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Transient grating experiments on supercooled molecular liquids II: microscopic derivation of the phenomenological equations

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Abstract. The constitutive equations including the energy conservation aspect, for the long-wavelength dynamics of a liquid comprised of identical, axially symmetric, rigid molecules are microscopically derived. These equations are extended to the case where the dynamics is generated by the interactions of two coherent lasers (the pumps) with the liquid. This interaction corresponds to a weak energy absorption and also to the coupling of the pumps with fluctuations in the mass density, the molecular orientation density and the temperature of the liquid. The microscopic equations generalise those phenomenologically derived in Pick et al. [1] where the role of the temperature fluctuations was ignored. Constraints on the relaxation functions related to the temperature fluctuations and to their coupling with density are derived.

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1 Introduction

This paper is the fourth of a series devoted to the optical study of (supercooled) liquids formed of axially symmetric molecules [1–3]. Since the discovery, at the end of the 19th century [4], of flow birefringence in such liquids, it was recognized that their shear flow leads to an orientational order, i.e. to a non-zero tensorial, orientational density proportional to this shear. Indeed, because the polarisability of such molecules is also anisotropic, the optical anisotropy of the liquid is linearly related to this orientational order. Yet, one had to wait until the beginning of the seventies [5] to recognize that such a property still exists at the optical wavelength scale; this was the explanation of the Rytov dip that had just been detected [6,7] in depolarised light scattering of molecular liquids such as nitrobenzene, quinoline and aniline.

After the pioneer work of de Gennes in liquid crystals [8], Quentrec [9] was the first to recognize that the equations proposed by Keyes and Kivelson or Anderson and Pecora [5] to explain this dip were equivalent to introducing in the usual Navier-Stokes equations describing the dynamics of a liquid, an additional (tensorial) variable representing this orientational density. Consequently, the usual set of equations had to be supplemented by another equation describing this orientational variable and its coupling to the shear flow. These equations were, nev-

ertheless, unable to properly describe the situation of very viscous liquids, and a first step was made by Wang [10] who introduced memory functions into the coupling between the different variables. Yet, a phenomenological set of such equations able to explain the dynamics of these liquids even in the presence of relaxation times tending to infinity was only proposed more than 10 years after [11]. This set was shown to describe properly the depolarised spectra of liquids such as metatoluidine [12], salol [13], or OTP [14], at all temperatures.

Longitudinal phonons correspond both to a local bulk and to a local shear deformation so that, in a polarised Brillouin scattering (BS) experiment, one must take into account, following that analysis, the changes in the local dielectric tensor, $\delta\bar{\bar{\epsilon}}(\mathbf{r}, t)$, related both to the bulk deformation (mass density modulation, $\rho(\mathbf{r}, t)$) and to the orientational density, $\bar{\bar{Q}}(\mathbf{r}, t)$, where $\bar{\bar{Q}}$ is a second rank, traceless, symmetrical tensor

$$\delta\epsilon_{ij}(\mathbf{r}, t) = a\rho(\mathbf{r}, t)\delta_{ij} + bQ_{ij}(\mathbf{r}, t). \qquad (1.1)$$

Such a model was developed in [2] with the help of the Navier-Stokes equations of [11]. New features in the polarised light scattering specra of supercooled liquids formed of anisotropic molecules could be predicted from this approach. Zhang et al. have recently detected one of them [13].

Simultaneously, a microscopic Mori-Zwanzig derivation of these phenomenological equations was given in [3].

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It allowed, inter alia, to prove that all the relaxation functions appearing in these Navier-Stokes equations are well behaved at long time, and that there exist relations between some of them. A series of inequalities results for the imaginary part of the Laplace transforms of these relaxation functions, or for their product (Onsager relations). These inequalities ensure that all the light scattering spectra deduced from equation (1.1) will be positive, whatever will be the relative contribution of the mass density and the orientational density modulations.

Reference [1], hereafter referred to as I, discussed transient grating (TG) experiments in the same liquids, using a phenomenological approach similar to that of [2]. Yet, two extra features had to be introduced. First, when discussing BS experiments, one can work in the adiabatic approximation because heat transfer between the acoustic phonon under study and the rest of the liquid takes place at times longer (frequency much lower) than detected in the experiments. Conversely, in a TG experiment, physically important information is deduced from the coupling of the energy absorbed by (irreversibly transferred from the pump lasers to) the liquid with the relaxation processes through which the liquid thermalises. An additional Navier-Stokes equation related to energy conservation, and the contribution of temperature to the stress tensor have to be included in the theory, both aspects involving new relaxation processes. Second, sources have to be added to each material dependent equation of the set. An already mentioned one is the heat absorption, which must be introduced into the energy balance equation. Two other processes have to be taken into account. One is the well known electrostrictive effect [15], which introduces a source into the equation of evolution of the stress tensor. The second is the orientational role of the electric field of the pumps; its introduction is necessary to describe experiments concentrating on the orientational dynamics of supercooled liquids, such as the Optical Kerr Effect (OKE) [16–19] or the density induced heterodyne amplified rotational dynamics (DIHARD) experiments [20]. The same source also consistently explains the dependence of the TG signal on the polarisation of the detection and probe beams, as observed, e.g. in metatoluidine [21].

The existence of sources in both the stress equation and the orientational density equation introduces a new problem. Since the pioneer work of Herman and Gray [15] (see e.g. Shen [22]) it was known that the electrostrictive source was proportional to $a = \frac{1}{3} \partial [\text{Trace}\, \overline{\overline{\epsilon}}]/\partial \rho$. Nevertheless, this electrostrictive effect and the heat absorption are the only sources introduced in the classical discussion of TG experiments. Because one of them is related to the imaginary part of $\overline{\overline{\epsilon}}$ and the other to a modulation of its real part (see Sect. 4), there is no practical connection between them: the relation between heat absorption and 'a' can be ignored. The situation changes when $\delta\overline{\overline{\epsilon}}$ is described by equation (1.1). Both the electrostrictive and the optical Kerr effects originate from the coupling of $\delta\overline{\overline{\epsilon}}$ to the square of the electric field of the pumps. The ratio of the strength of the two corresponding sources must be proportional to

a/b. This proportionality was demonstrated in I making use of the proposed Navier-Stokes equations. It allowed to differentiate between two contributions to the TG signal. One arises from those last two sources, was called the generalised ISBS (impulsive stimulated Brillouin scattering) signal and it is related through the fluctuation-dissipation theorem to some BS spectrum. The second is the ISTS (impulsive stimulated thermal scattering) signal which originates from the the thermal absorption.

The primary goal of the present paper is to prove, with the help of an extended Mori-Zwanzig formalism [23], the set of phenomenological equations used in I, i.e.:

– on the one hand, the generalisation of the Navier-Stokes equation describing the conservation of energy to the case where relaxation processes have to be taken into account. In fact, we shall derive in Section 3 a form of the energy balance equation that is more general than the one used in I;

– on the other hand, the relationship between the electrostrictive source and the Optical Kerr Effect.

There is a second, and more formal, goal for this paper. Though the Navier-Stokes equations of I contained $\rho(\mathbf{r}, t)$, $\overline{\overline{Q}}(\mathbf{r}, t)$ and the temperature, $T(\mathbf{r}, t)$, as dynamical variables, we did not introduce the latter as another origin of the modulation of $\delta\overline{\overline{\epsilon}}(\mathbf{r}, t)$; though it would have been formally consistent to replace equation (1.1) by

$$\delta\epsilon_{ij}(\mathbf{r}, t) = a\rho(\mathbf{r}, t)\delta_{ij} + bQ_{ij}(\mathbf{r}, t) + cT(\mathbf{r}, t)\delta_{ij}, \quad (1.2)$$

the last term of equation (1.2) was ignored. Its introduction leads to non-trivial new sources. The neglect of the last term of equation (1.2) was, nevertheless, not accidental: it gives for density and temperature fluctuations around equilibrium a contribution to the BS spectra numerically negligible with respect to the first two. The relationship between the BS spectra and the generalised ISBS signal indicates that this contribution will also be negligible for this signal. But there is no reason for this property to remain valid for the ISTS signal. In fact, during the completion of I, a TG experiment performed on water [24] close to 0 °C showed that this neglect would lead in that case to some misinterpretation of the data. We found thus necessary to explore thoroughly a consistent form of the theory to understand under which conditions and for which part of the signal the use of equation (1.2) was necessary. Consequently, this paper is organised as follows:

– Section 2 recalls the model of the supercooled molecular liquid used in [3], summarises the methods used in that paper and some of the results obtained.

– We introduce, in Section 3, $T(\mathbf{r}, t)$ as an additional variable, discuss the modification it introduces in the equation of motion of the stress tensor and derive the evolution equation of $T(\mathbf{r}, t)$ (Sect. 3.1) which, as usual, is expressed as a conservation law for the local energy density. In Section 3.2, we explain the physical meaning of the new relaxation functions, $\delta\beta(t)$, related to the tension (or thermal pressure) and $\delta c_V(t)$, related to the specific heat, introduced by the theory. This evolution equation

contains a term that did not need to be considered in I. We shall show that the complete equation leads to an expression of the BS spectra that has the correct symmetry even if the modulation of the dielectric tensor takes into account its purely thermal contribution. Finally, we derive in Section 3.3, the properties of, and the relations between $\delta c_V(t), \delta \beta(t)$ and the bulk viscosity, $\eta_b(t)$. We show that they are sufficient to ensure that the BS spectra are positive at all frequencies whatever are the relative values of a, b, and c in equation (1.2).

Section 4 introduces the sources in the three material dependent equations. In analogy with the electrostrictive effect, due to $\rho(\mathbf{r}, t)$, we call 'electrothermal' effects the sources originating from $cT(\mathbf{r}, t)$. We extend the results of I to this new situation, giving the expression of the Navier-Stokes equations with sources in Section 4.1, and their solution for a TG experiment in Section 4.2. This solution is analysed in Section 4.3 where we show that, as in the simpler case discussed in I, it splits into a generalised ISBS term, related to the corresponding BS spectrum by the Fluctuation-Dissipation theorem, and a generalised ISTS term. The special role played in the detection of the latter by the thermal modulation of the dielectric tensor is also discussed.

A brief conclusion, Section 5, summarises our results. It allows readers not familiar with the theoretical approach used in this paper to learn about the main results that have been derived, giving him confidence in the general validity of the approach and of the conclusions of I. We also specify the limitations of that paper as well as of the present one.

2 The non-energy-conserving Navier Stokes equations

2.1 Notations

Let us briefly recall in this Section the method and some of the results obtained in [3]. In that paper, we considered a dense liquid of N linear, rigid, identical, molecules of mass m at temperature T enclosed in a volume V. The thermodynamic limit, $N \to \infty$, with fixed particle density, $n = N/V$, was implied throughout.

The unperturbed Hamilton function of the system reads

$$H_0 = \sum_\alpha K_\alpha + V(\{\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha\}), \qquad (2.1)$$

where the kinetic energy of the α-th molecule is[1]

$$K_\alpha = \frac{\mathbf{P}_\alpha^2}{2m} + \frac{M_{\alpha X}^2 + M_{\alpha Y}^2}{2I}. \qquad (2.2)$$

Here $\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha$ denote the center-of-mass position and the polar angles of the molecule following the definition

of [25], $\mathbf{P}_\alpha$ is the canonical momentum associated to $\mathbf{R}_\alpha$, while I is the moment of inertia of the molecule for rotations around any axis perpendicular to its axis of symmetry and passing through its center of mass; X and Y are the body-fixed directions of two such axes, perpendicular one to the other and $M_{\alpha X}$ (resp. $M_{\alpha Y}$) are the corresponding angular momenta. Finally, V is the potential energy of the interacting molecules.

The partition sum is given by

$$Z = \int \prod_\alpha d\mathbf{R}_\alpha d\cos\theta_\alpha d\phi_\alpha d\mathbf{P}_\alpha dM_{\alpha X} dM_{\alpha Y} e^{-H_0/k_B T}; \qquad (2.3)$$

averaging over the angular momenta is just Gaussian and averaging over the polar angles amounts to averaging over the unit sphere.

We introduced in [3] the dynamics of the fluctuating molecular orientation tensor, written directly in the reciprocal space through

$$Q_{ij}(\mathbf{q}) = N^{-1/2} \sum_{\alpha=1}^N \left(\hat{u}_{\alpha i} \hat{u}_{\alpha j} - \frac{1}{3} \delta_{ij} \right) \exp\left(i\mathbf{q} \cdot \mathbf{R}_\alpha\right), \qquad (2.4)$$

where the degrees of freedom of the α-th molecule are specified by a unit vector, $\hat{\mathbf{u}}_\alpha = (\sin\theta_\alpha \cos\phi_\alpha, \sin\theta_\alpha \sin\phi_\alpha, \cos\theta_\alpha)$ for its orientation and by $\mathbf{R}_\alpha$. The wave vector $\mathbf{q}$ characterises the spatial modulation with respect to the fixed laboratory frame of a fluctuation, and latin indices denote cartesian components. The nine components of $Q_{ij}(\mathbf{q})$ are not independent, since the orientation tensor is symmetric and traceless, reducing the number of independent components to five. The normalisation of $Q_{ij}(\mathbf{q})$ and of all the variables to be introduced below was chosen such that the correlation functions are intensive.

We then introduced the orientational current,

$$\dot{Q}_{ij}(\mathbf{q}) = i\mathcal{L} Q_{ij}(\mathbf{q}), \qquad (2.5)$$

where $\mathcal{L}$ is the Liouville operator, the fluctuations in the mass density,

$$\rho(\mathbf{q}) = mN^{-1/2} \sum_{\alpha=1}^N \exp\left(i\mathbf{q} \cdot \mathbf{R}_\alpha\right), \qquad (2.6)$$

and the cartesian components of the mass current,

$$J_i(\mathbf{q}) = N^{-1/2} \sum_{\alpha=1}^N P_{\alpha i} \exp\left(i\mathbf{q} \cdot \mathbf{R}_\alpha\right). \qquad (2.7)$$

2.2 Static averages

We then expressed the static correlation functions to lowest order in q.

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

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[1] We do not take into account the kinetic energy related to rotations around the molecule's axis of symmetry, because, for such molecules, these rotations do not couple to the remainder of the dynamics.

special properties for the correlation functions of two second rank traceless tensor (see, e.g., Eq. (2.11)) and correlators between any second rank traceless tensor variable and any scalar variable will vanish in the long-wavelength limit.

Because of the compressibility sum rule [26], the static average of the density could be expressed as

$$(\rho(\mathbf{q})|\rho(\mathbf{q})) = m^2 v^2 / c_i^2 + \mathcal{O}(q^2), \qquad (2.8)$$

where c_i is the isothermal sound velocity and $v = \sqrt{k_B T_m/m}$ denotes the thermal velocity.

Also because of equation (2.3), the current correlations read

$$(J_i(\mathbf{q})|J_k(\mathbf{q})) = \delta_{ik} m^2 v^2 = \delta_{ik} m k_B T_m, \qquad (2.9)$$

an expression valid whatever $\mathbf{q}$, while to lowest order in $\mathbf{q}$, the equal-time correlators of the tensor variables were shown to be expressed as

$$(Q_{ij}(\mathbf{q})|Q_{kl}(\mathbf{q})) = S^2 \Delta_{ij,kl} + \mathcal{O}(q^2), \qquad (2.10)$$

where

$$\Delta_{ij,kl} = \left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{kl} \right) \qquad (2.11)$$

is a fourth-rank tensor the structure of which is governed by rotational symmetry, and S^2 is a quantity which is, as in equation (2.8), proportional in leading order to $k_B T_m$.

Similarly,

$$(\dot{Q}_{ij}(\mathbf{q})|\dot{Q}_{kl}(\mathbf{q})) = \Omega^2 \Delta_{ij,kl}, \qquad (2.12)$$

where the characteristic frequency Ω was shown to be equal to

$$\Omega = \sqrt{\frac{k_B T_m \Lambda'}{n}}, \qquad (2.13a)$$

with

$$\Lambda' = \frac{2n}{5I}. \qquad (2.13b)$$

The ratio of the static averages of the orientation to the orientational current, $\omega_R = \Omega/S$, defines the axial libration frequency, which is, as c_i, independent of temperature to leading order. Equations (2.13) and the definition of ω_R allow to express Ω^2 and S^2 as functions of $k_B T_m, n, \Lambda'$ and ω_R.

All the static averages involving different variables were found to be equal to zero, in the $q \to 0$ limit, either because of rotational symmetry, or because of time reversal considerations. Yet, $(\dot{Q}_{ij}(\mathbf{q})|J_k(\mathbf{q}))$ did not fall into any of those two categories; it deserved a special treatment but we showed in [3] that this static average is also equal to zero, at any order in $\mathbf{q}$, when the reference point of each molecule, $\mathbf{R}_\alpha$, is at its center of mass.

2.3 Constitutive equations for equilibrium fluctuations

The next step consisted in obtaining the constitutive equations for the time evolution of small fluctuations around equilibrium when the time scale is short enough to neglect the energy conservation problem.

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

$$\partial_t \rho(\mathbf{q},t) = iq_k J_k(\mathbf{q},t). \qquad (2.14)$$

Similarly, the conservation of momentum yields

$$\partial_t J_k(\mathbf{q},t) = iq_l \Pi_{kl}(\mathbf{q},t), \qquad (2.15)$$

where $\Pi_{kl}(\mathbf{q},t)$ denotes the fluctuating momentum current tensor. In order to close the system, we needed constitutive equations for the momentum current tensor, $\Pi_{kl}(\mathbf{q},t)$, and for the orientational tensor force $\ddot{Q}_{ij}(\mathbf{q},t)$. This was achieved through generalised Langevin equations which introduce appropriate memory kernels. We first defined a projection operator, P, which projects onto the subspace spanned by the density, the mass current, the symmetric traceless parts of the orientation tensor and of its time derivative:

$$P = \frac{1}{mk_B T_m} \Big[|\rho(\mathbf{q})) c_i^2 (\rho(\mathbf{q})| + |J_k(\mathbf{q}))(J_k(\mathbf{q})| \\ + \frac{\rho_m}{2\Lambda'} \big\{ |Q_{kl}(\mathbf{q})) \omega_R^2 (Q_{kl}(\mathbf{q})| \\ + | \dot{Q}_{kl}(\mathbf{q}))(\dot{Q}_{kl}(\mathbf{q})| \big\} \Big] + \mathcal{O}(q^2), \quad (2.16)$$

where the sum over repeated indices is implied and where $\rho_m = mn$. 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 $P^2 = P \cdot P$.

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

$$R(t) = R(t)P + \int_0^t R(s) Pi\mathcal{L}R'(t-s)ds + R'(t), \quad (2.17)$$

with the reduced operator $R'(t) = Q\exp(iQ\mathcal{L}Qt)Q$, where $Q = 1 - P$, and a short proof of equation (2.17) was given in Appendix B of [3]. The benefit of that procedure is that $R'(t)$ devoids the hydrodynamic singularities (longitudinal and transverse acoustic modes) present in $R(t)$ because of the conservation laws, equations (2.14) and (2.15). The matrix elements of $R'(t)$ could thus be taken in the $\mathbf{q} = 0$ limit. They lead to q-independent memory functions, at the lowest order (see, e.g., Eq. (2.23a)). We decided to treat the $Q_{ij}(\mathbf{q})$ and $\dot{Q}_{ij}(\mathbf{q})$ fluctuations on the same footing as $\rho(\mathbf{q})$ and $J_k(\mathbf{q})$ and thus to extract them from $R(t)$ though that was a matter of convenience and not of necessity.

We further transformed the second term of the r.h.s of equation (2.17) by letting the operator $i\mathcal{L}$ act on the 'bra' part of the projection operator P, which made appear

some derivatives of those 'bras'. Because of the $Q = 1 - P$ operator at the l.h.s. of $R'(t)$, this simply leads to

$$Pi\mathcal{L}R'(t-s) = -|\dot{Q}_{kl}(\mathbf{q}))\frac{\rho_m}{2mk_BT_m\Lambda'}(\ddot{Q}_{kl}(\mathbf{q})|R'(t-s)$$
$$+ iq_l|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(\Pi_{kl}(\mathbf{q})|R'(t-s). \quad (2.18)$$

Separating $\Pi_{ij}(\mathbf{q})$ into its diagonal part, $\delta_{ij}p(\mathbf{q})$, and its traceless part, $\pi_{ij}(\mathbf{q})$:

$$\Pi_{ij}(\mathbf{q},t) = p(\mathbf{q},t)\delta_{ij} + \pi_{ij}(\mathbf{q},t), \quad (2.19)$$

where

$$p(\mathbf{q},t) = [\Pi_{xx}(\mathbf{q},t) + \Pi_{yy}(\mathbf{q},t) + \Pi_{zz}(\mathbf{q},t)]/3, \quad (2.20)$$

equation (2.17) was applied to both components of $\Pi_{ij}(\mathbf{q},t)$. First, a lengthy calculation detailed in [3] lead to

$$R(t)Pp(\mathbf{q}) = c_i^2\rho(\mathbf{q},t), \quad (2.21)$$

$$\int_0^t R(s)Pi\mathcal{L}R'(t-s)p(\mathbf{q})ds = i\int_0^t \eta_b(t-s)q_kv_k(\mathbf{q},s)ds, \quad (2.22)$$

with

$$\eta_b(t) = (p|R'(t)|p)\frac{n}{k_BT_m}, \quad (2.23a)$$

$$v_i(\mathbf{q}) = J_i(\mathbf{q})/\rho_m, \quad (2.23b)$$

while $R'(t)p(\mathbf{q})$ produced a noise term. Similarly, $R(t)P\pi_{ij}(\mathbf{q})$ produced a term which is $\mathcal{O}(q^2)$ while equation (2.18) allowed $\pi_{ij}(\mathbf{q})$ to couple both to $\ddot{Q}_{kl}$ and Π_{kl}, yielding

$$\pi_{ij}(\mathbf{q},t) = -\int_0^t \eta_s(t-s)\tau_{ij}(\mathbf{q},s)ds + \int_0^t \mu(t-s)\dot{Q}_{ij}(\mathbf{q},s)ds, \quad (2.24)$$

with

$$\eta_s(t) = \frac{3}{4}\frac{n}{k_BT_m}(\pi_{zz}|R'(t)|\pi_{zz}), \quad (2.25)$$

$$\mu(t) = -\frac{3}{4}\frac{n}{k_BT_m\Lambda'}(\ddot{Q}_{zz}|R'(t)|\pi_{zz}), \quad (2.26)$$

$$\tau_{ij}(\mathbf{q},t) = -i\frac{q_lJ_k}{m}\Delta_{ij,kl}, \quad (2.27)$$

where $\tau_{ij}(\mathbf{q},t)$ is the Fourier transform of the strain rate tensor.

Grouping together equations (2.21), (2.22), and (2.24) we thus obtained

$$\Pi_{ij}(\mathbf{q},t) = \left[c_i^2\rho(\mathbf{q},t) + \int_0^t \eta_b(t-s)iq_kv_k(\mathbf{q},s)ds\right]\delta_{ij}$$
$$- \int_0^t \eta_s(t-s)\tau_{ij}(\mathbf{q},s)ds$$
$$+ \int_0^t \mu(t-s)\dot{Q}_{ij}(\mathbf{q},s)ds + \text{noise}. \quad (2.28)$$

Identification of equation (2.28) with the usual Navier-Stokes equation for the conservation of the linear momentum density makes clear that $\eta_b(t)$ is the bulk viscosity memory function, and $\eta_s(t)$ the corresponding shear viscosity function, while $\mu(t)$ appears as the orientation-translation (that we called rotation-translation) memory function.

To derive an equation of motion for $\ddot{Q}_{ij}(\mathbf{q})$, we again made use of equation (2.17). This yielded

$$R(t)P\ddot{Q}_{ij}(\mathbf{q}) = -\omega_R^2Q_{ij}(\mathbf{q},t), \quad (2.29)$$

while, from equation (2.18) and the definition of $\tau_{ij}(\mathbf{q},t)$, we obtained

$$Pi\mathcal{L}R'(t-s)\ddot{Q}_{ij}(\mathbf{q}) =$$
$$-|\dot{Q}_{ij}(\mathbf{q}))\Gamma'(t-s) + \Lambda'|\tau_{ij}(\mathbf{q}))\mu(t-s), \quad (2.30)$$

where the rotational memory function $\Gamma'(t)$ is defined by

$$\Gamma'(t) = \frac{3n}{4k_BT_m\Lambda'}(\ddot{Q}_{zz}|R'(t)|\ddot{Q}_{zz}). \quad (2.31)$$

Equations (2.29) and (2.30) were finally grouped into

$$\ddot{Q}_{ij}(\mathbf{q},t) = -\omega_R^2Q_{ij}(\mathbf{q},t) - \int_0^t \Gamma'(t-s)\dot{Q}_{ij}(\mathbf{q},s)ds$$
$$+\Lambda'\int_0^t \mu(t-s)\tau_{ij}(\mathbf{q},s)ds + \text{noise}. \quad (2.32)$$

Equations (2.28) and (2.32) completed the set of equations (2.14) and (2.15), the memory function $\mu(t)$ allowing for the coupling between the dynamics of the mass current and of the molecular orientation, thus appearing on the same footing in the two equations.

The relationship between those two equations appeared also under a somewhat different aspect. We showed in [3] that the Laplace transform of $(A|R'(t)|A)$ of any variable A with a definite symmetry with respect to time reversal was analytic with positive imaginary part for complex frequencies ω such that $\text{Im}(\omega) \leq 0$. This is true, in particular, for $(p|R'(t)|p)$ and for

$$(r\ddot{Q}_{zz} + s\pi_{zz}|R'(t)|r\ddot{Q}_{zz} + s\pi_{zz}) =$$
$$\frac{4k_BT_m\Lambda'}{3n}\left[r^2\Gamma'(t) - 2rs\mu(t) + s^2\frac{\eta_s(t)}{\Lambda'}\right], \quad (2.33)$$

for real numbers r, s. This implied that, for $\text{Im}(\omega) \leq 0$,

$$\text{Im}\,\eta_b(\omega) \geq 0, \quad (2.34a)$$

$$\text{Im}\,\eta_s(\omega) \geq 0, \quad (2.34b)$$

$$\text{Im}\,\Gamma'(\omega) \geq 0, \quad (2.34c)$$

and

$$[\text{Im}\,\Gamma'(\omega)][\text{Im}\,\eta_s(\omega)] - \Lambda'[\text{Im}\,\mu(\omega)]^2 \geq 0. \quad (2.34d)$$

These conditions were shown to be sufficient to ensure that the spectrum of the correlation function of $\delta\epsilon_{ij}(\mathbf{r},t)$, as expressed in equation (1.1), would be positve for any wave vector and real frequency, whatever are a and b.

3 The full Navier-Stokes equations

3.1 Derivation of the equations

Because of the heat absorbed in a transient grating experiment, a first step in its theory consists in enlarging the set of equations recalled in Section 2 to include the conservation of energy in the Navier-Stokes equations. This requires, within the microscopic approach taken here, first to define a local temperature variable, second to derive an equation for its time evolution following the method summarised in the preceding section, as well as to rederive the preceding equations when this new variable is taken into account.

The $\mathbf{q}$ component of the kinetic energy density of the liquid is defined by

$$e_K(\mathbf{q}) = N^{-1/2} \sum_\alpha K_\alpha \exp(i\mathbf{q} \cdot \mathbf{R}_\alpha), \qquad (3.1)$$

where the kinetic energy of particle α has been given in equation (2.2).

The thermal mean value of K_α, $\langle K_\alpha \rangle$ is easily computed from equation (2.3) to be

$$\langle K_\alpha \rangle = f \frac{k_B T_m}{2} \equiv \frac{c_V^\infty}{n} T_m, \qquad (3.2a)$$

where f is the number of degrees of freedom of the molecule ($f = 5$), and c_V^∞ is the specific heat per unit volume at constant volume for the non-interacting rigid molecules.

In the linear regime, the kinetic energy fluctuations have two distinct origins. A first one is the density fluctuations at constant mean kinetic energy per particle. In the remainder of this paper, we shall be interested in the second one, $T(\mathbf{q})$, related to the fluctuations of the kinetic energy without density change. The latter must then be defined by

$$c_V^\infty T(\mathbf{q}) = e_K(\mathbf{q}) - \frac{\rho(\mathbf{q})}{m} \frac{c_V^\infty}{n} T_m, \qquad (3.2b)$$

i.e.

$$T(\mathbf{q}) = \frac{e_K(\mathbf{q})}{c_V^\infty} - \frac{T_m}{\rho_m} \rho(\mathbf{q}). \qquad (3.2c)$$

Furthermore, the same equations (2.2) and (2.3) yield

$$\langle K_\alpha^2 \rangle = f(f-1) \left(\frac{k_B T_m}{2} \right)^2$$
$$+ f \times 3 \left(\frac{k_B T_m}{2} \right)^2$$
$$= f(f+2) \left(\frac{k_B T_m}{2} \right)^2, \qquad (3.3a)$$

which results in

$$\langle K_\alpha K_\beta \rangle = \left(f \frac{k_B T_m}{2} \right)^2 + 2f \left(\frac{k_B T_m}{2} \right)^2 \delta_{\alpha\beta}. \qquad (3.3b)$$

This implies that the static average $(e_K(\mathbf{q})|e_K(\mathbf{q}))$ splits into a coherent term and an incoherent term. The first one (cf. Eq. (2.8)) is equal to $(v^2/c_i^2)(c_V^\infty T_m/n)^2$, so that

$$(e_K(\mathbf{q})|e_K(\mathbf{q})) = \frac{v^2}{c_i^2} \left(\frac{c_V^\infty T_m}{n} \right)^2 + \frac{c_V^\infty}{n} k_B T_m^2. \qquad (3.4)$$

Equations (2.8) and (3.2a) show that the coefficient of $\rho(\mathbf{q})$ in the r.h.s. of equation (3.2b) may be written as

$$\frac{c_V^\infty}{n} T_m \frac{mv^2}{c_i^2} \left(\frac{m^2 v^2}{c_i^2} \right)^{-1} = \frac{(\rho(\mathbf{q})|e_K(\mathbf{q}))}{(\rho(\mathbf{q})|\rho(\mathbf{q}))}. \qquad (3.5)$$

This means that (see Eq. (3.2c))

$$(T(\mathbf{q})|\rho(\mathbf{q})) = 0. \qquad (3.6a)$$

With the help of equations (3.2c), (3.5), and (3.6a), we obtain

$$(T(\mathbf{q})|T(\mathbf{q})) = \frac{1}{c_V^\infty}(T(\mathbf{q})|e_K(\mathbf{q}))$$
$$= \frac{1}{(c_V^\infty)^2} \left[(e_K(\mathbf{q})|e_K(\mathbf{q})) - \frac{[(e_K(\mathbf{q})|\rho(\mathbf{q}))]^2}{(\rho(\mathbf{q})|\rho(\mathbf{q}))} \right]. \qquad (3.6b)$$

By construction, the coherent part of $(e_K(\mathbf{q})|e_K(\mathbf{q}))$ is equal to $\{(e_K(\mathbf{q})|\rho(\mathbf{q}))[(\rho(\mathbf{q})|\rho(\mathbf{q}))]^{-1/2}\}^2$. The r.h.s of equation (3.6b) thus involves only the incoherent part of $(e_K(\mathbf{q})|e_K(\mathbf{q}))$:

$$(T(\mathbf{q})|T(\mathbf{q})) = \frac{k_B T_m^2}{nc_V^\infty}. \qquad (3.6c)$$

The potential energy of the liquid, $V(\{\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha\})$ can always be written as

$$V(\{\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha\}) = \sum_\alpha v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha), \qquad (3.7a)$$

where $v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha)$ is a function of the relative positions $\{\mathbf{R}_\gamma - \mathbf{R}_\alpha\}$ of all the other molecules and of the orientation, $\theta_\alpha, \phi_\alpha, \{\theta_\gamma, \phi_\gamma\}$ of all the molecules. One can thus define, in analogy with equation (3.1), the $\mathbf{q}$ component of the potential energy density of the liquid

$$e_P(\mathbf{q}) = N^{-1/2} \sum_\alpha e^{i\mathbf{q} \cdot \mathbf{R}_\alpha} v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha). \qquad (3.7b)$$

Since $e_P(\mathbf{q})$ depends only on the positions and the orientations of all the molecules, while K_β depends only on the kinetic energy of the molecule β, we show in Appendix F, that

$$(e_P(\mathbf{q})|e_K(\mathbf{q})) = \frac{1}{N} \langle \sum_{\alpha,\beta} e^{i\mathbf{q} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)} v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha) K_\beta \rangle$$
$$= \frac{c_V^\infty T_m}{\rho_m}(e_P(\mathbf{q})|\rho(\mathbf{q})). \qquad (3.7c)$$

This implies for the correlator between the temperature and the potential energy density

$$(e_P(\mathbf{q})|T(\mathbf{q})) =$$
$$\frac{1}{c_V^\infty}(e_P(\mathbf{q})|e_K(\mathbf{q})) - \frac{T_m}{\rho_m}(e_P(\mathbf{q})|\rho(\mathbf{q})) = 0; \quad (3.8)$$

$e_P(\mathbf{q})$ which, for tensorial and time reversal symmetry reasons, could project, at the lowest order in $\mathbf{q}$, on both $\rho(\mathbf{q})$ and $T(\mathbf{q})$, has in fact no correlation with the temperature.

For the same symmetry reason, the static averages of $T(\mathbf{q})$ with all the other variables of the problem are again equal to zero to lowest order in $\mathbf{q}$. Taking into account this new variable, the projection operator, P, in equations (2.16) and (2.17), has to be replaced by

$$\tilde{P} = P + |T(\mathbf{q}))\frac{nc_V^\infty}{k_B T_m^2}(T(\mathbf{q})|, \quad (3.9)$$

while $\tilde{R}'(t)$, which replaces the reduced time evolution operator $R'(t)$ of equation (2.17), is defined through a projection operator $\tilde{Q} \equiv 1 - \tilde{P}$. Consequently, equation (2.18) is transformed into

$$\tilde{P}i\mathcal{L}\tilde{R}'(t-s) = Pi\mathcal{L}\tilde{R}'(t-s)$$
$$- |T(\mathbf{q}))\frac{nc_V^\infty}{k_B T_m^2}(\dot{T}(\mathbf{q})|\tilde{R}'(t-s) \quad (3.10)$$

and the additional terms in equations (3.9) and (3.10) modify the results obtained in Section 2. On the one hand, in the definition of the four memory functions $\eta_b(t), \eta_s(t), \mu(t)$ and $\Gamma'(t)$, $R'(t)$ has to be replaced by $\tilde{R}'(t)$. On the other hand, as $T(\mathbf{q})$ and $\dot{T}(\mathbf{q})$ are scalar variables, the introduction of the temperature fluctuations does not affect the dynamics of the tensorial traceless variables, either the orientational variable, $Q_{ij}(\mathbf{q})$, or the traceless part of $\Pi_{ij}(\mathbf{q})$, $\pi_{ij}(\mathbf{q})$. Conversely, the temperature couples to the $p(\mathbf{q})\delta_{ij}$ part of $\Pi_{ij}(\mathbf{q})$ and this coupling acts at two different places.

First

$$R(t)\tilde{P}p(\mathbf{q}) = R(t)Pp(\mathbf{q})$$
$$+ T(\mathbf{q}, t)\frac{nc_V^\infty}{k_B T_m^2}(T(\mathbf{q})|p(\mathbf{q})); \quad (3.11)$$

equation (3.11) introduces an instantaneous coupling between $\Pi_{ij}(\mathbf{q})$ and $T(\mathbf{q}, t)$. With reference to the usual Navier-Stokes equation where this coupling coefficient has the form

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \rho_m \beta, \quad (3.12a)$$

we define the instantaneous tension coefficient β^∞ through

$$\beta^\infty = \frac{c_V^\infty}{m k_B T_m^2}(T|p). \quad (3.12b)$$

Second, the additional term in the r.h.s of equation (3.10) brings a retarded interaction between $p(\mathbf{q}, t)$ and $T(\mathbf{q}, t)$,

namely

$$- \int_0^t T(\mathbf{q}, s)\frac{nc_V^\infty}{k_B T_m^2}(\dot{T}|\tilde{R}'(t-s)|p)ds. \quad (3.13)$$

The memory function appearing in the preceding equation is best understood if we define

$$\delta\beta(t) = \frac{1}{m k_B T_m^2}(e_P|\tilde{R}'(t)|p). \quad (3.14)$$

Then

$$m k_B T_m^2 \delta\dot{\beta}(t) = (e_P|i\tilde{Q}\mathcal{L}\tilde{R}'(t)|p)$$
$$= -(i\mathcal{L}\tilde{Q}e_P|\tilde{R}'(t)|p). \quad (3.15a)$$

Since $e_P(\mathbf{q})$ is orthogonal to $T(\mathbf{q})$, equation (3.8), whatever $\mathbf{q}$

$$\tilde{Q}e_P(\mathbf{q}) = e_P - \tilde{P}e_P(\mathbf{q})$$
$$= e_P(\mathbf{q}) - \rho(\mathbf{q})\frac{c_i^2}{m k_B T_m}(\rho(\mathbf{q})|e_P(\mathbf{q})). \quad (3.15b)$$

The Liouville operator acting on $\tilde{Q}e_P(\mathbf{q} = 0)$ produces an $\dot{e}_P(\mathbf{q} = 0)$ term plus a $\dot{\rho}(\mathbf{q} = 0)$ term which is equal to zero because of mass conservation so that

$$m k_B T_m^2 \delta\dot{\beta}(t) = -(\dot{e}_P|\tilde{R}'(t)|p). \quad (3.15c)$$

Conservation of the total energy implies for the long-wavelength limit of the potential energy density

$$-\dot{e}_P = \dot{e}_K = c_V^\infty\left[\dot{T} + \frac{T_m}{\rho_m}\dot{\rho}\right], \quad (3.15d)$$

where, once more, $\dot{\rho}$ vanishes in equation (3.15d); thus,

$$\rho_m\delta\dot{\beta}(t) = \frac{nc_V^\infty}{k_B T_m^2}(\dot{T}|\tilde{R}'(t)|p), \quad (3.15e)$$

and

$$- \int_0^t T(\mathbf{q}, s)\frac{nc_V^\infty}{k_B T_m^2}(\dot{T}|\tilde{R}'(t-s)|p)ds =$$
$$- \rho_m \int_0^t T(\mathbf{q}, s)\delta\dot{\beta}(t-s)ds. \quad (3.15f)$$

The additional terms, equations (3.11) and (3.15f), with the definition of β^∞, equation (3.12b), have to be added to equation (2.28) and yield

$$\Pi_{ij}(\mathbf{q}, t) = \left[c_i^2\rho(\mathbf{q}, t) + \rho_m \int_0^t \beta(t-s)T(\mathbf{q}, s)ds\right.$$
$$\left. + \int_0^t \eta_b(t-s)iq_k v_k(\mathbf{q}, s)ds\right]\delta_{ij}$$
$$- \int_0^t \eta_s(t-s)\tau_{ij}(\mathbf{q}, s)ds$$
$$+ \int_0^t \mu(t-s)\dot{Q}_{ij}(\mathbf{q}, s)ds + \text{noise}, \quad (3.16a)$$

with

$$\beta(t) = \beta^\infty \delta(t - 0) - \delta\dot\beta(t). \qquad (3.16b)$$

The introduction of the temperature variable replaces equation (2.28) of Section 2 by equation (3.16a), while equation (2.32) is not modified.

Let us finally look for the equation of motion of $\dot T(\mathbf{q}, t)$. Due to time reversal and rotational symmetry, in leading order of the wavenumber, the only nonzero term of $\tilde P\dot T(\mathbf{q})$ arises from the current contribution J_k. As shown in Appendix A, this contribution can be expressed as

$$R(t)|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(J_k(\mathbf{q})|\dot T(\mathbf{q})) = \frac{T_m}{c_V^\infty}\beta^\infty\dot\rho(\mathbf{q}, t). \qquad (3.17)$$

There is an instantaneous coupling between $T(\mathbf{q})$ and $\dot\rho(\mathbf{q})$.

We now turn to the retarded couplings. From symmetry considerations, only the two scalar terms are involved. The first originates from

$$iq_l|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(\Pi_{kl}|\tilde R'(t - s)|\dot T), \qquad (3.18a)$$

where, as usual, we have taken the $q = 0$ limit of the thermal average involving $\tilde R'(t)$ and where we have only to consider the $p\delta_{kl}$ contribution; it can be transformed (see Appendix A) into

$$|\dot\rho(\mathbf{q}))\frac{T_m}{c_V^\infty}\delta\dot\beta(t - s). \qquad (3.18b)$$

The second retarded term originates from the last term of the r.h.s. of equation (3.10) and reads

$$-|T(\mathbf{q}))\frac{nc_V^\infty}{k_BT_m^2}(\dot T(\mathbf{q})|\tilde R'(t - s)|\dot T(\mathbf{q})). \qquad (3.19)$$

Let us first study the $q \to 0$ limit of the coefficient of $T(\mathbf{q})$ and define

$$\delta c_V(t) = \frac{1}{nk_BT_m^2}(e_P|\tilde R'(t)|e_P). \qquad (3.20)$$

Appendix A shows that, up to terms in second order in q, one has

$$nk_BT_m^2\frac{\partial^2}{\partial t^2}\delta c_V(t) = -(c_V^\infty)^2(\dot T|\tilde R'(t)|\dot T). \qquad (3.21)$$

We can thus write, up to a second order term in q

$$\frac{nc_V^\infty}{k_BT_m^2}(\dot T(\mathbf{q})|\tilde R'(t - s)|\dot T(\mathbf{q})) =$$
$$- \frac{\delta\ddot c_V(t - s)}{c_V^\infty} + q^2\frac{\lambda(t - s)}{c_V^\infty} + \mathcal{O}(q^3), \qquad (3.22)$$

which defines a heat diffusion retarded interaction, $\lambda(t)$.

Grouping together equations (3.17), (3.18b), and (3.22), we finally obtain

$$c_V^\infty\dot T(\mathbf{q}, t) = T_m\int_0^t \beta(t - s)\dot\rho(\mathbf{q}, s)ds$$
$$+ \int_0^t \left[\delta\ddot c_V(t - s) - q^2\lambda(t - s)\right] T(\mathbf{q}, s)ds + \text{noise}. \qquad (3.23)$$

We shall, in the rest of the paper, keep the retarded character of $\lambda(t - s)$ though, because of its physical origin, this retardation aspect is presumably negligible under any circumstance.

3.2 Discussion I: form of the Navier-Stokes equations

The set of equations (3.16a), (2.32), and (3.23) is nearly identical to the Navier-Stokes equations that have been proposed in I. Equation (3.16a) is exactly the opposite of the generalisation of the stress tensor $\overline{\overline\sigma}$ presented in equation (2.18) of I. The tension coefficient $\beta(t)$ is the sum of an instantaneous interaction, $\beta^\infty\delta(t - 0)$, and of a retarded contribution, $-\delta\dot\beta(t)$, where $\delta\beta(t)$ is a natural relaxation function (see Eq. (3.14)). The formal expression of $\beta(t)$, and its role in equation (3.16a), give a simple physical meaning to $\delta\beta(t)$. If $T(\mathbf{q}, s)$ has the form $T(\mathbf{q})H(s)$, where $H(s)$ is the Heaviside function, the term in $\beta(t)$ of equation (3.16a) yields a pressure at time t, $\Delta p(\mathbf{q}, t)$, equal to

$$\Delta p(\mathbf{q}, t) = \rho_mT(\mathbf{q})[\beta^\infty + \delta\beta^0 - \delta\beta(t)]$$
$$\equiv \rho_mT(\mathbf{q})[\beta^{th} - \delta\beta(t)], \quad (3.24a)$$

where, as in I, $f^0 \equiv f(t = 0)$; as $\delta\beta(t)$ tends to zero when $t \to \infty$,

$$\delta\beta(t) = \frac{\Delta p^{th}(\mathbf{q}) - \Delta p(\mathbf{q}, t)}{\rho_mT(\mathbf{q})}, \qquad (3.24b)$$

where $\Delta p^{th}(\mathbf{q})$ is the pressure increase at infinite time.

As argued in I, the orientational dynamics contains no coupling with the temperature so that its microscopic derivation yields the same result as obtained in [3]. Conversely, equation (3.23), which represents the conservation of energy, has not exactly the same expression as proposed in I. As in our phenomenological approach, the same $\beta(t)$ function couples the temperature fluctuations to $\overline{\overline\sigma}$ in equation (3.16a) and the time derivative of the mass density fluctuation to the time derivative of the local temperature in equation (3.23). Yet, equation (3.23) differs from equation (2.17) of I because the retarded part of the specific heat does not couple to $\dot T(\mathbf{q}, s)$ but to $T(\mathbf{q}, s)$, the temperature fluctuation. However, after integration by parts, one obtains

$$c_V^\infty\dot T(\mathbf{q}, t) - \int_0^t \delta\ddot c_V(t - s)T(\mathbf{q}, s)ds =$$
$$\int_0^t c_V(t - s)\dot T(\mathbf{q}, s)ds - \delta\dot c_V(t)T^0(\mathbf{q}), \quad (3.25a)$$

where, as in I,

$$c_V(t) = c_V^\infty \delta(t-0) - \delta\dot{c}_V(t), \qquad (3.25b)$$

and where

$$T^0(\mathbf{q}) = T(\mathbf{q}, t=0) \qquad (3.25c)$$

is the temperature fluctuation at time $t = 0$, equation (3.25a) taking into account that $\delta c_V(t)$ is an even function of time (see Eq. (3.20)).

The l.h.s. of equation (3.25a) yields a physical interpretation of $\delta c_V(t)$ similar to that of $\delta\beta(t)$. This l.h.s. represents the energy increase per unit volume and unit time, $\Delta\dot{Q}(\mathbf{q}, t)$, at constant density, when heat diffusion is not taken into account. For the same temperature variation as above, $T(\mathbf{q}, s) = T(\mathbf{q})H(s)$, one obtains

$$\begin{aligned}\Delta Q(\mathbf{q}, t) &= \int_0^t \Delta\dot{Q}(\mathbf{q}, t')dt' \\ &= T(\mathbf{q})[c_V^\infty + \delta c_V^0 - \delta c_V(t)] \\ &\equiv T(\mathbf{q})[c_V^{th} - \delta c_V(t)].\end{aligned} \qquad (3.25d)$$

Thus

$$\delta c_V(t) = \frac{\Delta Q^{th}(\mathbf{q}) - \Delta Q(\mathbf{q}, t)}{T(\mathbf{q})}, \qquad (3.25e)$$

where $\Delta Q^{th}(\mathbf{q})$ is the heat absorbed per unit volume at infinite time. The formal expression of $\delta c_V(t)$, equation (3.20), ensures that $\delta c_V^0 \equiv \delta c_V(t=0)$ is positive while $\delta c_V(t)$ tends to zero when $t \to \infty$.

Let us now discuss the r.h.s. of equation (3.25a). In I, the initial temperature fluctuation $T^0(\mathbf{q})$ was taken to be identical to zero, since in a TG experiment the temporal evolution of the dynamical variables is dominated by the excitation by the pump beams: the microscopic derivation precisely reproduces the equations proposed in I under this assumption. Additionally, one can use either the form of the energy conservation equation derived here or the form proposed in I to derive expression for the BS spectra. One obtains the same result with both forms when one uses the scattering model of equation (1.1) (density and orientation only). Nevertheless, the form derived microscopically is necessary to obtain expressions for the BS spectra that have the proper symmetry when one enlarges, as here, the scattering model to take into account the change in temperature as an additional light scattering mechanism:

$$\delta\overline{\overline{\epsilon}}(\mathbf{q}, t) = a\rho(\mathbf{q}, t)\overline{\overline{I}} + b\overline{\overline{Q}}(\mathbf{q}, t) + cT(\mathbf{q}, t)\overline{\overline{I}}. \qquad (3.26)$$

Indeed, a straightforward calculation, strictly following the method used in [3] and summarised in Appendix B, yields for VV scattering, i.e. for incident and scattered photons polarised perpendicular to the scattering plane

(see Appendix B)

$$\begin{aligned}I_{VV}(\mathbf{q}, \omega) = \frac{mk_B T_m}{\omega}\mathrm{Im}&\left[\frac{a^2}{c_i^2} + \frac{4b^2}{3}\frac{\Lambda'}{\rho_m\omega_R^2}\left(1 - \frac{\omega_R^2}{D(\omega)}\right)\right. \\ &\left.- c^2\frac{T_m}{\rho_m}\frac{1}{c_V(\omega)}\frac{\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}\right] \\ + \frac{mk_B T_m}{\omega}\mathrm{Im}&\left[q^2 C(\omega)P_L'(q,\omega)C(\omega)\right],\end{aligned}$$

$$(3.27a)$$

with

$$C(\omega) = a + \frac{2b\Lambda'}{3\rho_m}r(\omega) + c\frac{T_m\beta(\omega)}{c_V(\omega)}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}. \qquad (3.27b)$$

Here $P_L'(q, \omega)$ is the propagator of the longitudinal phonon

$$P_L'(q, \omega) = \left[\omega^2 - q^2(c_i^2 + \rho_m^{-1}\omega\eta_L(\omega) + g(q,\omega))\right]^{-1}, \qquad (3.28a)$$

$$g(q, \omega) = -i\rho_m T_m\frac{\beta(\omega)^2}{c_V(\omega)}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}, \qquad (3.28b)$$

where

$$\tau_h(q, \omega) = \frac{c_V(\omega)}{q^2\lambda(\omega)}, \qquad (3.28c)$$

$$\eta_L(\omega) = \eta_b(\omega) + \frac{4}{3}\left[\eta_s(\omega) - \frac{\Lambda'}{\omega}D(\omega)r(\omega)^2\right], \qquad (3.28d)$$

$$D(\omega) = \omega_R^2 + \omega\Gamma'(\omega) - \omega^2, \qquad (3.28e)$$

$$r(\omega) = \omega\mu(\omega)\left[D(\omega)\right]^{-1}. \qquad (3.28f)$$

$\eta_b(\omega), \eta_s(\omega), \mu(\omega), \Gamma'(\omega), \beta(\omega), c_V(\omega)$ and $\lambda(\omega)$ are, respectively, the Laplace transforms of $\eta_b(t), \eta_s(t)$, etc., the retarded interactions[2] appearing in equations (3.16a), (2.32) and (3.23). The physical meaning of the different functions defined in equations (3.28) has been discussed in I.

Equation (3.27a) generalises the result obtained in [2] and I for such a scattering geometry. Its first bracket is independent of the phonons and contains an incoherent

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[2] As $\beta(t)$ appears only under the form of convolution products with $T(\mathbf{q}, t)$ or $\rho(\mathbf{q}, t)$, equations (3.16a) and (3.23), with a similar expression for $c_V(t)$ (see the r.h.s. of Eq. (3.25a)), we have found convenient, in I and here, to define $\beta(\omega)$ and $c_V(\omega)$ as usual Laplace transforms: $f(\omega) = i\int_0^\infty f(t)e^{-i\omega t}dt$. Another definition, namely $\tilde{\beta}(\omega) = -i\beta(\omega)$, $\tilde{c}_V(\omega) = -ic_V(\omega)$, could have been chosen. It would have lead, e.g., to $\tilde{\beta}(\omega) = \beta^{th} - \omega\delta\beta(\omega)$, stressing the fact that $\beta^{th} = \rho_m^{-1}\lim_{t\to\infty}(\delta p(t)/\delta T(0))_\rho$ is a susceptibility, the $-\omega\delta\beta(\omega)$ term corresponding to the extra contribution, in the frequency space, not contained in β^{th} and which has to be included to take retardation effects into account.

contribution from each scattering mechanism. Conversely, in the second bracket, those contributions act coherently through $C(\omega)^2$. The appearance of the square of $C(\omega)$ underlines that $I_{VV}(q,\omega)$ is the imaginary part of the Fourier-Laplace transform of the correlation function

$$\langle \delta\epsilon_{VV}(\mathbf{r},t)\delta\epsilon_{VV}(\mathbf{0},0)\rangle \qquad (3.29)$$

and that this correlation function is symmetric with respect to time reversal: the coherent fluctuations of the dielectric tensor are both the source of the longitudinal phonons and of their detection by light scattering.

Note that in practice, equation (3.27a) reduces to the results presented in [2] and I because, as discussed in Appendix E for a more general case, c/a is always much smaller than $c_V^{th}/(T_m\beta^{th})$ so that the c-contribution to the BS spectra can always be neglected with respect to the density contribution (a-term in Eq. (3.27a)).

3.3 Discussions II: the Onsager relations

The three material dependent equations related, respectively to $\Pi_{ij}(\mathbf{q},t)$, equation (3.16a), $\ddot{Q}_{ij}(\mathbf{q},t)$, equation (2.32), and $c_V^\infty \dot{T}(\mathbf{q},t)$, equation (3.23), are linear functions of $\rho(\mathbf{q},t)$, $Q_{ij}(\mathbf{q},t)$, $T(\mathbf{q},t)$ and/or of their time derivatives and they are coupled through some of their memory functions. The coupling between the two first equations appears though $\mu(t)$; as recalled in Section 2, its form translates into the relations between the three relaxation functions $\eta_s(t), \mu(t)$, and $\Gamma'(t)$, that were discussed in [3]. Conversely, in that paper which ignored the temperature fluctuations, the fourth relaxation function, $\eta_b(t)$ remained an isolated quantity.

The introduction of temperature fluctuations leads to the additional equation (3.23) and to its coupling to equation (3.16a), this coupling containing a time dependent part, $\delta\dot{\beta}(t)$. Equations (2.23a), (3.14), and (3.20) show that this time-dependent part introduces a relation between $\eta_b(t)$, $\delta\beta(t)$, and $\delta c_V(t)$. If

$$(rp + se_P|\tilde{R}'(t)|rp + se_P) = \frac{k_B T_m}{n}(r^2\eta_b(t)$$
$$+ 2rs\rho_m T_m\delta\beta(t) + s^2 T_m\delta c_V(t)), \quad (3.30)$$

as p and e_P have the same time reversal symmetry, the imaginary part of the Laplace transform of equation (3.30) must be non-negative for complex frequencies in the lower half of the complex plane, whatever r and s. This implies that for $\text{Im}(\omega) \leq 0$ and, in particular, for ω real,

$$\text{Im}\,\eta_b(\omega) \geq 0, \qquad (3.31a)$$

$$\text{Im}\,\delta c_V(\omega) \geq 0, \qquad (3.31b)$$

$$[\text{Im}\eta_b(\omega)][\text{Im}\delta c_V(\omega)] - T_m[\rho_m\text{Im}\delta\beta(\omega)]^2 \geq 0, (3.31c)$$

these equations bringing a complete symmetry between $\eta_s(t)$, $\mu(t)$, and $\Gamma'(t)$ on the one hand, $\eta_b(t)$, $\delta\beta(t)$, and $\delta c_V(t)$ on the other hand. Furthermore, the whole set of

equations (2.34) was necessary to ensure that any Brillouin spectrum analysed through the scattering model of equation (1.1) would be positive for all frequencies, whatever be the coefficients a and b. Similarly, the two sets of conditions, equations (2.34) and equations (3.31), ensure the same property for the scattering model of equation (3.26) with the three equations of motion equations (3.16a), (2.32), and (3.23), whatever are the values of a, b, c. The proof is rather lengthy and is sketched in Appendix C, for the case of VV scattering discussed in the preceding sub-section.

4 The Transient Grating signal

4.1 The Navier-Stokes equations with sources

In a TG experiment, the electric field that acts on the liquid is

$$\mathbf{E}(\mathbf{r},t) = \text{Re}[\mathbf{E}^1(\mathbf{r},t) + \mathbf{E}^2(\mathbf{r},t)], \qquad (4.1)$$

where $\mathbf{E}^1(\mathbf{r},t)$ (resp. $\mathbf{E}^2(\mathbf{r},t)$) is the electric field of the pump laser with wavevector $\mathbf{q}_1$ (resp. $\mathbf{q}_2$) and polarisation $\hat{\mathbf{e}}^1$ (resp. $\hat{\mathbf{e}}^2$)

$$\mathbf{E}^1(\mathbf{r},t) = E^1(t)\hat{\mathbf{e}}^1 \exp[i(q_l z - \omega t)]\exp(iqx/2), \quad (4.2)$$
$$\mathbf{E}^2(\mathbf{r},t) = E^2(t)\hat{\mathbf{e}}^2 \exp[i(q_l z - \omega t)]\exp(-iqx/2), (4.3)$$

$\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ being, in analogy with Appendix A.3, the internal and external bisectors of $\mathbf{q}_1$ and $\mathbf{q}_2$.

From a general point of view, the coupling of $\mathbf{E}(\mathbf{r},t)$ with the local relative dielectric tensor, $\bar{\bar{\epsilon}}(\mathbf{r},t)$, of the liquid as well as with the local fluctuating dipole moment, $\mathbf{M}(\mathbf{r},t)$, is the origin of the TG signal. The fluctuating dipole moments give rise to the usual absorption of electromagnetic radiation at frequencies corresponding to molecular vibrations, eventually leading to the increase of energy density of the liquid which is the origin of the ISTS signal. The interaction of the laser beams with the relative dielectric tensor, on the other hand, is the origin of the reversible coupling of these beams with the liquid, leading to effects such as the electrostrictive one.

Since our microscopic model of rigid axially symmetric molecules is too simple to account for the absorptive processes by molecular vibrations, or by their overtones, we use an ad hoc approach to model the increase of the energy per unit time and unit volume. In terms of the macroscopic complex dielectric function $[\epsilon^0]_\omega$, this contribution is given by

$$\Delta\dot{\mathcal{E}}(\mathbf{r},t) = \frac{\epsilon_0}{2}\mathbf{E}^1(t)\cdot\mathbf{E}^2(t)\text{Im}([\epsilon^0]_\omega)\cos(qx), \quad (4.4)$$

where $\omega/2\pi$ corresponds to the frequency of the pump lasers. Note that the absorption properties of the liquid are identified with those of the unperturbed liquid, the spatial modulation being entirely due to the interference pattern of the pump beams. Also, a space-independent increase of the energy results from the incoherent parts of the total squared electric fields; however, since this increase does

not give rise to a TG signal, it has been discarded. The absorption process, equation (4.4), is, by definition, the source of the generalised ISTS signal. To simplify notation, we suppress the dependence of the frequency of the pump beams and treat the absorption constant as a phenomenological parameter

$$\text{Im}([\epsilon^0]_\omega) = mH. \qquad (4.5)$$

The second part of the TG signal, called in I the generalised ISBS signal, originates from the first order change in the real part of $\epsilon_{ij}(\mathbf{r}, t)$. This corresponds to a change in the energy density that can be expressed as

$$\Delta\mathcal{E}(t) = \Delta\mathcal{E}(\mathbf{q}, t) + \Delta\mathcal{E}(-\mathbf{q}, t), \qquad (4.6)$$

with

$$\Delta\mathcal{E}(\mathbf{q}, t) = -\frac{\epsilon_0}{4} E^1(t) E^2(t) \hat{e}_i^1 \hat{e}_j^2 \delta\epsilon_{ij}(\mathbf{q}, t), \qquad (4.7)$$

where $\delta\epsilon_{ij}(\mathbf{q}, t)$ is given by equation (3.26).

If $A_\mu(\mathbf{q}, t)$, with $1 \le \mu \le 15$, represents the 15 variables introduced in Sections 2 and 3, $\rho(\mathbf{q}, t)$, $J_i(\mathbf{q}, t)$, $Q_{ij}(\mathbf{q}, t)$, $K_{ij}(\mathbf{q}, t) = -\dot{Q}_{ij}(\mathbf{q}, t)$, and $T(\mathbf{q}, t)$, equation (4.7) has the form

$$\Delta\mathcal{E}(\mathbf{q}, t) = -A_\mu(\mathbf{q}, t) f_\mu(\mathbf{q}, t), \qquad (4.8)$$

where the different non-zero $f_\mu(\mathbf{q}, t)$ are easily derived from equation (3.26). The $A_\mu(\mathbf{q}, t)$ being linearly coupled to the coefficients $f_\mu(\mathbf{q}, t)$ in equation (4.8), the latter appear as generalised forces acting on the corresponding dynamical variables. Also, with the help of $K_{ij}(\mathbf{q}, t)$, the whole set of equations (2.14 and 2.15), equation (3.16a), and equation (3.23), can be cast into the form

$$\dot{A}_\mu(\mathbf{q}, t) = -\int_0^t B_{\mu\nu}(\mathbf{q}, t-s) A_\nu(\mathbf{q}, s) ds + \text{noise}. \quad (4.9)$$

Equation (4.9) describes the deterministic evolution of the set $\{A_\mu(\mathbf{q}, t)\}$ when the liquid is perturbed from equilibrium by the random forces represented by the noise terms. When those random forces are replaced by the generalised forces $\{f_\mu(\mathbf{q}, t)\}$, these forces add to each fluctuation at time s, $A_\mu(\mathbf{q}, s)$, a deterministic term, $-\chi_{\mu\lambda}(\mathbf{q}) f_\lambda(\mathbf{q}, s)$, where $\chi_{\mu\lambda}(\mathbf{q})$ is the static susceptibility

$$\chi_{\mu\lambda}(\mathbf{q}) = \frac{n}{k_B T_m} (A_\mu(\mathbf{q}) | A_\lambda(\mathbf{q})), \qquad (4.10)$$

whence

$$\dot{A}_\mu(\mathbf{q}, t) = -\int_0^t B_{\mu\nu}(\mathbf{q}, t-s) [A_\nu(\mathbf{q}, s)$$
$$- \chi_{\nu\lambda}(\mathbf{q}) f_\lambda(\mathbf{q}, s)] ds. \quad (4.11)$$

The different $\chi_{\nu\lambda}(\mathbf{q})$ corresponding to the generalised forces, $f_\lambda(\mathbf{q}, t)$ are easily obtained, to lowest order in $\mathbf{q}$, from the results of Sections 2 and 3 and are diagonal in the type of variables, ρ, $\overline{\overline{Q}}$, and T.

Introducing, in analogy with [3],

$$U^g(t) = \frac{m\epsilon^0}{4} E^1(t) E^2(t) \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2, \qquad (4.12)$$

$$T_{ij}^g(t) = \frac{m\epsilon^0}{4} E^1(t) E^2(t) [e_i^1 e_j^2 + e_i^2 e_j^1 - \frac{2}{3} \delta_{ij} \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2], \qquad (4.13)$$

equation (4.11) shows that the coupling of the first order change, $\delta\epsilon_{ij}(\mathbf{q}, t)$, to the electric fields of the pumps changes

– $\rho(\mathbf{q}, t)$ into $\rho(\mathbf{q}, t) - (a/c_i^2) U^g(t)$ in equation (3.16a);
– $Q_{ij}(\mathbf{q}, t)$ into $Q_{ij}(\mathbf{q}, t) - (2b\Lambda'/\rho_m\omega_R^2) T_{ij}^g(t)$ in equation (2.32);
– $T(\mathbf{q}, t)$ into $T(\mathbf{q}, t) - (cT_m/\rho_m c_V^\infty) U^g(t)$ in equation (3.16a) and equation (3.23).

Furthermore, using equations (4.5) and (4.12), one can transform equation (4.4) into

$$\Delta\dot{\mathcal{E}}(t) = \Delta\dot{\mathcal{E}}(\mathbf{q}, t) + \Delta\dot{\mathcal{E}}(-\mathbf{q}, t), \qquad (4.14a)$$

with

$$\Delta\dot{\mathcal{E}}(\mathbf{q}, t) = \Delta\dot{\mathcal{E}}(-\mathbf{q}, t) = HU^g(t), \qquad (4.14b)$$

and the rate of increase of the energy density, $HU^g(t)$, has to be added to the r.h.s. of the equation of conservation of energy.

The three equations of motion for the material dependent variables now read

$$\Pi_{ij}(\mathbf{q}, t) = \left[c_i^2 \rho(\mathbf{q}, t) + \rho_m \int_0^t \beta(t-s) T(\mathbf{q}, s) ds \right.$$
$$\left. + \int_0^t \eta_b(t-s) i q_k \frac{J_k(\mathbf{q}, s)}{\rho_m} ds \right] \delta_{ij}$$
$$- \int_0^t \eta_s(t-s) \tau_{ij}(\mathbf{q}, s) ds$$
$$+ \int_0^t \mu(t-s) \dot{Q}_{ij}(\mathbf{q}, s) ds$$
$$- \delta_{ij} \left[aU^g(t) - \frac{cT_m}{c_V^\infty} \int_0^t \beta(t-s) U^g(s) ds \right], \qquad (4.15a)$$

$$\ddot{Q}_{ij}(\mathbf{q}, t) = -\omega_R^2 Q_{ij}(\mathbf{q}, t) - \int_0^t \Gamma'(t-s) \dot{Q}_{ij}(\mathbf{q}, s) ds$$
$$+ \Lambda' \int_0^t \mu(t-s) \tau_{ij}(\mathbf{q}, s) ds + \frac{2b\Lambda'}{\rho_m} T_{ij}^g(t), \qquad (4.15b)$$

$$c_V^\infty \dot{T}(\mathbf{q}, t) = T_m \int_0^t \beta(t-s) \dot{\rho}(\mathbf{q}, s) ds$$
$$+ \int_0^t \left[\delta\ddot{c}_V(t-s) - q^2 \lambda(t-s) \right] T(\mathbf{q}, s) ds$$
$$- \frac{cT_m}{\rho_m c_V^\infty} \int_0^t \left[\delta\ddot{c}_V(t-s) - q^2 \lambda(t-s) \right] U^g(s) ds$$
$$+ HU^g(t). \qquad (4.15c)$$

In the absence of a c-contribution to $\delta\epsilon_{ij}$, equations (4.15) are those proposed in I and the expressions of the sources proportional to a and b were derived in Appendix A of that paper through macroscopic arguments. The latter involved the equilibrium situation where the time dependence of $U^g(t)$ and $T^g_{ij}(t)$ are Heaviside functions. Conversely, the structure of the sources related to c seem difficult to obtain from the same type of arguments. The c-contribution adds sources to $\Pi_{ij}(\mathbf{q}, t)$ and to the rate of increase of the energy density, equation (4.15c), as already guessed by Shen [22]. Yet, his intuitive result largely differs from the additional terms of equations (4.15a) and (4.15c).

4.2 The Transient Grating signal

The expression of the TG signal was obtained in I under the hypothesis that $\delta\overline{\overline{\epsilon}}(\mathbf{q}, t)$ depended only on $\rho(\mathbf{q}, t)$ and $\overline{\overline{Q}}(\mathbf{q}, t)$. Concentrating on the case where only longitudinal phonons are involved, it was shown that any signal was a weighted sum of four independent signals each characterised by a parallel polarisation of the two pumps on the one hand, and of the probe and detection beams on the other hand. Those polarisations could be either along $\hat{\mathbf{x}}$ (H polarisation) or along $\hat{\mathbf{y}} = \hat{\mathbf{z}} \times \hat{\mathbf{x}}$ (V polarisation). The pump polarisation was labeled by the index ϵ_{ex} that takes the value 1 for a V polarisation and the value -1 for a H polarisation; in the same manner, the value of the index ϵ_p labeled the polarisation of the probe and detection beams. The results given in I (Eqs. (3.16) and (3.17)) corresponded to the case where $E^1(t)E^2(t)$ was proportional to $E^1E^2\delta(t-0)$ and where the heat diffusion process contained no relaxation contribution. Generalising those results to the case where such a relaxation process exists but keeping the same time dependence of the electric fields in order to give the expression of the response function of the system, the results of I could be expressed as

$$R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, t) = LT^{-1}[R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega)], \quad (4.16)$$

where $LT^{-1}[\,]$ indicates an inverse Laplace transform. $R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega)$ read

$$R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega) = i\left[b^2\frac{\Lambda'}{\rho_m}\frac{1+3\epsilon_p\epsilon_{ex}}{3}\frac{1}{D(\omega)}\right.$$
$$-q^2C^0(\epsilon_p,\omega)P'_L(\mathbf{q}, \omega)\left(C^0(\epsilon_{ex},\omega)\right.$$
$$\left.\left. -\frac{\rho_m\beta(\omega)}{c_V(\omega)}H\frac{\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}\right)\right], \quad (4.17)$$

with

$$C^0(\epsilon,\omega) = a + \frac{b\Lambda'}{\rho_m}\frac{3\epsilon-1}{3}r(\omega). \quad (4.18)$$

We defined the *generalised ISBS response functions* as the H independent part of equation (4.17) and showed that

$$R^{ISBS}_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, t) = \frac{-1}{mk_BT_m}\frac{d}{dt}(\delta\epsilon_{\epsilon_p}(\mathbf{q}, t)|\delta\epsilon_{ex}(\mathbf{q}, 0)), \quad (4.19)$$

where $\delta\epsilon_{\epsilon_p}(\mathbf{q}, t)$ is the ij component of $\delta\overline{\overline{\epsilon}}(\mathbf{q}, t)$ whose indices i and j are fixed by ϵ_p, with a similar meaning for $\delta\epsilon_{ex}(\mathbf{q}, t)$. Equation (4.19) simply expresses the Fluctuation-Dissipation Theorem: the part of $R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, t)$ which is the response to the generalised forces is the opposite, up to a mk_BT_m factor, of the time derivative of the correlation function of the corresponding components of the dielectric tensor.

When $\delta\overline{\overline{\epsilon}}$ is expressed by equation (1.2), a lengthy but straightforward calculation yields a generalisation of equations (4.17) and (4.18) that reads

$$R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega) = R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega) + R^2_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega), \quad (4.20)$$

with

$$R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega) = i\left[\frac{b^2\Lambda'}{\rho_m}\frac{1+3\epsilon_p\epsilon_{ex}}{3}\frac{1}{D(\omega)}\right.$$
$$\left.+\frac{c^2T_m}{\rho_mc_V^\infty} + c\frac{c\omega T_m/\rho_m + iH}{c_V(\omega)}\frac{\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}\right], \quad (4.21)$$

$$R^2_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega) = -iq^2C(\epsilon_p,\omega)P'_L(\mathbf{q}, \omega)\left[C(\epsilon_{ex},\omega)\right.$$
$$\left. -\frac{\rho_m\beta(\omega)}{c_V(\omega)}H\frac{\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}\right], \quad (4.22)$$

$$C(\epsilon,\omega) = a + \frac{b\Lambda'}{\rho_m}\frac{3\epsilon-1}{3}r(\omega)$$
$$+ cT_m\frac{\beta(\omega)}{c_V(\omega)}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}. \quad (4.23)$$

A derivation of equations (4.20–4.23) can also be obtained from the results of Section 3, those summarised below equation (4.13), and from equation (4.15c); it gives another insight to the physical content of those equations:

– First, in equation (4.22), $C(\epsilon_p,\omega)$ is the generalisation of the quantity $C(\omega)$ of equation (3.27b) which applies to a $\epsilon_p = 1$ experiment (V polarisation of the incident and scattered beams). This had to be expected: this factor represents the detection mechanism of the coherent part of the signal, which is the same in a BS and in a TG experiment: $C(\epsilon_p,\omega)$ simply generalises the expression of the detection mechanism, both for a BS and a TG experiment, for the different polarisations of the beams.
– Second, the term on the r.h.s. of $P'_L(\mathbf{q}, \omega)$ represents the sources that generate the longitudinal phonon; it is easily obtained from the same term in equation (4.17) by adding to the electrostrictive, orientational and heat absorption sources the three additional sources generated by the electrothermal contribution.
– Finally, the terms of $R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q}, \omega)$ which contain a factor 'c' have a somewhat different origin. The Laplace transform of equation (4.15c) reads

$$T(\mathbf{q}, \omega) = T_m \frac{\beta(\omega)}{c_V(\omega)} \frac{i\omega\tau_h(q,\omega)}{1 + i\omega\tau_h(q,\omega)} \rho(\mathbf{q}, \omega)$$
$$+ i \left[\frac{cT_m}{\rho_m c_V^\infty} \right.$$
$$\left. + \frac{c\omega T_m/\rho_m + iH}{c_V(\omega)} \frac{\tau_h(q,\omega)}{1 + i\omega\tau_h(q,\omega)} \right] U^g(\omega).$$
$$(4.24)$$

The term in brackets at the r.h.s. of equation (4.24) is detected only through the $cT(\mathbf{q},t)\delta_{ij}$ term of $\delta\epsilon_{ij}(\mathbf{q},t)$; it thus appears with a c factor as the second and last terms of equation (4.21). We can also note that the H-independent parts of these two terms correspond to two different effects. One is the counterpart, through the Fluctuation-Dissipation theorem, of the c^2 *incoherent* contribution to $I_{VV}(\mathbf{q},\omega)$ in equation (3.27a); it is a generalised ISBS contribution. Conversely, the $ic^2 T_m/(\rho_m c_V^\infty)$ term represents the instantaneous response of the liquid, through c_V^∞, to the pump beams: it has no equivalent in a BS experiment.

4.3 Discussion

Several comments are in order.

First, comparing equations (4.20–4.23) for $\epsilon_p = \epsilon_{ex} = 1$ (V polarisation for all the beams) with equation (3.27), it is apparent that the Fluctuation-Dissipation theorem is again fulfilled between the generalised ISBS signal and the $I_{VV}(\mathbf{q},\omega)$ spectrum, i.e. the H-independent terms of equations (4.21) and (4.22) fulfill equation (4.19)[3]. The generalised ISTS signal (terms proportional to H) has not only a contribution from $R^2_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ but also one from $R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ that originates from the c-contribution to $\delta\bar{\bar{\epsilon}}$, not considered in I.

Second, it was emphasised in I that the results of a polarised TG experiment could be analysed as the sum of six distinct, polarisation-independent contributions that we called Elementary Response Functions (ERFs). One of them is the first b^2 term of equation (4.17), which is the Optical Kerr Effect signal and is limited to times much shorter than the other ERFs. Three ERFs corresponded, through the Fluctuation-Dissipation theorem, to the longitudinal phonons generated by their mass density or by their orientational density contributions and detected by one of those two channels. Finally, the two last ERFs formed the generalised ISTS signal, which are generated by the heat absorption but are detected by the same mechanisms as above. Equations (4.20)–(4.23) introduce in principle more ERFs. Yet, the most important information is contained in the generalised ISTS signal, so that the TG experiments are, in fact, performed when the latter is non-negligible with respect to the generalised ISBS one. We show in Appendix E that, under such conditions, all the generalised ISTS contributions arising from

the c-contribution are negligible[4] when the two conditions

$$\frac{|c|}{a} \ll \frac{c_V^{th}}{T_m|\beta^{th}|}, \qquad (4.25a)$$

$$\frac{|c|}{a} \ll \frac{\rho_m|\beta^{th}|}{c_i^2}, \qquad (4.25b)$$

are fulfilled. The first condition implies that the electrothermal contribution may be neglected in $C(\epsilon,\omega)$ with respect to the electrostrictive one, i.e. in the r.h.s. of the stress tensor equation, equation (4.15a). This is always the case as it can be numerically checked for all known supercooled liquids. This contribution can thus be omitted in equation (4.22), as was done in I. The second condition means that the ISTS contribution to $R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ is negligible with respect to that of $R^2_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$, and that is also usually the case.

The analysis of $R_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ performed in I in terms of five ERFs thus breaks down only if condition (4.25b) is not fulfilled. This obviously takes place if there is a temperature at which $\beta^{th} = 0$, which implies the same thing for the thermal expansion coefficient, α^{th}, as $\beta^{th} = c_i^2\alpha^{th}$. This is the case in normal water where, at ambient pressure, α^{th} goes to zero at 4 °C. Equation (4.22) shows that the $R^2_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ contribution to the generalised ISTS signal, which is a decreasing exponential in the $t \sim \tau_h(q,\omega)$ time domain, will change sign at the same temperature as α^{th} does. Conversely, the $R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$ contribution to the ISTS signal, which is another exponential function with the same decay time, has a temperature independent amplitude. This second contribution explains that the change of sign of the exponential decay of the ISTS signal takes place at a temperature slightly different from 4 °C, as has been found by Taschin et al. [24]. Yet, condition (4.25a) is obviously fulfilled. This implies that even in that case the c-contribution can be ignored not only in the dynamics of the liquid, but also in the detection mechanism, except for this $R^1_{\epsilon_p,\epsilon_{ex}}(\mathbf{q},\omega)$, ISTS contribution.

5 Summary and final remarks

5.1 Summary

This paper offers a microscopic derivation of the set of phenomenological equations proposed in I. It also gives an extension of those results to the description of TG experiments performed on supercooled molecular liquids when the temperature contributions are systematically taken into account. I proposed that:

1) The material dependent Navier-Stokes equations for a liquid formed of rigid linear molecules (rigid symmetric tops) would read

$$\Pi_{ij}(\mathbf{q}, t) = \Pi_{ij}^b(\mathbf{q}, t), \qquad (5.1a)$$

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[3] Up to the $ic^2 T_m/(\rho_m c_V^\infty)$, see above.

[4] The terms involving b can always be separated out as they depend on the indices ϵ_p and ϵ_{ex}.

with

$$\Pi_{ij}^b(\mathbf{q}, t) = \left[c_i^2 \rho(\mathbf{q}, t) + \rho_m \int_0^t \beta(t - s) T(\mathbf{q}, s) ds \right.$$

$$+ \left. \int_0^t \eta_b(t - s) i q_k v_k(\mathbf{q}, s) ds \right] \delta_{ij}$$

$$- \int_0^t \eta_s(t - s) \tau_{ij}(\mathbf{q}, s) ds$$

$$+ \int_0^t \mu(t - s) \dot{Q}_{ij}(\mathbf{q}, s) ds, \tag{5.1b}$$

$$\ddot{Q}_{ij}(\mathbf{q}, t) = \ddot{Q}_{ij}^b(\mathbf{q}, t), \tag{5.2a}$$

with

$$\ddot{Q}_{ij}^b(\mathbf{q}, t) = -\omega_R^2 Q_{ij}(\mathbf{q}, t)$$

$$- \int_0^t \Gamma'(t - s) \dot{Q}_{ij}(\mathbf{q}, s) ds$$

$$+ \Lambda' \int_0^t \mu(t - s) \tau_{ij}(\mathbf{q}, s) ds, \tag{5.2b}$$

$$\int_0^t c_V(t - s) \dot{T}(\mathbf{q}, s) ds = c_V^\infty \dot{T}^b(\mathbf{q}, t), \tag{5.3a}$$

with

$$c_V^\infty \dot{T}^b(\mathbf{q}, t) = T_m \int_0^t \beta(t - s) \dot{\rho}(\mathbf{q}, s)$$

$$- q^2 \int_0^t \lambda(t - s) T(\mathbf{q}, s) ds. \tag{5.3b}$$

$\beta(t)$ and $c_V(t)$ were respectively expressed as

$$\beta(t) = \beta^\infty \delta(t - 0) - \delta\dot{\beta}(t), \tag{5.4a}$$

$$c_V(t) = c_V^\infty \delta(t - 0) - \delta\dot{c}_V(t), \tag{5.4b}$$

where $\delta\beta(t)$ and $\delta c_V(t)$ have the usual properties of correlation functions. Those equations allowed to express $\delta\overline{\overline{\epsilon}}(\mathbf{r}, t)$ in terms of thermal fluctuations when $\delta\overline{\overline{\epsilon}}(\mathbf{r}, t)$ is expressed by equation (1.1) and, incidentally, to obtain from it, the expression of the BS scattering intensities.

2) In a TG experiment, the sources that generate the signal have two distinct origins. One is a weak absorption of the energy of the two pump lasers that is instantaneously transformed into heat. The second is the reversible coupling of the electric fields of these two lasers to the liquid through the real part of its local dielectric tensor. The introduction of this second type of sources required a special treatment. Admitting that the coupling acts by perturbing only the mass (electrostrictive effect) and the orientational (Optical Kerr Effect) densities, equation (1.1) was used to obtain from an energy minimisation procedure, the expression of these two last sources.

The Navier-Stokes equations including the three sources and neglecting the thermal fluctuations read

$$\Pi_{ij}(\mathbf{q}, t) = \Pi_{ij}^b(\mathbf{q}, t) - a U^g(t) \delta_{ij}, \tag{5.5}$$

$$\ddot{Q}_{ij}(\mathbf{q}, t) = \ddot{Q}_{ij}^b(\mathbf{q}, t) + \frac{2b\Lambda'}{\rho_m} T_{ij}^g(t), \tag{5.6}$$

$$\int_0^t c_V(t - s) \dot{T}(\mathbf{q}, s) ds = c_V^\infty \dot{T}^b(\mathbf{q}, t) + H U^g(t). \tag{5.7}$$

$U^g(t)$ and $T_{ij}^g(t)$ are defined in equations (4.12) and (4.13) and describe the time evolution of the amplitudes of the pumps as well as, for $T_{ij}^g(t)$, their polarisation while H describes the energy absorption process.

3) Finally, expressions for the TG signals were derived. The signal depends on the polarisation of the pump lasers, of the probe and of the detection beams. In case of parallel polarisation of the pumps, on the one hand, of the probe and detection beams, on the other hand, the signal could be split into a generalised ISTS signal and a generalised ISBS signal that were discussed in the Introduction.

On top of presenting a microscopic derivation of these results (see below), the present paper has extended the results of I to the case where the modulation of the local dielectric tensor includes the direct influence of temperature changes, equation (1.2). This derivation has been achieved through the Mori-Zwanzig technique already used in [3] and with the same model of rigid molecular tops as in I.

In this model, the potential energy of the liquid depends only on its configuration (position and orientation of the molecule). Conversely, the kinetic energy that the molecule can acquire is only related to the motion of their centers of mass and to their rotations around axes perpendicular to their axis of symmetry.

This model allowed us, first, to define the coefficient c_V^∞ of equation (5.4b) as the part of the specific heat per unit volume due to a change of kinetic energy, $c_V^\infty = (5/2)n k_B$. The temperature modulation, $T(\mathbf{q})$ around the mean temperature T_m was then defined by

$$c_V^\infty T(\mathbf{q}) = e_K(\mathbf{q}) - \rho(\mathbf{q}) \frac{c_V^\infty T_m}{\rho_m}, \tag{5.8}$$

where $e_K(\mathbf{q})$ is the kinetic energy modulation. Equation (5.8) makes clear that a temperature modulation is the part of $e_K(\mathbf{q})$ which does not correspond to a density modulation at constant kinetic energy per molecule.

The evolution equation of $T(\mathbf{q})$ was then obtained. The only difference with the formulation of [3] was the addition of $T(\mathbf{q})$ to the relevant (distinguished) variables $\rho(\mathbf{q}), \mathbf{J}(\mathbf{q}), \overline{\overline{Q}}(\mathbf{q})$ and $\dot{\overline{\overline{Q}}}$ of that paper. The set of dynamical equations obtained contained equations (5.1) and (5.2). The derivation of equation (5.1) provided a microscopic definition of β^∞ and $\delta\beta(t)$, equation (5.4a). $\delta\beta(t)$ appeared, up to a material dependent factor, as the matrix element of the reduced time evolution operator, $\tilde{R}'(t)$, (see Eq. (3.9) and three lines below it) for the potential energy and the pressure variable, equation (3.14). Also, β^∞ was proportional to the static correlator of the temperature with the same pressure variable, equation (3.12b).

The evolution equation of $T(\mathbf{q})$ appeared under a form equivalent, see equations (3.23) and (3.25), though not identical to equation (5.3). It was also more complete as it contained the contribution of a possible temperature modulation at time $t = 0$, not included in I. Indeed, this equation could be written as

$$\int_0^t c_V(t-s)\dot{T}(\mathbf{q},s)ds = c_V^\infty \dot{T}^b(\mathbf{q},t) \\ - \delta\dot{c}_V(t)T^0(\mathbf{q}) + \text{noise}, \quad (5.9)$$

where $T^0(\mathbf{q})$ is that temperature modulation. The additional term of equation (5.9) allows the expression of the BS spectra to have the proper symmetry even when the light scattering model contains a direct contribution of the temperature fluctuations.

A microscopic expression of $\delta c_V(t)$, equation (3.20), also resulted from the Mori-Zwanzig technique. $\delta c_V(t)$ was expressed as the matrix element of $\tilde{R}'(t)$ related to the potential energy modulation. Because the bulk viscosity memory function, $\eta_b(t)$, is the corresponding matrix element for the fluctuations of the pressure, we obtained conditions on the Laplace transforms of $\eta_b(t)$, $\delta\beta(t)$, and $\delta c_V(t)$ and of some of their products. These conditions ensure, with results obtained in [3], that the BS spectra would be positive whatever are the relative contributions of $\rho(\mathbf{q})$, $\overline{\overline{Q}}(\mathbf{q})$, and $T(\mathbf{q})$ to the modulation of the dielectric tensor.

We finally used our microscopic model to derive the equations of motion of our three variables when the liquid is coupled to a temporally and spatially varying electric field, the coupling including now first order changes of the local dielectric tensor in $\rho(\mathbf{q})$, $\overline{\overline{Q}}(\mathbf{q})$, and $T(\mathbf{q})$. This allowed, first, to demonstrate the validity of equations (5.5–5.7), up to their H contribution, when the $T(\mathbf{q})$ contribution is ignored, second, to extend it to the case when this contribution is included. Yet, our model of rigid molecules does not allow for a non-negligible heat absorption, The latter (H contribution) had still to be added in an ad hoc manner. This lead to the three equations

$$\Pi_{ij}(\mathbf{q},t) = \Pi_{ij}^b(\mathbf{q},t) - \delta_{ij}\left[aU^g(t) \right. \\ \left. - \frac{cT_m}{c_V^\infty}\int_0^t \beta(t-s)U^g(s)ds \right], \quad (5.10)$$

$$\ddot{Q}_{ij}(\mathbf{q},t) = \ddot{Q}_{ij}^b(\mathbf{q},t) + \frac{2b\Lambda'}{\rho_m}T_{ij}^g(t), \quad (5.11)$$

$$\int_0^t c_V(t-s)\dot{T}(\mathbf{q},s) = c_V^\infty \dot{T}^b(\mathbf{q},t) \\ - \frac{cT_m}{\rho_m c_V^\infty}\int_0^t \left[\delta\ddot{c}_V(t-s) - q^2\lambda(t-s) \right]U^g(s)ds + HU^g(t). \\ (5.12)$$

Expressions of the TG signal were then derived, equations (4.20) to (4.23), that generalise those obtained in I; the introduction of the electrothermal effect (term in c)

preserves the distinction between the generalised ISTS and the generalised ISBS signals, with the connection of the latter to the corresponding BS spectrum. This result stresses the reversible character of the coupling of the pump lasers to the real part of the local dielectric tensor.

We also showed that one needs very special conditions, namely the passing through zero of the thermal expansion coefficient, for having to take into account the electrothermal effect. Except for this case, the formulae obtained in I are sufficient to analyse the results of TG experiments.

5.2 Remarks

The microscopic model we have used in the present paper has been sufficient to derive the Navier-Stokes equations without, equations (5.1), (5.2), and (5.9), and with, equations (5.10) to (5.12), sources corresponding to the model of dielectric fluctuations given by equation (1.2). Our derivation relies on two assumptions that need to be underlined.

One is the axial symmetry (symmetric top) of the molecules. This hypothesis makes the derivation and the form of the resulting equations relatively easy to handle. Nevertheless, one can show that a description of the orientational degrees of freedom of non-axial molecules in terms Wigner rotation matrices leads to light scattering spectra which can be cast into the form of the equations used in the present paper [27].

The second assumption is the rigidity of the molecules, which is fundamentally incorrect and has two different consequences. One is related to the energy absorption process. In real supercooled molecular liquids, this process takes place through a weak absorption of the pump laser light by the combination of bands and/or overtones of some molecular internal vibrations. The very short lifetime of these vibrational modes results in a quasi instantaneous heating of the liquid. The local dielectric function of a real glass-forming liquid contains the signature of those absorption processes, with the corresponding decay channels, while they are absent in the model of rigid molecules. This explains the need for an ad hoc introduction of the H term (Eq. (4.5)) in Section 4, instead of giving a rigorous, microscopic basis to the absorption process.

The rigid molecule hypothesis has a more obvious consequence. Whatever is the temperature of the (supercooled) liquid, the thermalisation of the internal molecular vibrations takes place through intramolecular anharmonic processes, and through interactions with neighboring molecules. Both processes take place on the picosecond time scale; they are not sensitive to the structural relaxation process and must be included into c_V^∞/n, as experimentally measured. This explains why one deduces, e.g., from the measurements[5] of Laughlin and Uhlmann [28] in salol at T_g that c_V^∞/n is $21.4k_B$, i.e. one

---

[5] For such dense liquids, the difference between the specific heat at constant pressure and constant volume are negligible with respect to the order of magnitude we discuss here.

order of magnitude larger than the $5k_B/2$ value expected in the rigid molecule model.

Similarly, the structural relaxation consists not only of a change in the density and in the orientational static correlation functions, but also in a modification of the mean internal structure of the molecules. The latter involves an important energy change that contributes to δc_V^0, the time integral of $-\delta \dot{c}_V(t)$; the latter turns out to be, for all the supercooled liquids where it has been measured, of the same order of magnitude as c_V^∞. For instance, one deduces from the measurements of Laughlin and Uhlmann [28] in salol at T_g, $\delta c_V^0 / c_V^\infty = 0.72$. Values of the same order of magnitude, $c_V^\infty / n = 12.5k_B$, $\delta c_V^0 / c_V^\infty = 0.80$ can be deduced from the modulated specific heat measurements of Birge [29] in glycerol at T_g. The introduction of such effects are certainly out of the scope of the present paper.

Appendix A

We give below the derivation of results given in Section 3 that require some mathematical manipulations.

A.1 Equation (3.17)

The current contribution to $\tilde{P}\dot{T}(\mathbf{q})$ reads, in leading order of the wave vector:

$$
R(t)|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(J_k(\mathbf{q})|\dot{T}(\mathbf{q})) =
$$
$$
- J_k(\mathbf{q},t)\frac{1}{mk_BT_m}(\dot{J}_k(\mathbf{q})|T(\mathbf{q}))
$$
$$
= -J_k(\mathbf{q},t)\frac{1}{mk_BT_m}(iq_l\Pi_{kl}|T)
$$
$$
= -J_k(\mathbf{q},t)\frac{1}{mk_BT_m}(iq_l\delta_{kl}p|T)
$$
$$
= iq_k J_k(\mathbf{q},t)\frac{1}{mk_BT_m}(p|T)
$$
$$
= \frac{T_m}{c_V^\infty}\beta^\infty\dot{\rho}(\mathbf{q},t). \qquad (A.1)
$$

Note that the last line of equation (A.1) requires the definition of β^∞, equation (3.12b).

A.2 Equation (3.18b)

The $p\delta_{kl}$ contribution to Π_{kl} in equation (3.18b) can be successively transformed into:

$$
iq_l|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(\Pi_{kl}|\tilde{R}'(t-s)|\dot{T}) =
$$
$$
iq_k|J_k(\mathbf{q}))\frac{1}{mk_BT_m}(p|\tilde{R}'(t-s)|\dot{T})
$$
$$
= \frac{1}{mk_BT_m}|\dot{\rho}(\mathbf{q}))(p|\tilde{R}'(t-s)|\dot{T})
$$
$$
= -\frac{1}{mk_BT_m}|\dot{\rho}(\mathbf{q}))(\dot{T}|\tilde{R}'(t-s)|p)
$$
$$
= |\dot{\rho}(\mathbf{q}))\frac{T_m}{c_V^\infty}\delta\dot{\beta}(t-s). \quad (A.2)
$$

The last but one line of this series of equalities results from the fact that $\dot{T}(t)$ and $p(t)$ have opposite time reversal symmetries.

A.3 Equation (3.21)

The technique used to obtain the formal expression of $\delta\beta(t)$ applies also to $\delta c_V(t)$. Repeating twice the arguments one obtains successively

$$
nk_BT_m^2\frac{\partial^2}{\partial t^2}\delta c_V(t) = \frac{\partial}{\partial t}(e_P|i\tilde{Q}\mathcal{L}\tilde{R}'(t)|e_P)
$$
$$
= -\frac{\partial}{\partial t}(i\mathcal{L}\tilde{Q}e_P|\tilde{R}'(t)|e_P)
$$
$$
= c_V^\infty\frac{\partial}{\partial t}(\dot{T}|\tilde{R}'(t)|e_P)
$$
$$
= c_V^\infty(\dot{T}|\tilde{R}'(t)|i\mathcal{L}\tilde{Q}e_P)
$$
$$
= -(c_V^\infty)^2(\dot{T}|\tilde{R}'(t)|\dot{T}). \qquad (A.3)
$$

Appendix B: Expression of $I_{VV}(\mathbf{q},\omega)$

We compute here the VV Brillouin scattering intensity, $I_{VV}(\mathbf{q},\omega)$, resulting from the use of equation (1.2), i.e. from fluctuations of $\delta\overline{\overline{\epsilon}}(\mathbf{q},t)$ due to changes in mass density, $\rho(\mathbf{q},t)$, orientational density $\overline{\overline{Q}}(\mathbf{q},t)$, and temperature $T(\mathbf{q},t)$. The equations of motion are given by equations (3.16a), (2.32), and (3.23). The computation follows closely the methods used in [2]. Yet, to keep in line with the notations in I, the wave vectors of the incident light, $\mathbf{q}_i$, and of the scattered light, $\mathbf{q}_f$, are in the $\hat{\mathbf{x}} - \hat{\mathbf{z}}$ plane, $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ being respectively the external and internal bisectors of $\mathbf{q}_i$ and $\mathbf{q}_f$; $\hat{\mathbf{y}}$ is defined as $\hat{\mathbf{y}} = \hat{\mathbf{z}} \times \hat{\mathbf{x}}$. VV scattering thus represents polarisation of the incident and scattered photons parallel to $\hat{\mathbf{y}}$.

Combining equations (2.14) and (2.15) with equation (3.16a) yields

$$-(c_i^2 q^2 + \rho_m^{-1}\omega k_L(\omega) - \omega^2)\left[\rho(\mathbf{q},\omega) - \frac{\rho^0(\mathbf{q})}{\omega}\right]$$

$$- q^2\omega\mu(\omega)\left[Q_{xx}(\mathbf{q},\omega) - \frac{Q_{xx}^0(\mathbf{q})}{\omega}\right]$$

$$+ iq^2\beta(\omega)T(\mathbf{q},\omega) = c_i^2 q^2 \frac{\rho^0(\mathbf{q})}{\omega}, \quad (\text{B.1a})$$

with

$$k_L(\omega) = \eta_b(\omega) + \frac{4}{3}\eta_s(\omega). \quad (\text{B.1b})$$

Similarly, the Laplace transform of equation (2.32) yields for $Q_{xx}(\mathbf{q},\omega)$

$$Q_{xx}(\mathbf{q},\omega) - \frac{Q_{xx}^0(\mathbf{q})}{\omega} = -\frac{4}{3}\frac{\Lambda'}{\rho_m}\left[\rho(\mathbf{q},\omega) - \frac{\rho^0(\mathbf{q})}{\omega}\right]$$

$$- \frac{\omega_R^2}{D(\omega)}\frac{Q_{xx}^0(\mathbf{q})}{\omega}, \quad (\text{B.2})$$

while one obtains from equation (3.23)

$$T(\mathbf{q},\omega) = \frac{1}{c_V(\omega)}\frac{i\tau_h(q,\omega)}{1+i\omega\tau(q,\omega)}\left[T_m\omega\beta(\omega)\left(\rho(\mathbf{q},\omega)\right.\right.$$

$$\left.\left. - \frac{\rho^0(\mathbf{q})}{\omega}\right) + ic_V^\infty T^0(\mathbf{q})\right]. \quad (\text{B.3})$$

Inserting equations (B.2) and (B.3) into equation (B.1) yields

$$\rho(\mathbf{q},\omega) - \frac{\rho^0(\mathbf{q})}{\omega} = \frac{q^2}{\omega}P_L'(\mathbf{q},\omega)A(\mathbf{q},\omega), \quad (\text{B.4})$$

with

$$A(\mathbf{q},\omega) = c_i^2\rho^0(\mathbf{q}) - \omega_R^2 r(\omega)Q_{xx}^0(\mathbf{q})$$

$$+ \frac{\rho_m\omega\beta(\omega)}{c_V(\omega)}\frac{ic_V^\infty}{1+i\omega\tau_h(q,\omega)}T^0(\mathbf{q}). \quad (\text{B.5})$$

Furthermore, one can write

$$\delta\epsilon_{yy}(\mathbf{q},t) = a\rho(\mathbf{q},t) - \frac{b}{2}\left[Q_{xx}(\mathbf{q},t)\right.$$

$$\left. - (Q_{yy}(\mathbf{q},t) - Q_{zz}(\mathbf{q},t))\right] + cT(\mathbf{q},t), \quad (\text{B.6})$$

while equation (2.32) applied to the yy and zz components of $\overline{\overline{Q}}$ yields

$$Q_{yy}(\mathbf{q},\omega) - Q_{zz}(\mathbf{q},\omega) =$$

$$\left(1 - \frac{\omega_R^2}{D(\omega)}\right)\left(\frac{Q_{yy}^0(\mathbf{q})}{\omega} - \frac{Q_{zz}^0(\mathbf{q})}{\omega}\right). \quad (\text{B.7})$$

With the help of the static averages (see Sect. 2.2) one successively obtains

$$(\rho(\mathbf{q},\omega)|\delta\epsilon_{yy}^0(\mathbf{q})) =$$

$$\frac{mk_BT_m}{\omega}\left[q^2 P_L'(\mathbf{q},\omega)C(\omega) + \frac{a}{c_i^2}\right], \quad (\text{B.8})$$

$$(Q_{xx}(\mathbf{q},\omega)|\delta\epsilon_{yy}^0(\mathbf{q})) =$$

$$\frac{mk_BT_m}{\omega}\left[-\frac{4}{3}\frac{\Lambda'}{\rho_m}r(\omega)q^2 P_L'(\mathbf{q},\omega)C(\omega)\right.$$

$$\left. - \frac{2b}{3}\frac{\Lambda'}{\rho_m}\frac{1}{\omega_R^2}\left(1 - \frac{\omega_R^2}{D(\omega)}\right)\right], \quad (\text{B.9})$$

$$(T(\mathbf{q},\omega)|\delta\epsilon_{yy}^0(\mathbf{q})) = \frac{mk_BT_m}{\omega}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}$$

$$\times\left[\frac{T_m\beta(\omega)}{c_V(\omega)}q^2 P_L'(\mathbf{q},\omega)C(\omega) - c\frac{T_m}{\rho_m}\frac{1}{ic_V(\omega)}\right], \quad (\text{B.10})$$

with

$$C(\omega) = a + \frac{2b}{3}\frac{\Lambda'}{\rho_m}r(\omega) + cT_m\frac{\beta(\omega)}{c_V(\omega)}\frac{i\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}. \quad (\text{B.11})$$

This yields

$$\left(a\rho(\mathbf{q},\omega) + \frac{b}{2}Q_{xx}(\mathbf{q},\omega) + cT(\mathbf{q},\omega)|\delta\epsilon_{yy}^0(\mathbf{q})\right) =$$

$$\frac{mk_BT_m}{\omega}\left[\frac{a^2}{c_i^2} + \frac{b^2}{3}\frac{\Lambda'}{\rho_m}\frac{1}{\omega_R^2}\left(1 - \frac{\omega_R^2}{D(\omega)}\right)\right.$$

$$- c^2\frac{T_m}{\rho_m}\frac{1}{c_V(\omega)}\frac{\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}$$

$$\left. + q^2 C(\omega)P_L'(\mathbf{q},\omega)C(\omega)\right], \quad (\text{B.12})$$

while, because of equations (B.7) and (2.10)

$$\frac{b}{2}(Q_{yy}(\mathbf{q},\omega) - Q_{zz}(\mathbf{q},\omega)|\delta\epsilon_{yy}^0(\mathbf{q})) =$$

$$\frac{mk_BT_m}{\omega}\frac{b^2\Lambda'}{\rho_m}\frac{1}{\omega_R^2}\left(1 - \frac{\omega_R^2}{D(\omega)}\right). \quad (\text{B.13})$$

Grouping together those two results, one obtains

$$LT\left[(\delta\epsilon_{yy}(\mathbf{q},t)|\delta\epsilon_{yy}^0(\mathbf{q}))\right](\omega) = \frac{mk_BT_m}{\omega}\left[\left\{\frac{a^2}{c_i^2}\right.\right.$$

$$+ \frac{4b^2}{3}\frac{\Lambda'}{\rho_m}\frac{1}{\omega_R^2}\left(1 - \frac{\omega_R^2}{D(\omega)}\right)$$

$$\left. - c^2\frac{T_m}{\rho_m}\frac{1}{c_V(\omega)}\frac{\omega\tau_h(q,\omega)}{1+i\omega\tau_h(q,\omega)}\right\}$$

$$\left. + q^2 C(\omega)P_L'(\mathbf{q},\omega)C(\omega)\right]. \quad (\text{B.14})$$

Appendix C: Positivity of the $I_{VV}(\mathbf{q}, \omega)$ spectrum

Appendix B makes clear that one can write $I_{VV}(\mathbf{q}, \omega)$ as

$$I_{VV}(\mathbf{q}, \omega) = \mathrm{Im}\left[LT\left[(a\rho(\mathbf{q}, t) - \frac{b}{2}Q_{xx}(\mathbf{q}, t) \right.\right.$$

$$\left.\left. + cT(\mathbf{q}, t)|a\rho^0(\mathbf{q}) - \frac{b}{2}Q_{xx}^0(\mathbf{q}) + cT^0(\mathbf{q}))\right](\omega)\right]$$

$$+ \mathrm{Im}\left[LT\left[(\frac{b}{2}(Q_{yy}(\mathbf{q}, t) - Q_{zz}(\mathbf{q}, t))|\frac{b}{2} \right.\right.$$

$$\left.\left. \times (Q_{yy}^0(\mathbf{q}) - Q_{zz}^0(\mathbf{q})))\right](\omega)\right], \quad (\text{C.1})$$

i.e. that $I_{VV}(\mathbf{q}, \omega)$ is the sum of two quadratic forms. One is based on the imaginary part of the Laplace Transforms of the correlation functions of the three variables $\rho(\mathbf{q}, t)$, $Q_{xx}(\mathbf{q}, t)$, and $T(\mathbf{q}, t)$, while the second corresponds to the same quantity for the correlation function of $Q_{yy}(\mathbf{q}, t) - Q_{zz}(\mathbf{q}, t)$. Let us write

$$\tilde{A}_1(q, t) = \rho(q, t), \quad (\text{C.2a})$$

$$\tilde{A}_3(q, t) = Q_{xx}(q, t), \quad (\text{C.2b})$$

$$\tilde{A}_5(q, t) = T(q, t), \quad (\text{C.2c})$$

$$\tilde{A}_6(q, t) = Q_{yy}(q, t) - Q_{zz}(q, t), \quad (\text{C.2d})$$

with $\mathbf{q} = q\hat{x}$, and further introduce

$$\tilde{A}_2(q, t) = -\dot{\tilde{A}}_1(q, t), \quad (\text{C.3a})$$

$$\tilde{A}_4(q, t) = -\dot{\tilde{A}}_3(q, t), \quad (\text{C.3b})$$

$$\tilde{A}_7(q, t) = -\dot{\tilde{A}}_6(q, t). \quad (\text{C.3c})$$

With such notations, $I_{VV}(\mathbf{q}, \omega)$ reads

$$I_{VV}(\mathbf{q}, t) = \sum_{\mu,\nu=1}^{5} \mathrm{Im}\left(a_\mu \tilde{C}_{\mu\nu}(q, \omega)a_\nu \right)$$

$$+ \sum_{\mu,\nu=6}^{7} \mathrm{Im}\left(a_\mu \tilde{C}_{\mu\nu}(q, \omega)a_\nu \right), \quad (\text{C.4})$$

with

$$\tilde{C}_{\mu\nu}(q, \omega) = LT[(\tilde{A}_\mu(q, t)|\tilde{A}_\nu^0(q))](\omega), \quad (\text{C.5a})$$

$$a_2 = a_4 = a_7 = 0. \quad (\text{C.5b})$$

We show below that the two quadratic forms appearing in equation (C.4) are, independently, positive definite.

Let us start by discussing the first one. The five equations of motion for $\tilde{A}_\mu(q, t)$ are easily obtained from equations (2.14), (2.15), and (3.16a) and equation (3.23). Because, in such a geometry, $\tau_{xx} = (4/3)\mathrm{div}\,\mathbf{v}$, these five equations may be written under the form

$$\dot{\tilde{A}}_\mu(q, t) = -\int_0^t \tilde{B}_{\mu\nu}(q, t-s)\tilde{A}_\nu(q, s)ds, \quad (\text{C.6a})$$

where the elements $\tilde{B}_{\mu\nu}(q, t)$ are

0	$\delta(t-0)$	0	0	0
$-q^2 c_i^2$	$q^2 \rho_m^{-1} k_L(t)$	0	$q^2 \mu(t)$	$-q^2 \rho_m \beta(t)$
0	0	0	$\delta(t-0)$	0
0	$\frac{4}{3}\frac{\Lambda'}{\rho_m}\mu(t)$	$-\omega_R^2 \delta(t-0)$	$\Gamma'(t)$	0
0	$\frac{T_m}{c_V^\infty}\beta(t)$	0	0	$-\frac{\delta\ddot{c}_V(t)-q^2\lambda(t)}{c_V^\infty}$

$$(\text{C.6b})$$

Note that equation (C.6a) represent an extension of equations used, e.g. by Mountain [30], or Allain and Lallemand [31], $\tilde{A}_2(q, t)$ being their variable $\psi(t)$, when relaxation phenomena as well as the additional rotational variable $Q_{xx}(q, t)$ (with $K_{xx}(q, t) = -\dot{Q}_{xx}(q, t)$) have to be taken into account.

Making the product of both sides of equation (C.6a) with $\tilde{A}_\lambda^0(q)$, taking the thermal average and performing the Laplace transform yields

$$\tilde{M}_{\mu\nu}(q, \omega)\tilde{C}_{\nu\lambda}(q, \omega) = k_B T_m \tilde{\chi}_{\mu\lambda}(q), \quad (\text{C.7a})$$

with

$$\tilde{M}_{\mu\nu}(q, \omega) = \omega\delta_{\mu\nu} - \tilde{B}_{\mu\nu}(q, \omega), \quad (\text{C.7b})$$

$$\tilde{\chi}_{\mu\nu}(q) = \frac{1}{k_B T}(\tilde{A}_\mu^0(q)|\tilde{A}_\nu^0(q)), \quad (\text{C.7c})$$

where $\tilde{B}_{\mu\nu}(q, \omega)$ is the Laplace transform of $\tilde{B}_{\mu\nu}(q, t)$. The value of the matrix elements of the static susceptibility matrix $\tilde{\chi}_{\mu\nu}(q)$ at the lowest order in $\mathbf{q}$ are easily derived from the definitions of the various $\tilde{A}_\mu(\mathbf{q})$ and from the results of Section 2.2. One finds, in particular, that this matrix is diagonal with all its elements positive. We show in Appendix D that a sufficient condition for the form $\mathrm{Im}(\tilde{C}_{\mu\nu}(q, \omega)$ to be positive definite is that the form $R_{\mu\nu}$, defined by

$$\bar{\bar{R}} = \frac{-1}{2i}[\bar{\bar{\chi}}\,\bar{\bar{M}}^+ - \bar{\bar{M}}\,\bar{\bar{\chi}}], \quad (\text{C.8})$$

and by $\tilde{M}_{\mu\nu}^+ = \tilde{M}_{\nu\mu}^*$, is also positive definite.

A lengthy but straightforward calculation yields for the elements of $\tilde{R}_{\mu\nu}(q, \omega)$ Because we look for sufficient

$$
\begin{pmatrix}
-\mathrm{Im}(\frac{\omega}{c_i^2}) & 0 & 0 & 0 & 0 \\
0 & -q^2\mathrm{Im}(\omega) + q^4\rho_m^{-1}\mathrm{Im}(k_L(\omega)) & 0 & \frac{4}{3}q^2\frac{\Lambda'}{\rho_m}\mathrm{Im}(\mu(\omega)) & iq^2\frac{T_m}{c_V^\infty}\mathrm{Re}(\beta(\omega)) \\
0 & 0 & -\frac{4}{3}\frac{\Lambda'}{\rho_m}\frac{1}{\omega_R^2}\mathrm{Im}(\omega) & 0 & 0 \\
0 & \frac{4}{3}q^2\frac{\Lambda'}{\rho_m}\mathrm{Im}(\mu(\omega)) & 0 & -\frac{4}{3}\frac{\Lambda'}{\rho_m}\mathrm{Im}(\omega - \Gamma'(\omega)) & 0 \\
0 & -iq^2\frac{T_m}{c_V^\infty}\mathrm{Re}(\beta(\omega)) & 0 & 0 & -\frac{T_m}{\rho_m c_V^\infty}\mathrm{Im}(\omega + \frac{\delta\ddot{c}_V(\omega)-q^2\lambda(\omega)}{c_V^\infty})
\end{pmatrix}. \tag{C.9}
$$

conditions for the form $\tilde{R}_{\mu\nu}$ to be non-negative, it is sufficient to prove that it can split into a sum of forms that individually have the same property. Furthermore, as we are interested in a light scattering spectrum, we need only to study the case of real frequencies, $\mathrm{Im}(\omega) = 0$. The non-trivial part of $\tilde{R}_{\mu\nu}$ is then a 3×3 matrix that can be split into three independent forms.

– One form involves only $\tilde{R}_{55}$, namely $(q^2 T_m/\rho_m(c_V^\infty)^2)\mathrm{Im}\lambda(\omega)$. Assuming that no relaxation process is included in the heat diffusion process, $\lambda(\omega) = i\lambda^0$; this leads to the obvious condition

$$\lambda^0 > 0. \tag{C.10}$$

– To obtain the two other forms, let us first factorise out the q^2 terms in line 2 and in column 2 of the matrix (C.9), then split $k_L(\omega)$ into its $\eta_b(\omega)$ and $\eta_s(\omega)$ parts, see equation (B.1b). One of these form is related to the indices 2 and 4. Once $4\rho_m/3$ has been factorised in that matrix, the remaining form reads

$$
\begin{array}{|c|c|}
\hline
\mathrm{Im}(\eta_s(\omega)) & \Lambda'\mathrm{Im}(\mu(\omega)) \\
\hline
\Lambda'\mathrm{Im}(\mu(\omega)) & \Lambda'\mathrm{Im}(\Gamma'(\omega)) \\
\hline
\end{array}. \tag{C.11}
$$

This form is positive definite provided that the three conditions (Eqs. (2.34b) to (2.34d)) are satisfied. As recalled in Section 2, these conditions result from the respective expressions of $\eta_s(t)$, $\mu(t)$, and $\Gamma'(t)$.

- The last form involves only the indices 2 and 5 of the same matrix, namely

$$
\begin{array}{|c|c|}
\hline
\frac{1}{\rho_m}\mathrm{Im}(\eta_b(\omega)) & i\frac{T_m}{c_V^\infty}\mathrm{Re}(\beta(\omega)) \\
\hline
-i\frac{T_m}{c_V^\infty}\mathrm{Re}(\beta(\omega)) & -\frac{T_m}{\rho_m(c_V^\infty)^2}\mathrm{Im}(\delta\ddot{c}_V(\omega)) \\
\hline
\end{array}. \tag{C.12}
$$

For ω real,

$$\mathrm{Re}(\beta(\omega)) = \omega\mathrm{Im}(\delta\beta(\omega)), \tag{C.13a}$$
$$-\mathrm{Im}(\delta\ddot{c}_V(\omega)) = \omega^2\mathrm{Im}(\delta c_V(\omega)). \tag{C.13b}$$

The conditions for the form given in equation (C.12) to be positive definite are thus those given by equations (3.31): they are automatically fulfilled because of the respective expressions of $\eta_b(t)$, $\delta\beta(t)$ and $\delta c_V(t)$.

The six conditions listed above, which are direct consequences of our theoretical approach, ensure that the first quadratic form of equation (C.4) is non-negative for real frequencies.

The second form appearing in equation (C.4) is again non-negative for real frequencies. Indeed, for the variable $\tilde{A}_6$ and $\tilde{A}_7$, the matrix $\tilde{B}_{\mu\nu}$ reads

$$
\begin{array}{|c|c|}
\hline
0 & -\delta(t-0) \\
\hline
-\omega_R^2\delta(t-0) & \Gamma'(t) \\
\hline
\end{array}, \tag{C.14}
$$

which is the part of the matrix appearing in equation (C.6b) corresponding to the indices 3 and 4. Furthermore,

$$\tilde{\chi}_{66} = 3\tilde{\chi}_{33}, \tag{C.15a}$$
$$\tilde{\chi}_{77} = 3\tilde{\chi}_{44}. \tag{C.15b}$$

The corresponding matrix $\overline{\overline{\tilde{R}}}$ is thus, up to a factor $3^2 = 9$, the part of the matrix $\overline{\overline{\tilde{R}}}$, equation (C.9), corresponding to the two indices 3 and 4. Equation (2.34c) ensures that it is positive definite.

$I_{VV}(\mathbf{q}, \omega)$ is thus non-negative for ω real whatever are the coefficients a, b and c entering into the expression of the fluctuation $\delta\epsilon_{ij}$.

Appendix D: Positive definite character of the form $\mathrm{Im}(\tilde{C}_{\mu\nu})$

We prove here that a sufficient condition for the form $\mathrm{Im}(\tilde{C}_{\mu\nu})$, where $\tilde{C}_{\mu\nu}$ is defined by equation (C.5a), to be positive definite is that the matrix $R_{\mu\nu}$ defined by equation (C.8) has the same property. Let us write equation (C.7a) as

$$\overline{\overline{\tilde{M}}}\,\overline{\overline{\tilde{C}}} = a\overline{\overline{\tilde{\chi}}}, \tag{D.1}$$

where $\overline{\overline{\tilde{\chi}}}$ is diagonal and real, a being a positive number. Multiplying equation (D.1) on its r.h.s. by $\overline{\overline{\tilde{M}}}^+$, where $\overline{\overline{\tilde{M}}}^+$ is the hermitian conjugate of $\overline{\overline{\tilde{M}}}$ ($\tilde{M}_{\mu\nu}^+ = \tilde{M}_{\nu\mu}^*$) yields

$$\overline{\overline{\tilde{M}}}\,\overline{\overline{\tilde{C}}}\,\overline{\overline{\tilde{M}}}^+ = a\overline{\overline{\tilde{\chi}}}\,\overline{\overline{\tilde{M}}}^+. \tag{D.2}$$

Furthermore, as $\overline{\overline{\tilde{C}}}$ is a symmetric matrix, $\overline{\overline{\tilde{C}}}^+ = \overline{\overline{\tilde{C}}}^*$, and as $\overline{\overline{\tilde{\chi}}}$ is real and diagonal,

$$[\overline{\overline{\tilde{M}}}\,\overline{\overline{\tilde{C}}}]^+ = \overline{\overline{\tilde{C}}}^*\,\overline{\overline{\tilde{M}}}^+ = a\overline{\overline{\tilde{\chi}}}. \tag{D.3}$$

$$(e_P(\mathbf{q})|e_K(\mathbf{q})) = \frac{1}{N} \frac{\int \left(\sum_{\alpha\beta} e^{i\mathbf{q}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)} v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha) e^{-V_0/k_B T_m} \right) \prod_\lambda d\mathbf{R}_\lambda d\cos\theta_\lambda d\phi_\lambda}{\int e^{-V_0/k_B T_m} \prod_\lambda d\mathbf{R}_\lambda d\cos\theta_\lambda d\phi_\lambda} K_\beta^{th}, \qquad (F.4)$$

Multiplying equation (D.3) on its l.h.s. by $\overline{\overline{\widetilde{M}}}$ and subtracting the result from equation (D.2) yields

$$\overline{\overline{\widetilde{M}}}\,\mathrm{Im}(\overline{\overline{\widetilde{C}}})\,\overline{\overline{\widetilde{M}}}^+ = \frac{a}{2i}(\overline{\overline{\widetilde{\chi}}}\,\overline{\overline{\widetilde{M}}} - \overline{\overline{\widetilde{M}}}\,\overline{\overline{\widetilde{\chi}}}) = a\overline{\overline{\widetilde{R}}}. \qquad (D.4)$$

Thus, if $\overline{\overline{\widetilde{R}}}$ is positive definite, the same is true for $\mathrm{Im}(\overline{\overline{\widetilde{C}}})$.

Appendix E

There are two different places where the electrostrictive contribution, characterised by a, and the electro-thermal contribution, characterised by c, compete. One is in $C(\epsilon, \omega)$, the other is in the relative weight of $R^1_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$ and $R^2_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$ in the generalised ISTS signal, once this first competition has been taken care of.

For simplicity, we neglect here the frequency dependence of $\beta(\omega)$ and $c_V(\omega)$ and identify them with ic_V^{th} and $i\beta^{th}$, respectively. The a and c contributions to $C(\epsilon, \omega)$ then read

$$\tilde{C}(\omega) = a + cT_m\frac{\beta^{th}}{c_V^{th}} - (-i)\frac{cT_m\beta^{th}}{c_V^{th}}\frac{1}{\tau_h}\frac{i\tau_h}{1 + i\omega\tau_h}. (E.1)$$

The second term of the r.h.s. of equation (E.1) is negligible with respect to the first one as long as

$$\frac{|c|}{a} \ll \frac{c_V^{th}}{T_m|\beta^{th}|}. \qquad (E.2)$$

This relation appears to be fulfilled for all the molecular liquids studied so far, and will obviously be the more valid the smaller is $|\beta^{th}|$. Also, because the frequency dependence of $\beta(\omega)$ and $c_V(\omega)$ does not change the order of magnitude of the real part of their ratio, one can safely neglect this dependence for the present discussion. Finally, the last term of the r.h.s. of equation (E.1) has been written in a way that makes clear that it generates a signal which is the convolution product of the signal generated by the second term with $\tau_h^{-1}\exp(-t/\tau_h)$. The τ_h^{-1} factor ensures that this signal is negligible with respect to this second term.

Condition (E.2) ensures that the electrothermal contribution may be neglected with respect to the electrostrictive one, as far as the generalised ISBS signal and/or the generalised ISTS part of $R^2_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$ are concerned.

Let us now compare the generalised ISTS contributions of $R^1_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$ and $R^2_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$, concentrating, for the $R^2_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$ part, on the electrostrictive detection. For such a discussion, one can approximate $P'_L(q, \omega)$ by $-(q^2 c_i^2)^{-1}$. We have thus to compare c (in $R^1_{\epsilon_p, \epsilon_{ex}}(\mathbf{q}, \omega)$)

with $(a/c_i^2)(\beta^{th}\rho_m)$, whence the additional condition to neglect the c-contribution

$$\frac{|c|}{a} \ll \frac{\rho_m|\beta^{th}|}{c_i^2}. \qquad (E.3)$$

Though this condition is also generally met in a supercooled liquid, it clearly breaks down if β^{th} tends to zero and this condition is always more stringent than relation equation (E.2) because

$$\frac{\rho_m|\beta^{th}|}{c_i^2} \ll \frac{c_V^{th}}{T_m|\beta^{th}|}. \qquad (E.4)$$

Indeed, if c_a is the adiabatic sound velocity and γ given by

$$\gamma = \frac{c_P^{th}}{c_V^{th}}, \qquad (E.5)$$

where c_P^{th} is the thermal value of the specific heat at constant pressure, one has (see e.g. I)

$$\frac{c_a^2 - c_i^2}{c_i^2} = \gamma - 1 = \frac{\rho_m T_m}{c_i^2}\frac{(\beta^{th})^2}{c_V^{th}}. \qquad (E.6)$$

$\gamma - 1$ is always a small positive number, which ensures that relation (E.4) is always satisfied.

Appendix F: Proof of equation (3.7c)

The unperturbed Hamilton function of the system, H_0, can be written as

$$H_0 = V_0 + K_0, \qquad (F.1)$$

where

$$V_0 = V(\{\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha\}) = \sum_\alpha v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha), \qquad (F.2a)$$

$$K_0 = \sum_\alpha K_\alpha, \qquad (F.2b)$$

K_0 not depending on the configuration of the liquid. Then

$$(e_P(\mathbf{q})|e_K(\mathbf{q})) = \frac{1}{N} \left\langle \sum_{\alpha\beta} e^{i\mathbf{q}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)} v(\mathbf{R}_\alpha, \theta_\alpha, \phi_\alpha) K_\beta \right\rangle \quad (F.3)$$

can be written as

See equation (F.4) above

with

$$K_\beta^{th} = \frac{\int K_\beta e^{-K_0/k_B T_m} \prod_\lambda d\mathbf{P}_\lambda dM_{\lambda X} dM_{\lambda Y}}{\int e^{-K_0/k_B T_m} \prod_\lambda d\mathbf{P}_\lambda dM_{\lambda X} dM_{\lambda Y}}. \quad \text{(F.5)}$$

As V_0 does not depend on the momenta, the integration over the momentum variables involves only equation (F.5), and one easily identifies K_β^{th} with $\langle K_\beta \rangle = c_V^\infty T_m/n$ (Eq. (3.2a)), a quantity independent of the molecule β. $(e_P(\mathbf{q})|e_K(\mathbf{q}))$ then appears as the product of two independent factors, whose first one is clearly $(e_P(\mathbf{q})|\rho(\mathbf{q})/m)$. This proves the identity

$$(e_P(\mathbf{q})|e_K(\mathbf{q})) = \frac{c_V^\infty T_m}{\rho_m}(e_P(\mathbf{q})|\rho(\mathbf{q})). \quad \text{(F.6)}$$

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