ \int_0^t R(s)P\mathrm{i}\mathcal{L}R'(t-s)p(\mathbf{q})\mathrm{d}s \\ &+ R'(t)p(\mathbf{q})\,. \qquad (17)\end{aligned}$$

The first term represents an instantaneous coupling to the distinguished variables of the projector. The second yields a retarded coupling and the last term is a rapidly fluctuating term that we shall call 'noise', *i.e.* which is uncorrelated for all times to the distinguished variables. Hence, this term can be ignored for the evaluation of the correlation functions of the distinguished variables. Nevertheless, the same term will be useful in establishing the Kubo formulae of Section 4, which will relate the time-dependent correlation functions of some variables to the memory kernels of the dynamical equations.

In order to evaluate the first term of equation (17), we need static correlations of the pressure with the distinguished variables. Time-inversion symmetry allows nonvanishing correlations only with the density and the orientational tensor. Since rotational invariance implies:

$$(\pi_{ij}(\mathbf{q})|\rho(\mathbf{q})) = \mathcal{O}(q^2), \qquad (18\text{a})$$

one can evaluate $(\rho(\mathbf{q})|p(\mathbf{q}))$ by using the conservation of momentum, equation (11), and equation (5), up to terms of order $\mathcal{O}(q^2)$:

$$\begin{aligned}(\rho(\mathbf{q})|p(\mathbf{q}))\mathrm{i}q_k &= (\rho(\mathbf{q})|p(\mathbf{q}))\mathrm{i}q_l\delta_{kl} \\ &= (\rho(\mathbf{q})|\mathrm{i}q_l\Pi_{kl}(\mathbf{q})) = (\rho(\mathbf{q})|\dot{J}_k(\mathbf{q})) \\ &= -(\dot{\rho}(\mathbf{q})|J_k(\mathbf{q})) = \mathrm{i}q_l(J_l(\mathbf{q})|J_k(\mathbf{q})) \\ &= \mathrm{i}q_km^2v^2. \qquad (18\text{b})\end{aligned}$$

This yields:

$$(\rho(\mathbf{q})|p(\mathbf{q})) = m^2v^2 + \mathcal{O}(q^2)\,. \qquad (18\text{c})$$

Conversely, rotational invariance implies, similarly to equation (7), that $(p(\mathbf{q})|Q_{ij}(\mathbf{q})) = \mathcal{O}(q^2)$. Collecting the terms appearing in P, the long-wavelength instantaneous coupling is then simply given by:

$$R(t)Pp(\mathbf{q}) = c^2\rho(\mathbf{q},t). \qquad (19)$$

Let's turn now to the retarded couplings. From equation (15b), one has to consider only the couplings of $p(\mathbf{q})$ with $\dot{Q}_{kl}(\mathbf{q})$ and with $J_k(\mathbf{q})$, and these couplings involve

$(\ddot{Q}_{kl}(\mathbf{q})|R'(t-s)|p(\mathbf{q}))$ and $(\Pi_{kl}(\mathbf{q})|R'(t-s)|p(\mathbf{q}))$. As $\ddot{Q}_{kl}(\mathbf{q})$ is traceless while $\Pi_{kl}(\mathbf{q})$ is not, the first term is $\mathcal{O}(q^2)$ while the second is of order unity. Consequently, to lowest order in q, we need to consider only the retarded coupling to $J_k(\mathbf{q})$. It is convenient to introduce the long-wavelength pressure correlator in the form:

$$(p|R'(t)|p)\,\frac{n}{k_BT} = \eta_b(t)\,. \tag{20}$$

(Here, and in the rest of the paper, omitting the wavenumber dependence indicates that the quantity is to be evaluated for $\mathbf{q}\to 0$.)

One thus obtains:

$$\begin{aligned}\mathrm{i}q_l(\Pi_{kl}(\mathbf{q})|R'(t-s)|p(\mathbf{q})) &= \\ &\mathrm{i}q_k\eta_b(t-s)k_BT/n + \mathcal{O}(q^3),\end{aligned} \tag{21}$$

once we make use of the fact that $(\pi_{kl}(\mathbf{q})|R'(t)|p(\mathbf{q}))$ is of order $\mathcal{O}(q^2)$. Introducing equation (21) into the expression of the retarded coupling and replacing, in equations (15), $J_k(\mathbf{q})$ by $mnv_k(\mathbf{q})$, one obtains the standard, retarded, constitutive equation for the fluctuating pressure:

$$\begin{aligned}p(\mathbf{q},t) = c^2\rho(\mathbf{q},t) + \mathrm{i}\int_0^t \eta_b(t-s)q_kv_k(\mathbf{q},s)\mathrm{d}s \\ +noise\,,\end{aligned} \tag{22a}$$

which is the Fourier transform of the usual equation:

$$\begin{aligned}-p(\mathbf{r},t) = -c^2\rho(\mathbf{r},t) + \int_0^t \eta_b(t-s)\ \mathrm{div}\ \mathbf{v}(\mathbf{r},s)\mathrm{d}s \\ +noise\,.\end{aligned} \tag{22b}$$

Let us now apply the same technique to $\pi_{ij}(\mathbf{q})$, the traceless part of $\Pi_{ij}(\mathbf{q})$. Multiplying equation (14) by $\pi_{ij}(\mathbf{q})$ from the right yields the Langevin equation for the traceless part of the momentum current tensor. In order to evaluate the instantaneous couplings, one needs to compute the static correlations of this tensor with the distinguished variables. Because of equation (18a) and of the time reversal symmetry, one is left with the sole evaluation of $(Q_{kl}(\mathbf{q})|\pi_{ij}(\mathbf{q}))$ for which neither tensorial nor time reversal symmetry constraints apply, in the long-wavelength limit. However from momentum conservation:

$$\begin{aligned}\mathrm{i}q_j(Q_{kl}(\mathbf{q})|\pi_{ij}(\mathbf{q})) &= (Q_{kl}(\mathbf{q})|\mathrm{i}\mathcal{L}J_i(\mathbf{q})) \\ &= -(\dot{Q}_{kl}(\mathbf{q})|J_i(\mathbf{q})),\end{aligned} \tag{23}$$

where the first equality is correct up to order $\mathcal{O}(q^2)$ due to the traceless character of $Q_{kl}(\mathbf{q})$. The r.h.s. of equation (23) is equal to zero at every order in q, equation (9), so that there is no instantaneous coupling of $\pi_{ij}(\mathbf{q})$ with the distinguished variables, in the leading order in q considered in the present paper. Hence, one is left with the evaluation of the memory kernel, which splits into two parts:

– the traceless momentum current tensor autocorrelator which, in line with equation (20), we write in the form:

$$(\pi_{kl}|R'(t)|\pi_{ij})\,\frac{n}{k_BT} = \eta_s(t)\Delta_{ij,kl}\,, \tag{24}$$

and we call $\eta_s(t)$ the time-dependent shear viscosity, as it couples the momentum current to the strain rate, see equation (28);

– the coupling of the traceless momentum current with the corresponding orientational force, that we write as:

$$\left(\ddot{Q}_{kl}|R'(t)|\pi_{ij}\right)\frac{1}{\Omega^2} = -\mu(t)\Delta_{ij,kl}\,. \tag{25}$$

For reasons similar to those used in equation (21):

$$\begin{aligned}\mathrm{i}q_l(\Pi_{kl}(\mathbf{q})|R'(t-s)|\pi_{ij}(\mathbf{q})) &= \\ \mathrm{i}q_l(\pi_{kl}(\mathbf{q})|R'(t-s)|\pi_{ij}(\mathbf{q})) &= \\ &\mathrm{i}q_l\eta_s(t-s)\frac{k_BT}{n}\Delta_{kl,ij},\end{aligned} \tag{26a}$$

and:

$$\begin{aligned}\mathrm{i}q_l\frac{J_k(\mathbf{q})}{n}\Delta_{kl,ij} &= \mathrm{i}m[q_iv_j(\mathbf{q}) + q_jv_i(\mathbf{q}) - \frac{2}{3}\delta_{ij}q_kv_k(\mathbf{q})] \\ &\equiv -m\tau_{ij}(\mathbf{q})\,,\end{aligned} \tag{26b}$$

where $\tau_{ij}(\mathbf{q})$ is the strain rate tensor, so that:

$$\begin{aligned}R(s)|J_k(\mathbf{q}))\frac{1}{mk_BT}\mathrm{i}q_l(\Pi_{kl}(\mathbf{q})|R'(t-s)|\pi_{ij}(\mathbf{q})) &= \\ -\,\tau_{ij}(\mathbf{q},s)\eta_s(t-s).\end{aligned} \tag{26c}$$

Similarly:

$$\begin{aligned}-\,R(s)|\dot{Q}_{kl}(\mathbf{q}))\frac{1}{2\Omega^2}(\ddot{Q}_{kl}(\mathbf{q})|R'(t-s)|\pi_{ij}(\mathbf{q})) &= \\ R(s)|\dot{Q}_{kl}(\mathbf{q}))\frac{1}{2}\Delta_{kl,ij}\mu(t-s)& \\ = \dot{Q}_{ij}(\mathbf{q},s)\mu(t-s).\end{aligned} \tag{27}$$

Then, the generalised constitutive equation for $\pi_{ij}(\mathbf{q},t)$ reads:

$$\begin{aligned}\pi_{ij}(\mathbf{q},t) = -\int_0^t \eta_s(t-s)\tau_{ij}(\mathbf{q},s)\mathrm{d}s \\ +\int_0^t \mu(t-s)\dot{Q}_{ij}(\mathbf{q},s)\mathrm{d}s + noise.\end{aligned} \tag{28}$$

Combining equation (22a) and equation (28), one obtains:

$$\begin{aligned}\Pi_{ij}(\mathbf{q},t) = \delta_{ij}c^2\rho(\mathbf{q},t) + \mathrm{i}\delta_{ij}\int_0^t \eta_b(t-s)q_kv_k(\mathbf{q},s)\mathrm{d}s \\ -\int_0^t \eta_s(t-s)\tau_{ij}(\mathbf{q},s)\mathrm{d}s \\ +\int_0^t \mu(t-s)\dot{Q}_{ij}(\mathbf{q},s)\mathrm{d}s + noise,\end{aligned} \tag{29}$$

which is exactly the Fourier transform of equation (3) of Part I, once one has noted that $\Pi_{ij}(\mathbf{q},t)$ is the opposite of the stress tensor, $\sigma_{ij}(\mathbf{q},t)$.

To derive an equation of motion for $\ddot{Q}_{ij}(\mathbf{q})$, we again make use of equation (14). For the instantaneous contribution, $R(t)P\ddot{Q}_{ij}(\mathbf{q})$, only the term involving the orientation in the projector P needs to be considered, the other terms dropping out for tensorial or time-reversal symmetry considerations. Since:

$$\begin{aligned}(Q_{kl}(\mathbf{q})|\ddot{Q}_{ij}(\mathbf{q})) &= -(\dot{Q}_{kl}(\mathbf{q})|\dot{Q}_{ij}(\mathbf{q}))\\ &= -\Omega^2\Delta_{kl,ij}\,, \qquad (30a)\end{aligned}$$

$$R(t)P\ddot{Q}_{ij}(\mathbf{q}) = -\omega_0^2 Q_{ij}(\mathbf{q},t)\,, \qquad (30b)$$

with the axial libration frequency:

$$\omega_0 = \Omega/S\,. \qquad (30c)$$

The evaluation of the retarded couplings proceeds along the same lines as for the momentum current tensor. Defining:

$$(\ddot{Q}_{kl}|R'(t)|\ddot{Q}_{ij})\frac{1}{\Omega^2} = \Gamma'(t)\Delta_{kl,ij}\,, \qquad (31a)$$

and:

$$\Lambda' = \frac{\Omega^2 n}{k_B T} = \frac{2n}{5I}\,, \qquad (31b)$$

one easily obtains, with the help of equations (15b), and (26b):

$$\begin{aligned}P\mathrm{i}\mathcal{L}R'(t-s)\ddot{Q}_{ij}(\mathbf{q}) &= -|\dot{Q}_{ij}(\mathbf{q}))\Gamma'(t-s)\\ &\quad+\Lambda'|\tau_{ij}(\mathbf{q}))\mu(t-s)\,, \qquad (31c)\end{aligned}$$

once one has noted that, because of the traceless character of $\ddot{Q}_{ij}(\mathbf{q})$:

$$(\Pi_{kl}|R'(t-s)|\ddot{Q}_{ij}) = (\pi_{kl}|R'(t-s)|\ddot{Q}_{ij})\,. \qquad (31d)$$

Collecting the various terms, one thus obtains:

$$\begin{aligned}\ddot{Q}_{ij}(\mathbf{q},t) &= -\omega_0^2 Q_{ij}(\mathbf{q},t) - \int_0^t \Gamma'(t-s)\dot{Q}_{ij}(\mathbf{q},s)\mathrm{d}s\\ &\quad+\Lambda'\int_0^t \mu(t-s)\tau_{ij}(\mathbf{q},s)\mathrm{d}s\\ &\quad+noise\,. \qquad (32)\end{aligned}$$

The same memory kernel, $\mu(t)$, occurs in the constitutive equation for the orientational force, equation (32), as response to a momentum gradient, and in the equation for the momentum current, equation (28), as a reaction to an orientational current. This can be considered as a general consequence of Onsager's principle, and it appears, here, naturally as the result of the use of the Zwanzig-Mori formalism. Equation (32) is, as expected, the Fourier transform of equation (4) of Part I, as briefly argued in [10]. The Zwanzig-Mori formalism thus leads to the microscopic derivation of the equations proposed, on a phenomenological basis, in [1,9]. There are, nevertheless, already two bonuses. One is the precise definitions of Λ', equation (31b), in terms of quantities *a priori* known, and of ω_0, equation (30c), which can be obtained from thermal averages of $(Q_{ij}|Q_{kl})$ and $(\dot{Q}_{ij}|\dot{Q}_{kl})$. The second bonus is the precise definitions, through $R'(t)$ of the four memory kernels, $\eta_b(t), \eta_s(t), \mu(t)$ and $\Gamma'(t)$, equations (20, 24, 25) and (31a). We shall show, in the next two sections, that these expressions allow:

- on the one hand (Sect. 3) to precisely define under which conditions, all the Brillouin intensities, derived or recalled in Part I, are positive whatever the frequency, within the scattering model used in [3];
- on the other hand (Sect. 4) to show, through Kubo's formulae, that these kernels can, directly or indirectly depending on which one is considered, be measured as correlation functions of $q \to 0$ dynamical variables.

3 The Onsager relations and the positiveness of the spectra

3.1 Summary of the light scattering results of Part I

In Part I, [3], making use of the equations of motions (Eqs. (10, 11, 29) and (32)), we gave an expression for the intensity of the VV light-scattering spectrum under the assumption that the fluctuations of the dielectric tensor could be written as the linear combination:

$$\epsilon_{ij}(\mathbf{q}) = a\delta_{ij}\rho(\mathbf{q}) + bQ_{ij}(\mathbf{q})\,, \qquad (33)$$

where a and b are phenomenological coefficients. Taking the convention that the Laplace transform of $f(t)$ would be $f(\omega) = LT[f(t)](\omega) = \mathrm{i}\int_0^\infty \mathrm{d}t f(t)\exp(-\mathrm{i}\omega t)$, this intensity was expressed (see Eq. (36), Part I) in terms of all the quantities defined in Section 2, and of $\langle|Q^0_{\perp\perp'}|^2\rangle = S^2$, see equation (6a). Using equations (30c) and (31b) which relate $\omega_0, \Lambda', \Omega$ and S, the result obtained in Part I can be cast into the form[3]:

$$\begin{aligned}I_{VV}(\mathbf{q},\omega) = \frac{1}{\omega}\mathrm{Im}\Bigg\{&-\frac{4b^2}{3}\frac{\Omega^2}{D(\omega)}\\ &+q^2\left[a+\frac{2b\Lambda'}{3mn}r(\omega)\right]^2 m^2v^2P_L(q,\omega)\Bigg\}\,, \qquad (34a)\end{aligned}$$

where $P_L(q,\omega)$ is the longitudinal phonon propagator:

$$P_L(q,\omega)^{-1} = \omega^2 - q^2c^2 - q^2\omega\eta_L(\omega)/mn\,, \qquad (34b)$$

with:

$$\begin{aligned}\eta_L(\omega) &= \eta_b(\omega) + \frac{4}{3}\left[\eta_s(\omega) - \frac{\Lambda'}{\omega}D(\omega)r(\omega)^2\right] \qquad (34c)\\ &\equiv k_L(\omega) - \frac{4}{3}\frac{\Lambda'}{\omega}D(\omega)r(\omega)^2 \qquad (34d)\\ &\equiv \eta_b(\omega) + \frac{4}{3}\eta_T(\omega)\,, \qquad (34e)\end{aligned}$$

$$D(\omega) = \omega_0^2 + \omega\Gamma'(\omega) - \omega^2\,, \qquad (35)$$

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[3] In this section, we neglect in the expression of the intensities, the $\delta(\omega)$ terms related to the $\mathrm{Im}(1/\omega)$ contributions.

$$r(\omega) = \frac{\omega\mu(\omega)}{D(\omega)}\,. \tag{36}$$

$\eta_T(t)$, defined through equation (34e) is what we shall call the transverse viscosity.

Similarly, the expression for the intensity of the VH light-scattering spectrum, already derived in [9,1] within the same model, was recalled in Part I (Eq. (48)); with the present notations, it reads:

$$I_{VH}(\mathbf{q},\omega) = \frac{b^2}{\omega}\mathrm{Im}\left\{\frac{-\Omega^2}{D(\omega)} + q^2\left[\frac{\Lambda' r(\omega)}{mn}\right]^2 \cos^2\frac{\theta}{2}m^2v^2P_T(q,\omega)\right\}, \tag{37a}$$

where θ is the scattering angle and:

$$P_T(q,\omega)^{-1} = \omega^2 - q^2\omega\eta_T(\omega)/mn \tag{37b}$$

is the transverse phonon propagator. It is convenient to separate out the angular contribution in equation (37a) by rewriting it in the form:

$$I_{VH}(\mathbf{q},\omega) = b^2\left[\sin^2\frac{\theta}{2}I_{BD}(\omega) + \cos^2\frac{\theta}{2}I_T(q,\omega)\right], \tag{37c}$$

with:

$$I_{BD}(\omega) = \frac{1}{\omega}\mathrm{Im}\left[\frac{-\Omega^2}{D(\omega)}\right], \tag{37d}$$

$$I_T(q,\omega) = \frac{1}{\omega}\mathrm{Im}\left\{\frac{-\Omega^2}{D(\omega)} + q^2m^2v^2\left[\frac{\Lambda' r(\omega)}{mn}\right]^2 P_T(q,\omega)\right\}. \tag{37e}$$

3.2 Necessary conditions on the memory kernels

In the present part of Section 3, we show some general properties of the four memory kernels $\eta_b(t), \eta_s(t), \mu(t)$ and $\Gamma'(t)$ that can be derived from their microscopic expressions. These properties are of interest for the light scattering spectra and, in particular, they are such that, when fulfilled, the spectra are positive whatever the frequency and the ratio b/a of equation (33).

Firstly, from their definitions, equations (20, 24, 25, 31a), one checks that the memory kernels are real and have even time parity. Furthermore, by taking the special linear combinations:

$$\pi_{20} = [2\pi_{zz} - \pi_{xx} - \pi_{yy}]/\sqrt{12}\,, \tag{38a}$$

$$Q_0 = [2Q_{zz} - Q_{xx} - Q_{yy}]/\sqrt{12}\,, \tag{38b}$$

$\eta_s(t)$ and $\Gamma'(t)$ can be written as auto-correlation functions similar to $\eta_b(t)$:

$$\eta_s(t) = \frac{n}{k_BT}(\pi_{20}|R'(t)|\pi_{20})\,, \tag{39a}$$

$$\Gamma'(t) = \frac{1}{\Omega^2}(\ddot{Q}_0|R'(t)|\ddot{Q}_0). \tag{39b}$$

Thus the Laplace-transforms of the memory kernels have the usual properties described, *e.g.*, in [11–13] (see also Appendix C). In particular, this Appendix shows that these Laplace transforms are analytic in the lower complex half plane and that the inequalities:

$$\mathrm{Im}\,\eta_b(\omega) \geq 0\,, \tag{40a}$$

$$\mathrm{Im}\,\eta_s(\omega) \geq 0\,, \tag{40b}$$

$$\mathrm{Im}\,\Gamma'(\omega) \geq 0\,, \tag{40c}$$

hold for all complex ω with $\mathrm{Im}\,\omega < 0$.

The mixed correlation function:

$$-\Omega^2\mu(t) = (\ddot{Q}_0|R'(t)|\pi_{20})\,, \tag{41a}$$

can be read as an off-diagonal element of the matrix correlator built on $\ddot{Q}_0$ and π_{20}. Since the imaginary part of the Laplace transform of this matrix is positive semidefinite (see Appendix C, equation (C.6)), one obtains, with the help of equation (31b), the inequality:

$$[\mathrm{Im}\eta_s(\omega)][\mathrm{Im}\Gamma'(\omega)] - \Lambda'[\mathrm{Im}\mu(\omega)]^2 \geq 0\,, \tag{41b}$$

for all ω in the lower complex half- plane. The system of inequalities equations (40, 41b) is a generalisation of Onsager's relations to finite frequencies: from the microscopic approach, one obtains that the imaginary part of the matrix of kinetic coefficients is positive definite for any frequency.

Let us mention one useful consequence. First by Fourier back-transform:

$$\begin{aligned}\Lambda'\mu(t)^2 &= \Lambda'\left[\int\frac{\mathrm{d}\omega}{\pi}\cos(\omega t)\mathrm{Im}\mu(\omega)\right]^2\\ &\leq \Lambda'\left[\int\frac{\mathrm{d}\omega}{\pi}\left|\mathrm{Im}\mu(\omega)\right|\right]^2\\ &\leq \left[\int\frac{\mathrm{d}\omega}{\pi}\mathrm{Im}\Gamma'(\omega)\right]\left[\int\frac{\mathrm{d}\omega}{\pi}\mathrm{Im}\,\eta_s(\omega)\right],\end{aligned} \tag{42a}$$

where in the last line we used equation (41b). The last relation implies that the translation-rotation coupling is bounded by:

$$\Lambda'\mu(t)^2 \leq \eta_s(t=0)\Gamma'(t=0)\,. \tag{42b}$$

3.3 Positiveness of the light scattering spectra and further relations

The four inequalities, equations (40, 41b), turn out to be sufficient to prove that the light-scattering spectra, equations (34a) and (37a), are positive for any frequency. The proof will be given for real frequencies only since the algebra greatly simplifies. By similar methods, one can extend the proof to hold for all frequencies in the lower complex half-plane. Let us first recall that if $\mathbf{A}$ is a symmetric complex matrix, then one can write

$\mathrm{Im}(\mathbf{A}^{-1}) = -[\mathrm{Im}\mathbf{A} + (\mathrm{Re}\mathbf{A})(\mathrm{Im}\mathbf{A})^{-1}(\mathrm{Re}\mathbf{A})]^{-1}$. If $\mathrm{Im}\mathbf{A}$ is a positive definite matrix, one proves that $(\mathrm{Re}\mathbf{A})(\mathrm{Im}\mathbf{A})^{-1}(\mathrm{Re}\mathbf{A})$ has the same property, so that $-\mathrm{Im}(\mathbf{A}^{-1})$ is also a positive definite matrix; in particular, its diagonal elements are positive [4]. Let us now make use of this property to prove the positiveness of the spectra, starting with the VH spectrum written as equation (37c).

First:

$$I_{BD}(\omega) = \frac{\omega_0^2 \mathrm{Im}\Gamma'(\omega)}{[\omega_0^2 - \omega^2 + \omega\mathrm{Re}\Gamma'(\omega)]^2 + [\omega\mathrm{Im}\Gamma'(\omega)]^2}, \tag{43}$$

so that $I_{BD}(\omega)$ is always positive. Second, consider the matrix:

$$\begin{bmatrix} F_T(q,\omega)/\Omega^2 & * \\ * & \omega^2 C_T(q,\omega)/(m^2v^2q^2) \end{bmatrix} = \\ -\begin{bmatrix} \omega D(\omega) & q\Omega\omega\mu(\omega)/(mv) \\ q\Omega\omega\mu(\omega)/(mv) & -\omega + q^2\eta_s(\omega)/mn \end{bmatrix}^{-1} \tag{44a}$$

(here the matrix elements we are not interested in are abbreviated by asterisks). One checks that, for real ω, the imaginary part of the matrix on the r.h.s is positive definite: indeed, its diagonal elements are positive (Eqs. (40b, 40c)) while the corresponding 2×2 determinant is proportional to the l.h.s. of equation (41b). Consequently, so does the imaginary part of the l.h.s. of equation (44a). In particular, the diagonal elements on the left-hand side are positive. After some algebra one finds that:

$$\mathrm{Im}\, F_T(q,\omega) = I_T(q,\omega)\,, \tag{44b}$$

$$\mathrm{Im}\, C_T(q,\omega) = \frac{q^2m^2v^2}{\omega}\mathrm{Im}\, P_T(q,\omega). \tag{44c}$$

As both $I_{BD}(\omega)$ and $I_T(q,\omega)$ are positive whatever ω real, the depolarised light-scattering spectrum, equation (37c) is always positive. Also, from the form of $P_T(q,\omega)$, equation (37b), the sign of $\mathrm{Im}P_T(q,\omega)$ is the same as that of $\eta_T(\omega)$; this implies:

$$\mathrm{Im}\,\eta_T(\omega) \geq 0\,. \tag{44d}$$

Thus, in spite of its intricate expression, equation (34e), one can prove that $\mathrm{Im}\eta_T(\omega)$ is always positive, a result which will be obtained again through the Green-Kubo technique in Section 4.

For the polarised spectrum, let us consider the similar matrix:

$$\begin{bmatrix} F_L(q,\omega)/\Omega^2 & \omega G_L(q,\omega)/(\Omega mvq) \\ \omega G_L(q,\omega)/(\Omega mvq) & \omega^2 C_L(q,\omega)/(m^2v^2q^2) \end{bmatrix} = \\ -\begin{bmatrix} \omega D(\omega) & \sqrt{4/3}q\dfrac{\Omega\omega\mu(\omega)}{mv} \\ \sqrt{4/3}q\dfrac{\Omega\omega\mu(\omega)}{mv} & \dfrac{c^2q^2-\omega^2}{\omega} + \dfrac{q^2k_L(\omega)}{mn} \end{bmatrix}^{-1}. \tag{45a}$$

Again, the imaginary part of the matrix on the r.h.s of equation (45a) is positive definite; its diagonal elements are positive, equations (40), while the corresponding 2×2 determinant is proportional to:

$$[\mathrm{Im}\,\Gamma'(\omega)][\mathrm{Im}\,\eta_b(\omega) + \frac{4}{3}\mathrm{Im}\,\eta_s(\omega)] - \frac{4}{3}\Lambda'[\mathrm{Im}\,\mu(\omega)]^2\,. \tag{45b}$$

This term is also positive, because of equations (41b) and (40a, 40c). Explicit evaluation of the inverse of the matrix on the r.h.s. of equation (45a) yields:

$$\mathrm{Im}F_L(q,\omega) = \frac{3}{\omega}\mathrm{Im}\Big\{\frac{-\Omega^2}{3D(\omega)} \\ + q^2\left[\frac{2}{3}\frac{\Lambda' r(\omega)}{mn}\right]^2 m^2v^2P_L(q,\omega)\Big\}, \tag{45c}$$

$$\mathrm{Im}G_L(q,\omega) = \frac{\sqrt{3}}{\omega}q^2m^2v^2\mathrm{Im}\left\{\frac{2}{3}\frac{\Lambda' r(\omega)}{mn}P_L(q,\omega)\right\}, \tag{45d}$$

$$\mathrm{Im}C_L(q,\omega) = \frac{q^2m^2v^2}{\omega}\mathrm{Im}P_L(q,\omega). \tag{45e}$$

Since the imaginary part of the matrix on the l.h.s. of equation (45a) is positive definite, this is also true for the matrix whose elements are $F_L(q,\omega), G_L(q,\omega)$ and $C_L(q,\omega)$. In consequence:

$$I_L(q,\omega) = a^2\mathrm{Im}C_L(q,\omega) + \frac{2}{\sqrt{3}}ab\,\mathrm{Im}\,G_L(q,\omega) \\ + \frac{b^2}{3}\mathrm{Im}F_L(q,\omega) \geq 0. \tag{45f}$$

Since

$$I_{VV}(q,\omega) = b^2 I_{BD}(\omega) + I_L(q,\omega)\,, \tag{45g}$$

the VV spectrum, equation (34a), is positive, whatever a and b. (Note that the same technique could be applied to the HH spectrum, equation (43) of Part I, to prove that it is also positive, whatever the scattering angle.) Equation (45e) can also be used to prove that $\mathrm{Im}\,\eta_L(\omega) > 0$, a conclusion which already resulted from equations (44d) and (40a). Let us stress that the positiveness of $I_{VV}(q,\omega)$ for any ω, whatever q, is not a trivial result as $I_L(q,\omega)$ is the sum of a q-independent term, proportional to $I_{BD}(\omega)$, and of a q-dependent term. One could naively think that $I_{VV}(q,\omega)$ could be always positive only if the same would be true for this q-dependent term. Figure 3 of Part I, [3] shows that this is not the case. In fact, though equation (41b) does not invoke q, it insures that $\mathrm{Im}\Gamma'(\omega)$ is large enough, whatever ω, for the sum of the two terms of $I_L(q,\omega)$ to be positive, independently of the value of q. A similar argument holds for the $I_{VH}(q,\omega)$ spectrum.

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[4] One easily includes the case where $\mathrm{Im}\mathbf{A}$ is not invertible due to a vanishing eigenvalue by adding an arbitrarily small imaginary multiple of the unit matrix; this simply changes the strict inequalities into weak ones. In order to avoid this complication, we shall use equations (40, 41b) as strict inequalities.

4 The Green-Kubo approach to the memory kernels

4.1 Preliminary remarks

The comparison between measured Brillouin spectra and their predicted intensities (Eqs. (34a) and (37a)) requires the knowledge of the four memory kernels $\eta_b(t), \eta_s(t), \mu(t)$ and $\Gamma'(t)$. Although microscopically well defined, those cannot be evaluated exactly, so that in practice, they are frequently taken as empirical fit functions. Whereas the correct memory kernels are guaranteed to reflect all the restrictions of the correlated motion of the translational and orientational degrees of freedom, *i.e.* automatically fulfill the relations, equations (40a, 40b, 40c) and (41b), this needs not be true for these empirical functions. Hence, one has to carefully choose their parameters so that these relations are fulfilled.

A possible intermediate approach consists in obtaining information on those memory kernels through MD calculations of some realistic model of the supercooled liquid under consideration. Because the memory kernels are $q \to 0$ limits of correlation functions of specific variables, they can, in principle, be computed from these MD calculations. Yet, these kernels, equations (20, 24, 25) and (31a), are written in terms of the reduced operator $R'(t)$. As the latter has no easy formulation, this apparently reduces drastically the value of the preceding remark. We show, in the present section, that the microscopic approach of Section 2 allows for the determination of expressions of $\eta_b(t)$, and $\eta_T(t)$, the bulk and transverse viscosities, which coincide with the usual Green-Kubo formulae: they can be directly determined as the correlation functions of variables accessible in a MD calculation.

Conversely, no such direct determination of $\Gamma'(t)$ and $\mu(t)$ is possible; their Laplace transforms, can be obtained through the computation of the Laplace transforms of the correlation functions of other dynamical variables but the determination of $\Gamma'(\omega)$ and $\mu(\omega)$ will be rather indirect, as we shall see; for technical reasons, we shall start with this second aspect and will turn, later on, to the determination of the viscosity kernels.

Let us start by recalling that, in equation (32), the 'noise term' is equal to $R'(t)\ddot{Q}_{ij}(\mathbf{q})$ so that one can rewrite this equation as:

$$\begin{aligned} R'(t)\ddot{Q}_0(\mathbf{q}) = \ddot{Q}_0(\mathbf{q},t) &+ \omega_0^2 Q_0(\mathbf{q},t) \\ &+ \int_0^t \Gamma'(t-s)\dot{Q}_0(\mathbf{q},s)\mathrm{d}s \\ &- \Lambda' \int_0^t \mu(t-s)\tau_0(\mathbf{q},s)\mathrm{d}s, \end{aligned} \tag{46}$$

with:

$$\tau_0(\mathbf{q}) = [2\tau_{zz}(\mathbf{q}) - \tau_{xx}(\mathbf{q}) - \tau_{yy}(\mathbf{q})]/\sqrt{12}. \tag{47}$$

When computing $\mu(t)$ or $\Gamma'(t)$ through equations (25, 31a), the $\mathbf{q} \to 0$ limit is taken, and $\tau_0(\mathbf{q})$ is $\mathcal{O}(q)$ (see equation (26b)); the last term of equation (46) may thus be dropped. Multiplying both sides of equation (46), from the left, by $\ddot{Q}_0$, performing a thermal average and a Laplace transform yields:

$$\begin{aligned} \Omega^2\Gamma'(\omega) &= LT[(\ddot{Q}_0|R'(t)|\ddot{Q}_0)](\omega) \\ &= (\omega_0^2 + \omega\Gamma'(\omega) - \omega^2)LT[(Q_0(t)|\ddot{Q}_0)](\omega) \\ &\quad +[\omega - \Gamma'(\omega)](Q_0|\ddot{Q}_0)\cdot \end{aligned} \tag{48a}$$

As $(\ddot{Q}_0|Q_0) = -(\dot{Q}_0|\dot{Q}_0) = -\Omega^2$, the $\Omega^2\Gamma'(\omega)$ drops out of equation (48a): $\Gamma'(\omega)$ is not directly determined by considering the 'noise term': its indirect determination is nevertheless possible through equation (48a) as:

$$LT[(Q_0(t)|\ddot{Q})](\omega) = \frac{\omega\Omega^2}{D(\omega)}\cdot \tag{48b}$$

The l.h.s. of equation (48b) can be obtained from the correlation of $Q_0(t)$ with $\ddot{Q}_0$. Nevertheless, it is simpler to write:

$$\begin{aligned} LT[(Q_0(t)|\ddot{Q}_0)](\omega) &= LT[(\ddot{Q}_0(t)|Q_0)](\omega) \\ &= -\omega^2 LT[(Q_0(t)|Q_0)](\omega) + \omega(Q_0|Q_0)\,. \end{aligned} \tag{48c}$$

Equations (48b, 48c) can be recast into the form:

$$LT[(Q_0(t)|Q_0)](\omega) = \frac{S^2}{\omega}\left[1 - \frac{\omega_0^2}{D(\omega)}\right]\cdot \tag{48d}$$

The fancy technique we have just used simply recovers equation (34) of Part I which was directly obtained from the phenomenological equations of motion. The latter have been microscopically derived in Section 2, and this derivation implied the neglect of the noise term term $R'(t)$. The above given proof of equation (48d) can be considered as a consistency check for the use of the 'noise term' to derive valuable results, a technique we shall now use to derive useful expressions for $\eta_b(t)$ and $\eta_T(t)$.

Before doing that, let us multiply the $q \to 0$ limit of equation (46), on the left, by π_{20}. Performing similar manipulations as above, one obtains:

$$\begin{aligned} -\Omega^2\mu(\omega) &= LT[(\pi_{20}|R'(t)|\ddot{Q}_0)](\omega) \\ &= D(\omega)LT[(Q_0(t)|\pi_{20})](\omega) \\ &\quad -[\omega - \Gamma'(\omega)](\pi_{20}|Q_0)\,, \end{aligned} \tag{49a}$$

where $(\pi_{20}|Q_0)$ is equal to zero, due to equations (23) and (9). This yields:

$$\mu(\omega) = -\frac{D(\omega)}{\Omega^2}LT[(Q_0(t)|\pi_{20})](\omega)\,, \tag{49b}$$

or, equivalently:

$$r(\omega) = -\frac{\omega}{\Omega^2}LT[(Q_0(t)|\pi_{20})](\omega)\,. \tag{49c}$$

It should be noted that $r(\omega)/\omega$ is of order $\mathcal{O}(\omega^{-3})$ for frequencies $\omega \gg \omega_0$; this is consistent with the 'sum rule' associated with $(Q_0|\pi_{20}) = 0$. $r(\omega)$ is the function which couples the (longitudinal and transverse) phonon propagator to the light scattering mechanism *via* the orientational part of these excitations, see equations (34a) and (37a). Equation (49c) shows that $r(t)$ can be directly obtained as the time derivative of the correlation function of $Q_0(t)$ with π_{20}, but that $\mu(t)$ is not directly accessible; it can be obtained only once $r(\omega)$ and $D(\omega)^{-1}$ have been determined by the MD calculation.

4.2 Expressions of $\eta_T(t)$ and $\eta_b(t)$ as time correlation functions

Let us now use the same 'noise term' technique to express $\eta_T(t)$ and $\eta_b(t)$ as auto-correlation functions of some dynamical variables. The 'noise term' of equation (28) is equal to $R'(t)\pi_{20}(\mathbf{q})$, and, in the same $q \to 0$ limit, this equation simplifies into:

$$R'(t)\pi_{20} = \pi_{20}(t) - \int_0^t \mu(t-s)\dot{Q}_0(s)\mathrm{d}s. \qquad (50a)$$

Multiplying this equation from the left by π_{20}, and performing the same manipulations as before yields, with the help of equation (24):

$$\frac{k_BT}{n}\eta_s(\omega) = LT[(\pi_{20}(t)|\pi_{20})](\omega) \\ -\mu(\omega)\{\omega LT[(Q_0(t)|\pi_{20})](\omega) - (Q_0|\pi_{20})\}\cdot \qquad (50b)$$

Using equations (49b), (23) and (9), equation (50b) transforms into:

$$\eta_s(\omega) = \frac{n}{k_BT}LT[(\pi_{20}(t)|\pi_{20})](\omega) + \frac{\Lambda'}{\omega}\frac{[\omega\mu(\omega)]^2}{D(\omega)}\cdot \qquad (50c)$$

From the definition of $\eta_T(t)$, equation (34e), this equation reads:

$$\eta_T(t) = \frac{n}{k_BT}(\pi_{20}(t)|\pi_{20}). \qquad (50d)$$

Equation (50d) is the link between the usual Navier-Stokes approach to the dynamics of supercooled liquids and the most sophisticated approach of the present series of papers, which takes explicitly into account the rotational motion of the molecules (the usual approach is recovered by formally putting $\mu(t) \equiv 0$). $\eta_T(\omega)$ (see equation (37b)) is the memory function which governs the transverse phonon propagator: within the Green-Kubo formalism of equation (50d), this transverse viscosity is proportional to the correlation of the traceless part of the stress tensor, π_{20}, independently of the existence of a rotation-translation coupling. In other words, the pure center-of-mass viscosity, $\eta_s(t)$, is not the quantity directly measured by the correlation function of π_{20}: $\eta_s(t)$ must be deduced from the simultaneous determination of $\eta_T(\omega), r(\omega)$ and $D(\omega)$, quantities which can all be obtained, at least in principle, as correlation functions of some properly chosen variables, as we have just shown. Equation (50d) also proves directly, see equation (44d), that $\mathrm{Im}\eta_T(\omega)$ is always positive, being the Fourier transform of a auto-correlation function.

The same type of technique can be used to determine $\eta_b(t)$. In the $q \to 0$ limit, equation (22a) reads:

$$R'(t)p = p(t) - c^2\rho(t) = R(t)[p - \rho(\rho|p)/(\rho|\rho)], \qquad (51a)$$

once equations (4) and (18c) have been taken into account, or:

$$R'(t)p = R(t)Q_np. \qquad (51b)$$

Equation (51b) introduces the variable Q_np, which is the part of the pressure which is orthogonal to the density. Because of the existence of a Q operator on the left hand side of $R'(t)$ (see Appendix B) which projects out the ρ variable:

$$(Q_np|R'(t) = (p|R'(t). \qquad (51c)$$

Thus, equation (20) can be written as:

$$\eta_b(t) = \frac{n}{k_BT}(Q_np(t)|Q_np). \qquad (51d)$$

Equation (51d) is the analog of the Green-Kubo formulation of the bulk viscosity within the usual Navier-Stokes formalism: as the rotation-translation coupling does not play a role in the bulk viscosity, this usual formulation remains exact in the more sophisticated present approach.

Here a comment is in order. Since we did not deal with energy fluctuations in the projector, the correlation function $\eta_b(t)$ decays to a non-zero constant even for times much larger than the structural relaxation time. It is therefore convenient to define a new correlation function $\tilde{\eta}_b(t)$ that vanishes at long times by an appropriate subtraction. One can work out the constant from thermodynamic considerations and find:

$$\eta_b(t) = \tilde{\eta}_b(t) + mn(\tilde{c}^2 - c^2), \qquad (52)$$

where $\tilde{c}$ is the adiabatic sound velocity. For the Laplace transforms this implies the relation:

$$\omega\eta_b(\omega) = \omega\tilde{\eta}_b(\omega) + mn(\tilde{c}^2 - c^2). \qquad (53)$$

In all correlation functions considered so far, the bulk viscosity appeared only *via* the longitudinal phonon propagator. Using the preceding equation $P_L(q,\omega)$ reads:

$$P_L(q,\omega)^{-1} = \omega^2 - \tilde{c}^2q^2 - \frac{q^2\omega}{mn}[\tilde{\eta}_b(\omega) + \frac{4}{3}\eta_T(\omega)], \qquad (54)$$

which shows that the adiabatic sound velocity governs the propagation of longitudinal phonons. To simplify notations, in the remaining part of the paper, we shall drop the tilde again and treat c as the adiabatic sound velocity and $\eta_b(t)$ as decaying to zero for long times.

5 Comparison with previous theoretical approaches

5.1 Introduction

The discussions performed in [1] and [9] have made clear that the set of equations (29) and (32) are convenient tools to describe the light scattering spectra of molecular liquids, in their normal and in their supercooled states, when those equations are supplemented by the dielectric model of equation (33). Indeed as soon as the four memory functions $\eta_b(t), \eta_s(t), \mu(t)$ and $\Gamma'(t)$ are mimicked by reasonably decreasing functions (characterised, inter alia, by relaxation times, τ, that increase with decreasing temperature) the most characteristic features of the VH spectra can be described:

– The back scattering spectrum is mostly characterised by a broad high-frequency libration mode, in the vicinity of a frequency $\omega_0/2\pi$, and by a low-frequency central mode, the line width of which decreases upon cooling. Both features can be approximately reproduced by equation (37d) with the help of the expression of $D(\omega)$ given by equation (35), as soon as a reasonable $\Gamma'(\omega)$ is chosen.

– The shape of the q-dependent part of the VH spectrum has been discussed in detail in [1]. It was shown that equations (37a) and (37b) allowed to adequately describe the existence of a Rytov dip [14] in a normal molecular liquid, this dip being a very narrow central peak, wave-number and scattering-angle dependent, which is subtracted from the much broader central mode. This dip appears in the high-temperature regime when, for all the frequencies of the central mode, $\omega\tau \ll 1$. The $\omega\tau \gg 1$ regime, which is characterised by the appearance of the Brillouin spectrum of a transverse propagative mode, is also well described by these equations, provided reasonably decreasing functions are also taken for the three remaining memory functions. In particular, the transverse sound velocity, characterised by the plateau value of $\omega\eta_T(\omega)$ at frequencies $1 \ll \omega\tau \ll \omega_0\tau$ is decreased by the coupling of the molecular orientation to the transverse phonon through $\mu(\omega)^2$. Finally, in view of the form of $\eta_L(\omega)$, see equation (34e), the same is true for the sound velocity of the longitudinal phonons.

In this section, we shall compare the results which can be obtained through equations (29) and (32) with those resulting from the two other papers (or series of papers) already mentioned which make use, in different ways, of a Mori-Zwanzig technique to describe the liquid dynamics.

5.2 The Andersen-Pecora approach

The Anderson and Pecora approach [4] was only used to study the VH spectrum of a molecular liquid at high temperature [5]. Indeed, their work was devoted to the explanation of the Rytov dip [14]; and their analysis made use of a dielectric fluctuation model identical to the one of the present paper.

In the work of Andersen and Pecora, the mass density, the mass current and a second-rank tensor proportional to Q_{ij} were the sole 'slow variables' of the theory, within the usual Zwanzig-Mori distinction between 'slow' and 'fast' variables. In other words, they implicitly assumed that $\dot{Q}_{ij}$ had a much faster dynamics than Q_{ij}, so that the former could be treated on the same footing as the other fast variables. Furthermore, they performed a Markov approximation on all the retarded interactions that needed to be taken into account, which is equivalent to taking the $\omega\tau \ll 1$ limit of the corresponding kernels.

A summary of the result of their theory, within this Markov approximation, can be found in the book of Berne and Pecora [12]. The corresponding equations read, with notations adapted to the present paper:

$$\pi_{ij}(\mathbf{q},t) = -\Gamma''_{11}\tau_{ij}(\mathbf{q},t) - \mathrm{i}\Gamma'_{12}Q_{ij}(\mathbf{q},t), \tag{55}$$

$$\dot{Q}_{ij}(\mathbf{q},t) = -\mathrm{i}\Gamma'_{21}\tau_{ij}(\mathbf{q},t) - \Gamma_{22}Q_{ij}(\mathbf{q},t). \tag{56}$$

Here, the kinetic coefficients $\Gamma''_{11}, \Gamma_{22}$ are real quantities, whereas $\Gamma'_{12}, \Gamma'_{21}$ are purely imaginary, and are related by Onsager's principle. Equation (55) makes it clear that $\pi_{ij}(\mathbf{q},t)$ depends, here, linearly on $Q_{ij}(\mathbf{q},t)$, and not on its time derivative, as is the case in equation (28), while equation (56) does not contain a second time derivative of $Q_{ij}(\mathbf{q},t)$, contrary to equation (32).

The form of the Zwanzig-Mori technique, see equation (14), used in the present paper allows to derive precise expressions for the three relaxation kernels associated with the variables of the problem (time dependent generalisations of $\Gamma''_{11}, \Gamma'_{12}$ and Γ_{22}), in terms of a reduced time evolution operator. Calculating from the corresponding equations of motion the VH spectrum and comparing the results with equations (37d, 37e), one can express the three Andersen-Pecora kernels as functions of $\eta_s(\omega), \mu(\omega), \Gamma'(\omega), \Lambda'$ and ω_0. One can thus study their $\omega\tau \ll 1$ and $\omega\tau \gg 1$ regimes. This study will show that the $\omega\tau \ll 1$ limit gives reasonable results, which are, as expected, in line with the Andersen-Pecora Markov approximation. Conversely, the $\omega\tau \gg 1$ limit yields a complicated behaviour for the same three kernels which cannot be easily modeled. This will make the Andersen-Pecora method inappropriate for the study of a molecular supercooled liquid, as we shall now see.

Indeed, using the same technique as in Section 2, one can derive the equations of motion related to $\Pi_{ij}(\mathbf{q},t)$ and $Q_{ij}(\mathbf{q},t)$ when one restricts the variables to the Anderson-Pecora set. This means that, *e.g.* the projection operator P of equation (13) has been replaced by:

$$\begin{aligned}\hat{P} = |Q_{kl}(\mathbf{q}))\frac{1}{2S^2}(Q_{kl}(\mathbf{q})| + |\rho(\mathbf{q}))\frac{c^2}{m^2v^2}(\rho(\mathbf{q})|\\ +|J_k(\mathbf{q}))\frac{1}{m^2v^2}(J_k(\mathbf{q})|\,.\end{aligned} \tag{57}$$

$\hat{P}$ leads to the new orthogonal projector $\hat{Q} = 1 - \hat{P}$, in terms of which a new reduced time evolution operator $\hat{R}(t)$ can be defined. One then finds that the equation for $p(\mathbf{q},t)$, equation (22a), is not modified, except for the change of $R'(t)$ into $\hat{R}'(t)$, which formally changes $\eta_b(t)$ into $\hat{\eta}_b(t)$. Evaluating the corresponding Green-Kubo relation reveals that $\hat{\eta}_b(t) = \eta_b(t)$. Since the pressure fluctuations are irrelevant for the VH spectrum discussed in [4],

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[5] We shall not discuss here the papers of Keyes and Kivelson [J. Chem. Phys. **54**, 1786 (1971), *ibid.* **56**, 1057 (1972)] which are, basically, along the same line.

we do not discuss further those aspects. Conversely, the equation for $\pi_{ij}(\mathbf{q},t)$ now turns out to be:

$$\pi_{ij}(\mathbf{q},t) = -\int_0^t \hat{\eta}_s(t-s)\tau_{ij}(\mathbf{q},s)\mathrm{d}s + \int_0^t \lambda(t-s)Q_{ij}(\mathbf{q},s)\mathrm{d}s + noise, \quad (58)$$

$\hat{\eta}_s(t)$ being the complete analog of $\eta_s(t)$. Equation (58) contains a linear term in $Q_{ij}(\mathbf{q},t)$, as in equation (55), and not in $\dot{Q}_{ij}(\mathbf{q},t)$, as was case for equation (28) while the corresponding retarded interaction is expressed by:

$$(\dot{Q}_{ij}|\hat{R}'(t)|\pi_{kl})\frac{1}{S^2} = -\lambda(t)\Delta_{ij,kl}\,, \quad (59)$$

where $\dot{Q}_{ij}$ and π_{kl} are respectively odd and even with respect to time inversion; thus $\lambda(t)$ is an odd function of t, contrary to all the memory functions considered up to now in the present paper. The most important change arises, nevertheless, from the fact that the equation of motion for $Q_{ij}(\mathbf{q},t)$ has to be derived from:

$$\partial_t Q_{ij}(\mathbf{q},t) = \dot{Q}_{ij}(\mathbf{q},t)\,, \quad (60)$$

an equation which replaces equation (12). A calculation similar in every respect to the one performed below equation (29) yields:

$$\dot{Q}_{ij}(\mathbf{q},t) = -\frac{\Lambda'}{\omega_0^2}\int_0^t \lambda(t-s)\tau_{ij}(\mathbf{q},s)\mathrm{d}s - \int_0^t M(t-s)Q_{ij}(\mathbf{q},s)\mathrm{d}s + noise, \quad (61)$$

with:

$$(\dot{Q}_{ij}|\hat{R}'(t)|\dot{Q}_{kl})\frac{1}{S^2} = M(t)\Delta_{ij,kl}. \quad (62)$$

Equations (58) and (61) are, obviously, the non-Markovian form of equations (55) and (56). Ignoring temperature fluctuations, the previous relations are exact, and allow us to relate the memory kernels $M(\omega), \hat{\eta}_s(\omega), \lambda(\omega)$ to the ones already used in this paper by deriving from equations (58,61), through the same methods as used in [1], the expression of the VH spectrum and comparing it with equation (48) of Part I. For $M(\omega)$, this can be done by simply computing the correlation function of $Q_{\perp\perp'}$ which is responsible for the pure back-scattering spectrum (see Part I for a definition of the geometry used). Solving equation (61) in this simple case yields:

$$LT[(Q_{\perp\perp'}(\mathbf{q},t)|Q_{\perp\perp'}(\mathbf{q}))](\omega) = \frac{S^2}{\omega - M(\omega)}\cdot \quad (63)$$

Comparison with equation (34) of Part I, with the help of equation (6a), leads to the relation between $\Gamma'(\omega)$ and $M(\omega)$:

$$M(\omega) = \frac{\omega_0^2}{\omega - \Gamma'(\omega)}\cdot \quad (64)$$

In order to gain some insight into the Markov approximation, *a priori* valid at high temperatures, let us discuss the properties of $M(\omega)$ upon cooling the system. To simplify the discussion, we consider a Maxwell model for $\Gamma'(\omega)$:

$$\Gamma'(\omega) = \mathrm{i}\gamma + \frac{\mathrm{i}\Gamma_0^2\tau}{1+\mathrm{i}\omega\tau}, \quad (65)$$

which mimics its frequency dependence for frequencies much lower than typical liquid frequencies, *i.e.* for $\omega \ll \omega_0$. Then, all the fast processes are hidden in a weakly temperature-dependent background, $\mathrm{i}\gamma$, whereas the temperature-sensitive structural relaxation is modeled by a decreasing exponential in the time domain, corresponding to a temperature insensitive amplitude, Γ_0^2, and a relaxation time, τ, that increases by orders of magnitude upon supercooling the liquid.

At high temperature, *i.e.* for $\omega\tau \ll 1$, under the possible conditions $\omega, \gamma, \omega_0 \ll \Gamma_0^2\tau$, which simply imply that even at high temperatures $\Gamma_0^2\tau$ is substantially larger than the width of the central peak, equation (37d), one obtains:

$$M(\omega) \simeq \mathrm{i}\frac{\omega_0^2}{\Gamma_0^2\tau}\cdot \quad (66)$$

This is the Andersen-Pecora result in its Markov approximation $M(\omega) = \mathrm{i}\Gamma_{22}$ with $\Gamma_{22} \sim \tau^{-1}$. Conversely, at low temperature, and under the same conditions, $M(\omega)$ will be approximated by:

$$M(\omega) \simeq \frac{-\omega_0^2\omega}{\Gamma_0^2 + \mathrm{i}\omega\gamma} \simeq -\frac{\omega_0^2\omega}{\Gamma_0^2}\,; \quad (67)$$

at low frequencies, $M(\omega)$ is a real quantity proportional to ω and independent of the relaxation time. The vanishing of the imaginary part of $M(\omega)$ at low frequencies implies that the area of $M(t)$ cancels at low temperatures. Whereas the shape of $M(t)$ is clearly model dependent, the cancellation of areas of $M(t)$ is a general feature of supercooled liquids. Contrary to $\Gamma'(t)$, there is no step process in $M(t)$ with a diverging time scale upon cooling. It is thus fruitless to try to model the temporal evolution of $M(t)$ since the common features of an increasing structural relaxation time are masked in this approach.

We can similarly evaluate the Andersen-Pecora memory kernels $\hat{\eta}_s(\omega)$, and $\lambda(\omega)$ by solving the dynamics for the variable $Q_{\perp\parallel}(\mathbf{q},t)$ that also contributes to the VH scattering. Using the methods of [1], one obtains:

$$LT[(Q_{\perp\parallel}(\mathbf{q},t)|Q_{\perp\parallel}(\mathbf{q}))](\omega) = \frac{S^2}{\omega - M(\omega)} - \left[\frac{\Lambda'}{mn\omega_0^2}\frac{\lambda(\omega)}{\omega - M(\omega)}\right]^2 \frac{q^2m^2v^2}{\omega - q^2\eta_T(\omega)/mn}, \quad (68)$$

with the transverse viscosity given by:

$$\eta_T(\omega) = \hat{\eta}_s(\omega) - \frac{\Lambda'}{\omega_0^2}\frac{\lambda(\omega)^2}{\omega - M(\omega)}\cdot \quad (69)$$

A comparison between the second term of the r.h.s of equations (68) and (37e) yields the relation between the two sets of memory kernels:

$$\lambda(\omega) = -\mathrm{i}\frac{\omega_0^2\mu(\omega)}{\omega - \Gamma'(\omega)} = -\mathrm{i}\mu(\omega)M(\omega), \qquad (70)$$

$$\hat{\eta}_s(\omega) = \eta_s(\omega) + \frac{\Lambda'\mu(\omega)^2}{\omega - \Gamma'(\omega)} \qquad (71a)$$

$$= \eta_s(\omega) + \frac{\Lambda'}{\omega_0^2}\mu(\omega)^2 M(\omega)\,. \qquad (71b)$$

The high-temperature limit of $M(\omega)$, equation (66), yields, with a Debye model for $\mu(\omega)$ and $\eta_s(\omega)$, the Markov limits obtained in [4]: $\lambda(\omega)$ becomes an imaginary number independent of τ, while $\hat{\eta}_s(\omega \to 0)$ is the sum of two terms, both imaginary and proportional to the relaxation time. One originates from $\eta_s(\omega \to 0)$, while the second, negative, is the $\omega \to 0$ limit of $\Lambda'\mu(\omega)^2 M(\omega)/\omega_0^2$; this explains why, in the Andersen-Pecora approach, the viscosity, $-\mathrm{i}\eta_s(\omega \to 0)$, is the sum of two positive terms.

Conversely, the difficulty of an *a priori* modeling of $M(\omega)$ transfers to the two other memory kernels, $\hat{\eta}_s(\omega)$ and $\lambda(\omega)$. This explains why a naïve modeling by simple, Debye-like, relaxation functions, consistent both with the high-temperature Markov results and the different time reversal symmetries of the kernels, is unable to yield correct physical results in the supercooled regime. Appendix D shows, indeed, that the low-temperature limit of such an attempt leads to the existence of transverse propagative modes coupled to molecular orientation motions, but this coupling increases the sound velocity instead of decreasing it.

Summarizing this part, we have shown that a Mori-Zwanzig procedure as applied by Andersen and Pecora [4] allows to derive constitutive equations through which the light scattering problem can be properly formulated as long the frequency dependence is kept on a formal level. Conversely, when one expresses these memory kernels in terms of those obtained in Section 2, one discovers that their modeling as time-dependent memory kernels is extremely difficult. This problem can be circumvented, if one models them directly, as inspired by equations (64, 70, 71a), but this procedure is equivalent to considering $\Gamma'(\omega)$, $\mu(\omega)$, and $\eta_s(\omega)$ as fundamental quantities.

5.3 Comparison with the general expressions for light scattering

The expressions for the VV and VH intensities obtained in Part I and discussed again in Section 4, equations (34a) and (37a), have been obtained under the physical assumption that the fluctuations of the local dielectric tensor, $\delta\epsilon_{ij}(\mathbf{q},t)$, could be expressed through equation (33), *i.e.* depend, in first order, only on the density and the orientational fluctuations. Conversely, the expressions obtained in [5] did not make use of a specific form for $\delta\epsilon_{ij}(\mathbf{q},t)$. We shall show, in this last part of Section 5, that those two expressions are, indeed, a specialization of the general results obtained in [5]. We also discuss the respective merits of these two complementary approaches.

The basic idea of [5] was to express the finite wavenumber fluctuations of the dielectric tensor in terms of the long-wavelength limit of the two special linear combinations:

$$s_{00}(\mathbf{q}) = [\epsilon_{xx}(\mathbf{q}) + \epsilon_{yy}(\mathbf{q}) + \epsilon_{zz}(\mathbf{q})]/3\,, \qquad (72a)$$

$$t_{20}(\mathbf{q}) = [2\epsilon_{zz}(\mathbf{q}) - \epsilon_{xx}(\mathbf{q}) - \epsilon_{yy}(\mathbf{q})]/\sqrt{12}\,. \qquad (72b)$$

Within the present light-scattering model, these two quantities reduce to the contributions of the density and the orientation fluctuations, respectively:

$$s_{00}(\mathbf{q}) = a\rho(\mathbf{q})\,, \qquad (73a)$$

$$t_{20}(\mathbf{q}) = bQ_0(\mathbf{q})\,. \qquad (73b)$$

In [5], the VV spectrum was expressed, using notations that have been adapted to the current paper, as:

$$\begin{aligned} I_{VV}(\mathbf{q},\omega) = \mathrm{Im}\Bigg\{ &\mathcal{S}(\omega) + \frac{4}{3}\mathcal{T}(\omega) + \frac{m^2v^2}{c^2\omega}\left(\frac{\partial s_{00}}{\partial\rho}\right)_T^2 \\ &+ \left[\left(\frac{\partial s_{00}}{\partial\rho}\right)_T - \omega a_{VV}(\omega)\right]^2 [LT[(\rho(\mathbf{q},t)|\rho(\mathbf{q}))](\omega) \\ &- \frac{m^2v^2}{c^2\omega}\Bigg] + \xi(\omega)^2 LT[(\Theta(\mathbf{q},t)|\Theta(\mathbf{q}))](\omega) \\ &+ 2\xi(\omega)\left[\left(\frac{\partial s_{00}}{\partial\rho}\right)_T - \omega a_{VV}(\omega)\right] LT[(\rho(\mathbf{q},t)|\Theta(\mathbf{q}))](\omega)\Bigg\}. \end{aligned} \qquad (74)$$

Similarly, the VH intensity was expressed as:

$$\begin{aligned} I_{VH}(\mathbf{q},\omega) = \mathrm{Im}\Bigg\{ &\mathcal{T}(\omega) \\ &+ \frac{q^2}{\omega}\cos^2\frac{\theta}{2}[\omega a_{VH}(\omega)]^2 m^2v^2 P_T(q,\omega)\Bigg\}. \end{aligned} \qquad (75)$$

The transverse phonon propagator is given directly in terms of the transverse viscosity, $\eta_T(\omega)$, as in equation (37b). As already alluded in the Introduction, the price to be paid for these two general results was the introduction of ten frequency-dependent quantities, namely, the scalar background spectrum $\mathcal{S}(\omega)$, the tensor background spectrum $\mathcal{T}(\omega)$, the two Pockels' coupling functions, $a_{VV}(\omega)$ for polarised and $a_{VH}(\omega)$ for depolarised scattering, and the temperature coupling $\xi(\omega)$, while the three hydrodynamic correlation functions related to the density, $\rho(\mathbf{q})$, and kinetic temperature, $\Theta(\mathbf{q})$, were expressed in terms of the transverse viscosity, $\eta_T(\omega)$, the longitudinal viscosity, $\eta_L(\omega)$, the heat conductivity, $\lambda(\omega)$, the dynamic specific heat, $c_V(\omega)$, and the tension coefficient, $\beta(\omega)$, respectively. The singular hydrodynamic behavior manifested itself explicitly in the three correlation functions just mentioned.

Let us relate those quantities to the one derived in the present paper and demonstrate numerous simplifications that occur in the density-and-orientational-decay-channels-only model. First, the temperature coupling is given by:

$$\xi(\omega) = \xi\frac{c_V(\omega)}{c_V} - \frac{c_V(\omega)}{c_V^0}\omega\frac{LT[(\tilde{Q}s_{00}(t)|\tilde{Q}e^P)](\omega)}{k_B T^2}, \quad (76)$$

where ξ is a linear function of the energy fluctuations in the $q \to 0$ limit and $\tilde{Q} = 1 - \tilde{P}$ is a projection operator orthogonal to the standard Kadanoff-Martin projector, $\tilde{P}$. The latter projects, in [5], on five variables, $\rho(\mathbf{q})$ and $\mathbf{J}(\mathbf{q})$, as in the present paper, and on the temperature fluctuations, $T(\mathbf{q})$, not introduced here, and proportional to the energy fluctuations, $e(\mathbf{q})$.

$$\begin{aligned}\tilde{P} = |\rho(\mathbf{q}))\frac{c^2}{m^2v^2}(\rho(\mathbf{q})| + |J_k(\mathbf{q}))\frac{1}{m^2v^2}(J_k(\mathbf{q})| \\ +|T(\mathbf{q}))\frac{c_V}{k_BT^2}(T(\mathbf{q})| + \mathcal{O}(q^2).\end{aligned} \quad (77)$$

Because energy fluctuations are not considered in the present approach, $\xi \equiv 0$. Also, $s_{00}(\mathbf{q})$ is proportional to $\rho(\mathbf{q})$, equation (73a), so that $\tilde{Q}s_{00} = 0, \xi(\omega) \equiv 0$.

Second, in [5], the scalar and the tensor background spectra are defined as:

$$\begin{aligned}\mathcal{S}(\omega) = -\frac{k_BT^2\xi(\omega)^2}{\omega c_V(\omega)} + \frac{k_BT^2}{\omega c_V}\xi^2 \\ +LT[(s_{00}(t)|\tilde{Q}s_{00})](\omega),\end{aligned} \quad (78a)$$

$$\mathcal{T}(\omega) = LT[(t_{20}(t)|t_{20})](\omega). \quad (78b)$$

The preceding results imply:

$$\mathcal{S}(\omega) \equiv 0, \quad (79a)$$

$$\mathcal{T}(\omega) = b^2LT[(Q_0(t)|Q_0)](\omega). \quad (79b)$$

Third, from equation (73a), $(\partial s_{00}/\partial\rho)_T = a$ while the dynamic Pockels' coupling functions are given, in [5], as:

$$a_{VH}(\omega) = LT[(\pi_{20}(t)|t_{20})](\omega)/m^2v^2, \quad (80a)$$

$$\begin{aligned}a_{VV}(\omega) = \frac{2}{3}a_{VH}(\omega) + \frac{\beta(\omega)T\xi(\omega)}{\omega c_V(\omega)} - \frac{\beta T\xi}{\omega c_V} \\ -LT[(p(t)|\tilde{Q}s_{00})](\omega)/m^2v^2.\end{aligned} \quad (80b)$$

As $\xi(\omega), \xi$ and $\tilde{Q}s_{00}$ are all equal to zero, one obtains:

$$a_{VV}(\omega) = \frac{2}{3}a_{VH}(\omega). \quad (80c)$$

Let us look at the results for the VV light scattering intensities. One observes that terms involving dynamic correlation functions of the kinetic temperature evaluate to zero. One is thus left with the density correlation functions which, if energy fluctuations are ignored, reads in agreement with equation (29a) of Part I:

$$\begin{aligned}LT[(\rho(\mathbf{q},t)|\rho(\mathbf{q}))](\omega) = \\ \frac{m^2v^2}{\omega}\left[\frac{1}{c^2} + \frac{q^2}{\omega^2 - q^2[c^2 + \omega\eta_L(\omega)/mn]}\right].\end{aligned} \quad (81)$$

Equation (81) allows to group the terms proportional to m^2v^2 and one ends up with:

$$\begin{aligned}I_{VV}(\mathbf{q},\omega) = \mathrm{Im}\Bigg\{\frac{4}{3}\mathcal{T}(\omega) + \frac{a^2m^2v^2}{c^2\omega} \\ + \left[a - \frac{2}{3}\omega a_{VH}(\omega)\right]^2\frac{m^2v^2q^2/\omega}{\omega^2 - q^2c^2 - q^2\omega\eta_L(\omega)/mn}\Bigg\},\end{aligned} \quad (82)$$

$\mathcal{T}(\omega)$ and $a_{VH}(\omega)$ being defined through equations (79b) and (80a), respectively. Furthermore in agreement with equation (48d) and equation (34) of Part I, $\mathcal{T}(\omega)$ can be written as

$$\mathcal{T}(\omega) = b^2\frac{S^2}{\omega}\left(1 - \frac{\omega_0^2}{D(\omega)}\right), \quad (83)$$

which is here a simple definition of $\omega_0^2/D(\omega)$. In the same manner, from equations (80a, 73b, 49c, 31b), one obtains:

$$-\omega a_{VH}(\omega) = \frac{b\Lambda'}{mn}r(\omega), \quad (84)$$

where, similarly to the case of $\omega_0^2/D(\omega), r(\omega)$ is simply defined through the Laplace transform of $(\pi_{20}(t)|t_{20})$, equation (80a). One sees that equation (82) has been cast into a form identical to equation (34a), while a similar identification holds between equation (75) and equation (37a).

The reduction of equations (74) and (75) to equations (34a) and (37a) shows the comparative interests of the approach of [5] and of the present one. The method of [5] does not depend on the system under study and allows for temperature (or energy) fluctuations: as soon as the scattering model, equation (33), is introduced, and the energy fluctuations are neglected, the equations of [5] reduce to those of the present model, depending on four functions $\mathcal{T}(\omega), a_{VH}(\omega), \eta_L(\omega)$ and $\eta_T(\omega)$, which are undetermined in this framework. Conversely, the more restricted approach developed in the present series of papers gives precise definitions of these four quantities in terms of more fundamental memory kernels $\Gamma'(\omega), \mu(\omega), \eta_b(\omega)$ and $\eta_s(\omega)$, and also gives the relationships through which the four first functions are related to the second ones *via* the constants Λ' and ω_0 for which definitions can be given. Yet the restricted approach has its own price to be paid: one has to start the whole work again if additional variables need to be introduced into the model.

6 Summary and final remarks

In a liquid formed of rigid molecules, the dynamics of the system has to take into account both the motion of the molecular centers of mass and the orientational motion of the molecules. In the long-wavelength limit, the first one gives rise to the hydrodynamic modes, to which the orientational motions are partly coupled, while this orientational dynamics also gives rise to motions that are wave-vector independent in the same limit. [9,1] and [3] proposed a phenomenological set of equations to describe this coupled dynamics in the case of linear molecules, and a phenomenological expression for the local fluctuation of the dielectric tensor: this fluctuation was expressed in terms of the density and orientational variables entering the dynamical equations.

The original objective of the present paper was twofold – one was to provide a complete, microscopic, derivation of these dynamical equations; the second was to compare the expression for the light scattering intensities resulting from these equations with those obtained with two other approaches [4,5].

Both goals have been achieved. On the one hand, the use of a Zwanzig-Mori formalism has allowed to completely derive these dynamical equations; in the course of this derivation, we have obtained the microscopic expressions of the two parameters and of the four memory functions entering those equations. On the other hand, the comparison with the two other Zwanzig-Mori approaches has also brought important results. One of them is related to the choice of Andersen and Pecora [4] of not including $\dot{Q}_{ij}(\mathbf{q})$ in their set of variables. This choice, which is sufficient at high temperature, when the Markov approximation can be made on the corresponding memory kernels, turns out to be inappropriate for the study of supercooled liquids: at low temperatures $\dot{Q}_{ij}(\mathbf{q},t)$ is as 'slow' a variable as $Q_{ij}(\mathbf{q},t)$. The most important consequence of the absence of $\dot{Q}_{ij}(\mathbf{q},t)$ in the set of selected variables is the change in the equation of motion of $Q_{ij}(\mathbf{q},t)$: it transforms it from a second order differential equation with a memory kernel acting on $\dot{Q}_{ij}(\mathbf{q})$ into a first order differential equation with a memory kernel acting on $Q_{ij}(\mathbf{q})$. The formal neglect of $\dot{Q}_{ij}(\mathbf{q})$ in the set of 'slow' variables is possible but the corresponding memory kernels have a non-trivial time evolution, which cannot be predicted without using the results of the present theory. The second result is that the present formulation of the theory is, indeed, a reduction of the general theory of [5] which can be derived from simplifications consistent with the phenomenological model of the dielectric tensor, and with the restricted set of variables used here.

The present Zwanzig-Mori approach also led to two important byproducts. One is the existence of conditions, equations (40, 41b), which have to be fulfilled by the Laplace transforms of the memory functions. These conditions are important because they are sufficient to insure that all the light scattering intensities will be positive, whatever the frequency, within the phenomenological model of the fluctuations of the dielectric tensor used here. A second byproduct is the set of Green-Kubo formulae we have derived in Section 4.3: we have shown that the correlation functions of some variables, not experimentally accessible by light scattering techniques, but which may be numerically obtained from MD computations of models of these molecular (supercooled) liquids, give access to definite combinations of the Laplace transforms of these memory functions. This is a possible way of obtaining an information on them.

Some results of the present paper provide a direct help to the experimentalists, when analysing the light scattering spectra of molecular supercooled liquids formed of rigid linear molecules, or of molecular liquids for which such an approximations is reasonable. One of them is the already mentioned necessary conditions on the memory functions. A second is that these functions exhibit the characteristic features of structural relaxation, *e.g.* rapidly increasing relaxation times upon lowering the temperature. Yet, the functional form of these memory kernels remains undetermined within this framework, except for the conventional analytic properties. Usually it is not possible to directly extract the frequency dependence of of the memory kernels from light-scattering experiments. Rather one has to rely on empirical functions and adjust a small number of parameters to obtain a reasonable description of experimental data. As a further step, one can supplement these empirical functions with features inspired from theoretical considerations, *e.g.* the fast β-process as discussed in the context of mode-coupling theory [2].

Time resolved optical spectroscopy of the same molecular liquids has recently developed into an important tool; this is particularly the case for the impulsive stimulated thermal scattering technique (ISTS) mentioned in the Introduction [6–8]. The most important part of the new information obtained from these measurements is derived from the coupling of the heat diffusion process with the stimulated hydrodynamics mode. We have not incorporated, in the microscopic derivation of the dynamical equations, a local temperature as a pertinent variable, contrary to what has been done in [5]. In order to properly exploit the information contained in these ISTS experiments, the whole procedure developed in the present paper has to be repeated with the inclusion of the variable(s) describing the local temperature of the supercooled liquid. It has to be found if this generalisation will require more memory functions than could be anticipated from a phenomenological extension of the full set of Navier-Stokes equations to the case of a supercooled (memory function aspect) molecular (inclusion of the rotation-translation coupling and of the molecular orientation dynamics) liquid [15].

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Appendix A: Static averages

The Hamilton function of identical, interacting, symmetric tops reads:

$$H = \sum_{\alpha} T_{\alpha} + V(\{\mathbf{R}_{\alpha}, \phi_{\alpha}, \Theta_{\alpha}\})\,, \qquad \text{(A.1)}$$

where the kinetic energy of the α-th molecule is given by:

$$T_\alpha = \frac{\mathbf{P}_\alpha^2}{2m} + \frac{(p_{\alpha\phi} - p_{\alpha\psi}\cos\Theta_\alpha)^2}{2I\sin^2\Theta_\alpha} + \frac{p_{\alpha\Theta}^2}{2I} + \frac{p_{\alpha\psi}^2}{2I'} \cdot \quad \text{(A.2)}$$

Here $\mathbf{R}_\alpha, \phi_\alpha, \Theta_\alpha, \psi_\alpha$ denote the center-of mass position and the Euler angles of the molecule following the definition of [16], and $\mathbf{P}_\alpha, p_{\alpha\phi}, p_{\alpha\Theta}, p_{\alpha\psi}$ the corresponding canonical momenta. The moments of inertia are denoted by I, I' for rotation perpendicular to and around the molecule's axis of symmetry. The potential energy of the interacting molecules is denoted by V. Note that, due to the symmetry, the interaction does not depend on the Euler angles ψ_α.

The orientational current, $\dot{Q}_{ij}(\mathbf{q}) = \mathrm{i}\mathcal{L}Q_{ij}(\mathbf{q}) = \{H, Q_{ij}(\mathbf{q})\}$, then splits naturally into two parts:

$$\dot{Q}_{ij}(\mathbf{q}) = N^{-1/2}\sum_{\alpha=1}^{N} \frac{\mathrm{i}\mathbf{q}\cdot\mathbf{P}_\alpha}{m}\left(\hat{u}_{\alpha i}\hat{u}_{\alpha j} - \frac{1}{3}\delta_{ij}\right)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha} + N^{-1/2}\sum_{\alpha=1}^{N}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha}\mathrm{i}\mathcal{L}\hat{u}_{\alpha i}\hat{u}_{\alpha j}, \quad \text{(A.3)}$$

where the first term corresponds to the translational motion of the center of mass and the second term describes molecular reorientations.

By definition:

$$(A(\mathbf{q})|B(\mathbf{q})) = \int \mathrm{d}\Gamma \mathrm{e}^{-H/k_BT}\delta A(\mathbf{q})^*\delta B(\mathbf{q}), \quad \text{(A.4)}$$

where $\mathrm{d}\Gamma = \prod_\alpha \mathrm{d}\mathbf{R}_\alpha \mathrm{d}\phi_\alpha \mathrm{d}\Theta_\alpha \mathrm{d}\psi_\alpha \mathrm{d}\mathbf{P}_\alpha \mathrm{d}p_{\alpha\phi}\mathrm{d}p_{\alpha\Theta}\mathrm{d}p_{\alpha\psi}$ denotes the canonical phase space volume element. Let us compute $(\dot{Q}_{ij}(\mathbf{q})|J_k(\mathbf{q}))$. In this thermal average appear two types of integrals (see equation (A.3)): one involving $(\mathbf{q}\cdot\mathbf{P}_\alpha)P_{\beta k}$, and the second $(\mathrm{i}\mathcal{L}\hat{u}_{\alpha i}\hat{u}_{\beta j})P_{\beta k}$. As

$$\mathrm{i}\mathcal{L}\hat{u}_{\alpha i}\hat{u}_{\beta j} = \left\{\sum_\gamma T_\gamma, \hat{u}_{\alpha i}\hat{u}_{\beta j}\right\} \quad \text{(A.5)}$$

involves only the angular variables, the only part dependent on the linear momentum in the second terms reads (*c.f.* Eqs. (A.1) and (A.2)):

$$\int \mathrm{e}^{-P_{\beta_k}^2/(2mk_BT)}P_{\beta k}dP_{\beta k} = 0. \quad \text{(A.6)}$$

One is thus left with the contributions of the first term. They read:

$$\begin{aligned}(\dot{Q}_{ij}(\mathbf{q})|J_k(\mathbf{q})) &= \\ N^{-1}&\sum_{\alpha,\beta=1}^{N}\left(\frac{\mathrm{i}\mathbf{q}\cdot\mathbf{P}_\alpha}{m}\left(\hat{u}_{\alpha i}\hat{u}_{\alpha j} - \frac{1}{3}\delta_{ij}\right)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha}\middle|P_{\beta k}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\beta}\right) \\ &= -\mathrm{i}q_k k_BTN^{-1}\sum_{\alpha=1}^{N}\left(\left(\hat{u}_{\alpha i}\hat{u}_{\alpha j} - \frac{1}{3}\delta_{ij}\right)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha}\middle|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_\alpha}\right) \\ &= -\mathrm{i}q_k k_BTN^{-1}\sum_{\alpha=1}^{N}\langle(\hat{u}_{\alpha i}\hat{u}_{\alpha j} - \frac{1}{3}\delta_{ij})\rangle = 0, \quad \text{(A.7)}\end{aligned}$$

where the last but one equality originates from averaging over the Gaussian variable, $\mathbf{P}_\alpha$, and the last one from the rotational symmetry of the problem. Equation (A.7) has been reported as equation (9) in the body of the present paper.

The kinetic energy expressed in terms of canonical momenta depends explicitly on the Euler angles, hence the evaluation of thermal averages is quite involved. This can be avoided by eliminating the canonical momenta in favour of the angular momenta [16]:

$$\begin{aligned}p_{\alpha\phi} &= -\tilde{J}_{\alpha x}\sin\Theta_\alpha\cos\psi_\alpha + \tilde{J}_{\alpha y}\sin\Theta_\alpha\sin\psi_\alpha \\ &\quad + \tilde{J}_{\alpha z}\cos\Theta_\alpha, & \text{(A.8a)} \\ p_{\alpha\Theta} &= \tilde{J}_{\alpha x}\sin\psi_\alpha + \tilde{J}_{\alpha y}\cos\psi_\alpha, & \text{(A.8b)} \\ p_{\alpha\psi} &= \tilde{J}_{\alpha z}. & \text{(A.8c)}\end{aligned}$$

One checks that the Jacobian is $\sin\Theta_\alpha$, while the corresponding part of the kinetic energy reads $T_\alpha = (\tilde{J}_{\alpha x}^2 + \tilde{J}_{\alpha y}^2)/2I + \tilde{J}_{\alpha z}^2/2I'$. Then the partition sum is given by

$$Z = \int\prod_\alpha \mathrm{d}\mathbf{R}_\alpha d\phi_\alpha d\cos\Theta_\alpha d\psi_\alpha d\mathbf{P}_\alpha d\tilde{\mathbf{J}}_\alpha \mathrm{e}^{-H/k_BT}. \quad \text{(A.9)}$$

Thus, averaging over the angular momenta is just Gaussian and averaging over the Euler angles amounts to averaging over the usual Haar measure of the rotation group.

In order to calculate the long-wavelength limit of the auto-correlation function of the orientational currents, it is sufficient to calculate it for one of its components, say $\dot{Q}_{zz}(\mathbf{q})$. Since $\hat{u}_{\alpha z} = \cos\Theta_\alpha$ and $\dot{\Theta}_\alpha = \{H, \Theta_\alpha\} = p_{\alpha\Theta}/I$, one finds, for $q \to 0$:

$$\dot{Q}_{zz}(\mathbf{q}) = -\frac{2}{I}N^{-1/2}\sum_{\alpha=1}^{N}[\tilde{J}_{\alpha x}\sin\psi_\alpha + \tilde{J}_{\alpha y}\cos\psi_\alpha]\cos\Theta_\alpha\sin\Theta_\alpha. \quad \text{(A.10)}$$

Then the long-wavelength correlation function of the orientational current can be evaluated:

$$\begin{aligned}(\dot{Q}_{zz}(\mathbf{q}=0)|\dot{Q}_{zz}(\mathbf{q}=0)) &= \\ \frac{4}{I^2}N^{-1}&\sum_\alpha\langle\left[\tilde{J}_{\alpha x}\sin\psi_\alpha + \tilde{J}_{\alpha y}\cos\psi_\alpha\right]^2\cos^2\Theta_\alpha\sin^2\Theta_\alpha\rangle \\ &= 4\frac{k_BT}{I}N^{-1}\sum_\alpha\langle\cos^2\Theta_\alpha\sin^2\Theta_\alpha\rangle = \frac{8k_BT}{15I}\cdot \quad \text{(A.11)}\end{aligned}$$

Comparison with equation (8) yields for the ideal gas libration frequency $\Omega^2 = 2k_BT/5I$.

Appendix B: Operator identity

The time evolution operator, $R(t) = \exp(\mathrm{i}\mathcal{L}t)$, may be split into two parts $R(t) = R_P(t) + R_Q(t)$ with $R_P(t) = R(t)P, R_Q(t) = R(t)Q$. From the equation of motion, $\partial_t R(t) = R(t)\mathrm{i}\mathcal{L}$, one finds:

$$\partial_t R_Q(t) = R_P(t)\mathrm{i}\mathcal{L}Q + R_Q(t)\mathrm{i}\mathcal{L}Q. \quad \text{(B.1)}$$

The solution of equation (B.1) can be expressed in terms of $R_P(t)$ as:

$$R_Q(t) = Q\mathrm{e}^{\mathrm{i}\mathcal{L}Qt} + \int_0^t R_P(s)\mathrm{i}\mathcal{L}Q\mathrm{e}^{\mathrm{i}\mathcal{L}Q(t-s)}\mathrm{d}s. \tag{B.2}$$

Furthermore, because $R'(t) = Q\mathrm{e}^{\mathrm{i}\mathcal{L}Qt}$ incorporates the projection operator Q, one easily finds, by *e.g.* expansion of the exponential, that $R'(t)$ may be written in the symmetric form:

$$R'(t) = Q\mathrm{e}^{\mathrm{i}Q\mathcal{L}Qt}Q. \tag{B.3}$$

Collecting terms, one arrives at equation (14).

Appendix C: Properties of the memory functions

The memory kernels of the type $(A|R'(t)|A)$ exhibit the same mathematical properties as auto-correlation functions, *viz.* for complex frequencies in the lower half plane, their Laplace transform is analytic with non-negative imaginary part. A non-rigorous proof can be adapted from Berne and Pecora [12]. Since $R'(t) = Q\exp(\mathrm{i}Q\mathcal{L}Qt)Q$, we formally introduce a complete set of eigenfunctions of the hermitian (with respect to the Kubo scalar product) operator $Q\mathcal{L}Q$:

$$Q\mathcal{L}Q\phi_\lambda = \lambda\phi_\lambda, \tag{C.1}$$

where all eigenvalues are real. Thus we can write:

$$\begin{aligned}(A|R'(t)|A) &= (QA|\mathrm{e}^{\mathrm{i}Q\mathcal{L}Qt}|QA)\\ &= \sum_\lambda (QA|\phi_\lambda)\mathrm{e}^{\mathrm{i}\lambda t}(\phi_\lambda|QA)\,.\end{aligned} \tag{C.2}$$

The Laplace transform yields:

$$LT[(A|R'(t)|A)](\omega) = \sum_\lambda \frac{1}{\omega-\lambda}|(QA|\phi_\lambda)|^2\,, \tag{C.3}$$

with complex frequencies in the lower half-plane. Since all the poles are located on the real axis, the Laplace transform is analytic for $\omega = \Omega - \mathrm{i}\epsilon, \epsilon > 0$. Furthermore:

$$\mathrm{Im}LT[(A|R'(t)|A)](\omega) = \sum_\lambda \frac{\epsilon}{(\Omega-\lambda)^2+\epsilon^2}|(QA|\phi_\lambda)|^2 \geq 0. \tag{C.4}$$

In particular, provided the limit $\epsilon \searrow 0$ exists, one obtains for real ω:

$$\mathrm{Im}LT[(A|R'(t)|A)](\omega) = \sum_\lambda \pi\delta(\omega-\lambda)|(QA|\phi_\lambda)|^2 \geq 0. \tag{C.5}$$

Consider now a collection of phase space variables $A_i, i = 1,..,l$ of identical time inversion parity. Then the real symmetric matrix $\mathrm{Im}LT[(A_i|R'(t)|A_j)](\omega)$ is positive semi-definite: since for arbitrary real numbers $y_i, i = 1,..,l$ the spectrum of the autocorrelation function of $Y = \sum_{i=1}^{l} y_iA_i$ is non-negative, one finds:

$$\sum_{i,j=1}^{n} y_iy_j\mathrm{Im}LT[(A_i|R'(t)|A_j)](\omega) \geq 0, \tag{C.6}$$

which implies the property. For frequencies $\omega \to 0$, one obtains Onsager's relations, *viz.* the matrix of the kinetic coefficients is symmetric with non-negative eigenvalues. Hence, equation (C.6) can be interpreted as the proper generalisation of Onsager's relations to finite frequencies.

Appendix D: Transverse phonons and the Andersen-Pecora approach in the low temperature limit

If one makes the (incorrect) supposition that the memory kernels of the Andersen-Pecora approach can be modeled by Debye relaxation processes consistent with their high-temperature Markov approximation and their time reversal symmetry, this yields:

$$M(\omega) = \mathrm{i}\frac{A^2}{\tau}\frac{1}{1+\mathrm{i}\omega\tau}, \tag{D.1}$$

$$\hat{\eta}_s(\omega) = \mathrm{i}\hat{\eta}_s^0\frac{\tau}{1+\mathrm{i}\omega\tau}, \qquad \hat{\eta}_s^0 > 0, \tag{D.2}$$

$$\lambda(\omega) = -\left[\mathrm{i}f_1 + f_2\frac{\omega\tau}{1+\mathrm{i}\omega\tau}\right], \qquad f_1, f_2 > 0. \tag{D.3}$$

The special form proposed for equation (D.3) derives from the fact that $\lambda(t)$ is an odd function of time. If we suppose it to be the time derivative of $f(t)$, the auto-correlation function of some variable, f_1 is its $t = 0$ value and we have chosen for its late-time evolution a smooth Debye-like behaviour.

Let us admit that, in the $\omega\tau \gg 1$ regime, the value of A is smaller than $1/\sqrt{2}$. Equation (D.1) then yields a VH backscattering spectrum with a pseudo-Lorentzian line shape and a line width approximately equal to $\tau^{-1}A^2(1-2A^2)^{-1/2}$. For ω larger than this line width, one can write for the q-dependent part of equation (68):

$$I(\mathbf{q},\omega) = -q^2\left(\frac{\Lambda'}{mn\omega_0^2}\right)^2\frac{m^2v^2}{\omega}\left[\mathrm{Re}\left(\frac{\omega\lambda(\omega)}{\omega-M(\omega)}\right)^2\right] \times\mathrm{Im}\frac{1}{\omega^2-q^2\omega\eta_T(\omega)/mn}. \tag{D.4}$$

In this $\omega\tau \gg 1$ limit, this reads:

$$I(\mathbf{q},\omega) = -q^2\left(\frac{\Lambda'}{mn\omega_0^2}\right)^2\frac{m^2v^2}{\omega}(f_1-f_2)^2 \times\mathrm{Im}\frac{1}{\omega^2-q^2c_T^2+\mathrm{i}\epsilon}, \tag{D.5}$$

ϵ being a small positive quantity. Equation (D.5) does represent the Brillouin spectrum of a transverse phonon, but the square of its the velocity is given by:

$$c_T^2 = \frac{\hat{\eta}_s^0}{mn} + \frac{\Lambda'}{mn\omega_0^2}(f_1 - f_2)^2. \tag{D.6}$$

In the spirit of the Andersen-Pecora approach, $\hat{\eta}_s(t)$ represents the contribution of the molecular center-of-mass motion to the shear viscosity (see, nevertheless, the remark below Eq. (71a)). Within the same spirit, $[\hat{\eta}_s^0/mn]^{1/2}$ should represent the contribution of the same motion to the transverse sound velocity. As announced, the bare sound velocity, $[\hat{\eta}_s^0/mn]^{1/2}$, is renormalized by a term in Λ'/ω_0^2, the signature of the rotation-translation coupling, but this renormalisation leads to an unphysical increase of the sound velocity, instead of the expected physical decrease.

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