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Light scattering from nonequilibrium steady states

T. Keyes
Sterling Chemistry Laboratory, Yale University, 225 Prospect Street, New Haven, Connecticut 06511

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We consider light scattering from nonequilibrium steady states (NESS) where both density fluctuations (already studied by others) and orientational fluctuations are important scattering mechanisms. When orientational fluctuations are important, the possibilities for new NESS scattering experiments seem to multiply considerably. A theory is given for two promising new experiments: VH (vertical-horizontal) scattering in the presence of a sound wave and VH–VV (vertical-horizontal–vertical-vertical) interference, which vanishes identically in equilibrium.

I. INTRODUCTION

In a series of papers,[1-6] Oppenheim and co-workers have shown how to calculate averages of dynamical variables in nonequilibrium steady states (NESS). By choosing the product of the density with itself at a later time as the dynamical variable, they obtained the NESS density-density correlation function, which determines light scattering by density fluctuations; they predicted most interesting new features, absent in equilibrium, in light scattering by NESS.

Density fluctuations, however, are only one source of light scattering. For systems composed of nonspherical molecules, orientational fluctuations also constitute an important scattering mechanism. If we ignore "collision-induced" or "multiple" scattering (such scattering may also show new features in NESS, but we ignore it in this first paper), then the light scattering spectrum per volume $I(k,\omega)$, in arbitrary units is[7]

$$I(k,\omega)=\frac{1}{V}\mathrm{Re}\int_0^\infty e^{i\omega t}dt\int_V d\vec{r}\,d\vec{r}\,'\,e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\langle\hat{n}_i\cdot\underline{S}(\vec{r},t)\cdot\hat{n}_f\hat{n}_i\cdot\underline{S}(\vec{r}\,',0)\cdot\hat{n}_f\rangle_{\mathrm{av}}\,, \tag{1}$$

where V is the scattering volume, $\hat{n}_i$ and $\hat{n}_f$ are unit vectors along the direction of incident and scattered polarization, respectively, $\vec{k}$ is the scattering vector, $\underline{S}(\vec{r},t)$ is the scattering source, and $\langle\;\rangle_{\mathrm{av}}$ denotes an average over the ensemble describing the system. For quasielastic scattering,

$$|k|=\frac{4\pi}{\lambda}\sin(\tfrac{1}{2}\theta)\,, \tag{2}$$

where λ is the wavelength of the incident radiation and θ the scattering angle.

The expression which we have found for $\underline{S}$ is[7]

$$\underline{S}(\vec{r},t)=\left(\frac{\epsilon+2}{3}\right)^2[\alpha_0^e\delta N(\vec{r},t)\underline{1}+\Delta\alpha^e\underline{Q}(\vec{r},t)]\,, \tag{3}$$

where ϵ is the optical dielectric constant, α_0^e and $\Delta\alpha^e$ the "effective" trace and anisotropy of the molecular polarizability, δN the density fluctuation, and $\underline{Q}$ the fluctuating second-rank orientational order tensor, discussed exhaustively elsewhere.[7]

According to Eqs. (1) and (3), light scattering is determined by density correlations, orientational correlations, and density-orientation cross correlations. In equilibrium, the cross correlations vanish, as do correlations between different tensorial components of $\underline{Q}$. Since the density correlations have already been studied for NESS, we should now, to complete the scattering calculation, look for new features in orientational correlation functions, which exist in equilibrium, and for possible nonzero values of correlation functions, which vanish in equilibrium. In this paper we examine both possibilities and, in each case, find new effects which should be observable. The number of possible scattering experiments, with different geometry, $\hat{n}_i$, $\hat{n}_f$, and $\vec{k}$ is very large. We have selected two experiments for study here which are probably the most promising; other interesting possibilities definitely remain.

II. BACKGROUND

A. Review of equilibrium hydrodynamics of fluids of nonspherical molecules

Due to the translational invariance of the equilibrium ensemble, the source correlation functions in Eq. (1) then depend on $\vec{r}-\vec{r}\,'$ only, and we have

$$I^{VH}(k,\omega)=\frac{1}{V}\mathrm{Re}\times\int_0^\infty dt\,e^{i\omega t}\langle\hat{n}_i\cdot\underline{S}_{\vec{k}}(t)\cdot\hat{n}_f\hat{n}_i\cdot\underline{S}_{\vec{k}}(0)\cdot\hat{n}_f\rangle\,, \tag{4}$$

where an equilibrium average is unsubscripted, and where a k subscript denotes a Fourier component. The S's are not really Fourier transformed variables, as the $\int d\vec{r}$ which defines them runs over V only, not all space. In equilibrium, all scattering volumes are equivalent and, furthermore, the correlation functions are usually short ranged with respect to the dimensions of V; under such circumstances, $\underline{S}_{\vec{k}}$ may be regarded as a Fourier component. Equation (3) then gives $\underline{S}_{\vec{k}}$ in terms of $\delta N_{\vec{k}}$ and $\underline{Q}_{\vec{k}}$.

In order to calculate the light scattering correlation functions at long times, the orientational variable $\underline{Q}$ must be "coupled"[8,9] to the hydrodynamic conserved variables, the number (N_k), energy (E_k), and momentum ($\vec{g}_k$) densities. In other words, an extended hydrodynamics is set up in which the elements of $\underline{Q}$ are added to the usual variables. If $\vec{A}_{\vec{k}}$ is a vector whose elements are the Fourier components of the chosen variables, then, on the (extended) hydrodynamic time scale,

$$\frac{\partial}{\partial t}\langle\vec{A}_{\vec{k}}(t)\vec{A}_{-\vec{k}}\rangle = \underline{M}_{\vec{k}}\cdot\langle\vec{A}_{\vec{k}}(t)\vec{A}_{-\vec{k}}\rangle\,, \tag{5}$$

where $\underline{M}_{\vec{k}}$ is the hydrodynamic matrix. Spatial isotropy causes $\underline{M}_{\vec{k}}$ to form blocks; for our choice of $\vec{k}$, $Q^{yz}_{\vec{k}}$ is uncoupled from other variables, with[8,9]

$$M_{Q^{yz}Q^{yz}} = -\Gamma\,, \tag{6}$$

where Γ is the collective, second-rank reorientation rate. The variable $Q^{xz}_{\vec{k}}$ is coupled to the z-component of the momentum density $\vec{g}_{\vec{k}}$ with,[8,9] for the order $(Q^{xz}_{\vec{k}}, g^{z}_{\vec{k}})$,

$$-M_k = \begin{pmatrix} \Gamma & ika \\ ikb & k^2(\eta-\eta_R) \end{pmatrix}\,. \tag{7}$$

The actual expressions for a and b are not needed here, but we will require

$$b = (\beta g^{(2)}/m)^{-1}a\,, \tag{8}$$

where $g^{(2)}$ is[7,9] the second-rank version of the Kirkwood g factor (a measure of static orientational order), $\langle Q^{\alpha\gamma}_{\vec{k}} Q^{\alpha\gamma}_{-\vec{k}}\rangle = Ng^{(2)}$, $\alpha\neq\gamma$, N is the number of particles in V, M the particle mass, $\beta = 1/k_B T$, k_B is Boltzmann constant, T the absolute temperature, and

$$\eta_R = ab/\Gamma\,. \tag{9}$$

η_R is the rotational contribution to the kinematic shear viscosity, arising from the possibility that stress can be relieved by rotation as well as translation, and η is the usual kinematic shear viscosity. The quantity R,

$$R \equiv \eta_R/\eta\,, \tag{10}$$

is known[10] for several liquids; typically $R \simeq 0.5$. Another block in the M matrix couples $(Q^{xx}_{\vec{k}} - Q^{yy}_{\vec{k}})$, $N_{\vec{k}}$, $E_{\vec{k}}$, and $g^{x}_{\vec{k}}$; we will discuss this block when we need it.

B. Correlation functions in NESS

Oppenheim *et al.* have shown[1-6] how to use the equilibrium M's, plus certain equilibrium averages, to calculate I^{VH} in NESS. They have given various methods for evaluating NESS correlation functions. We will use one of the most recent and most simple of these methods.

For NESS linearly displaced from equilibrium, Oppenheim finds,[1-6] for variables B and C,

$$\langle B(\vec{r},t)C(\vec{r}\,',0)\rangle_{\mathrm{av}} = \langle B(\vec{r},t)C(\vec{r}\,',0)\rangle + \int d\vec{x}\left(\langle B(\vec{r},t)C(\vec{r}\,',0)\vec{A}(\vec{x})\rangle - \tfrac{1}{2}\int_{-\infty}^{\infty} d\tau\langle B(\vec{r},t+\tau)C(\vec{r}\,',\tau)\vec{\dot{A}}^{\mathrm{Diss}}(\vec{x},0)\rangle\right)\cdot\vec{\phi}(\vec{x})\,, \tag{11}$$

where the angular brackets denote correlation functions, the dot product is to be taken in the space of hydrodynamic variables as well as in three-dimensional space, the $\dot{A}^{\mathrm{Diss}}$ are the dissipative parts of the time derivatives of the A's, and the ϕ's are the NESS values of the conjugate forces to the (extended) hydrodynamic variables,

$$\phi_N = \beta(\vec{r})[\mu(\vec{r}) - \mu^{\mathrm{eq}}]\,, \tag{12a}$$

$$\phi_E = \beta^{\mathrm{eq}} - \beta(\vec{r})\,, \tag{12b}$$

$$\phi_{\vec{g}} = \beta(\vec{r})\vec{v}(\vec{r})\,, \tag{12c}$$

μ is the chemical potential for a system at rest, $\vec{v}$ is the velocity field, and

$$\beta(\vec{r}) = \frac{1}{k_B T(\vec{r})}\,; \tag{13}$$

$\underline{\phi}_Q$ is not related to well known thermodynamic quantities.

In all the NESS calculations performed so far, the $\vec{A}$ have been the usual hydrodynamic variables, in which case

$$\dot{\vec{A}}^{\mathrm{Diss}} = -\vec{\nabla}\cdot\underline{I}^{\mathrm{Diss}}, \tag{14}$$

where the I^{Diss} are the dissipative fluxes. However, Eq. (14) does not hold for $\underline{Q}$, which is a nonconserved variable. Using Eq. (14) for the usual hydrodynamic variables and performing a partial integration over $\vec{x}$, while leaving $\dot{\underline{Q}}^{D}$ alone, one finds[1-6] (we write D instead of Diss from here on)

$$\begin{aligned}\langle B(\vec{r},t)C(\vec{r}\,',0)\rangle_{\mathrm{av}} = {} & \langle B(\vec{r},t)C(\vec{r}\,',0)\rangle \\ & + \int d\vec{x}\,\Big(\langle B(\vec{r},t)C(\vec{r}\,',0)\vec{A}(\vec{x})\rangle\cdot\vec{\phi}(\vec{x}) \\ & \qquad + \tfrac{1}{2}\int_{-\infty}^{\infty} d\tau\langle B(\vec{r},t+\tau)C(\vec{r}\,',\tau)\underline{I}^{\mathrm{Diss}}(\vec{x},0)\rangle\cdot\vec{\nabla}\vec{\phi}(\vec{x}) \\ & \qquad - \tfrac{1}{2}\int_{-\infty}^{\infty} d\tau\langle B(\vec{r},t+\tau)C(\vec{r}\,',\tau)\dot{\underline{Q}}^{D}(\vec{x},0)\rangle\cdot\underline{\phi}_{Q}(\vec{x})\Big)\end{aligned} \tag{15}$$

The next step is "localization" of the $\vec{x}$ integral. If the correlation functions in Eq. (15) are short ranged, $\vec{\phi}(\vec{x})$ can be expanded in a Taylor series about $x=r$; following Oppenheim *et al.*, we evaluate the right-hand side (rhs) of Eq. (15) to first order in the gradient of $\vec{\phi}$. The second term in Eq. (15) becomes[1-6]

$$\begin{aligned}\int d\vec{x}\langle B(\vec{r},t)C(\vec{r}\,',0)\vec{A}(\vec{x})\rangle\cdot\vec{\phi}(\vec{x}) = {} & \langle B(\vec{r},t)C(\vec{r}\,',0)\vec{A}_{\mathrm{tot}}\rangle\cdot\vec{\phi}(\vec{r}) \\ & + \int d\vec{x}\langle B(\vec{r},t)C(\vec{r}\,',0)\vec{A}(\vec{x})\rangle\cdot[(\vec{r}-\vec{x})\cdot\vec{\nabla}\vec{\phi}(\vec{r})] + O(\nabla\phi^{2}),\end{aligned} \tag{16}$$

where

$$\vec{A}_{\mathrm{tot}} = \int d\vec{x}\,\vec{A}(\vec{x}).$$

The first term on the rhs of Eq. (15) and the first term in Eq. (16) can be combined and the sum identified as the expansion to first order in $\vec{\phi}$ of the correlation function in an "homogeneous" system where the $\vec{\phi}$'s have constant values equal to $\vec{\phi}(\vec{r})$ in NESS. Such an homogeneous system is just an equilibrium system which may (if $\vec{v}\neq 0$) be in uniform motion, so no new tricks are needed to obtain this part of the correlation function, which we denote as $\langle\;\rangle^{1}_{\mathrm{Hom}}(\vec{r})$.

The second term in Eq. (16) is the "nonlocality correction," denoted $\langle\;\rangle^{1}_{\mathrm{NL}}(\vec{r})$. Evaluation may be complicated in general, but, for autocorrelation functions ($B=C$), it can be shown[1-3,6] that

$$\int d\vec{r}\,d\vec{r}\,'\,e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\langle B(\vec{r},t)B(\vec{r}\,'0)\rangle^{1}_{\mathrm{NL}}(\vec{y}) = \left(\frac{i}{2}\vec{\nabla}_{\vec{k}}\cdot\frac{\partial\langle B_{\vec{k}}(t)B_{-\vec{k}}\rangle_{\mathrm{Hom}}}{\partial\vec{\phi}}\right)_{\mathrm{eq}}\cdot\vec{\nabla}\vec{\phi}(\vec{y}), \tag{17}$$

So, the NL contribution to autocorrelation functions can also be derived from equilibrium properties. We will see later that Eq. (17) is sufficient to tell us all we need to know about the NL term.

The third term in Eq. (15) is already first order in $\vec{\nabla}\vec{\phi}$, so we simply replace $\vec{\nabla}\vec{\phi}(\vec{x})$ by $\vec{\nabla}\vec{\phi}(\vec{r})$, $\underline{I}(\vec{x})$ by $\underline{I}_{\mathrm{tot}}$, and we remove $\int d\vec{x}$. The last term might appear to require more manipulation. However, the only situations which we shall encounter in which $\underline{\phi}_{Q}$ is nonzero will be those where it is "switched on" by velocity gradients, i.e., flow birefringence. So, $\underline{\phi}_{Q}$ will be $O(\vec{\nabla}\vec{v})$ and we may localize the $\dot{\underline{Q}}$ term immediately, obtaining

$$\begin{aligned}\langle B(\vec{r},t)C(\vec{r}\,',0)\rangle_{\mathrm{av}} = {} & \langle B(\vec{r},t)C(\vec{r},t)C(\vec{r}\,')\rangle^{1}_{\mathrm{Hom}}(\vec{r}) + \langle B(\vec{r},t)C(\vec{r}\,')\rangle^{1}_{\mathrm{NL}}(\vec{r}) \\ & + \tfrac{1}{2}\int_{-\infty}^{\infty} d\tau[\langle B(\vec{r},t+\tau)C(\vec{r}\,',\tau)\underline{I}^{D}_{\mathrm{tot}}\rangle\cdot\vec{\nabla}\vec{\phi}(\vec{r}) - \langle B(\vec{r},t+\tau)C(\vec{r}\,',\tau)\dot{\underline{Q}}^{D}_{\mathrm{tot}}\rangle\cdot\underline{\phi}_{Q}(\vec{r})].\end{aligned} \tag{18}$$

All correlation functions $\langle B(\vec{r},t)C(\vec{r}\,',0)\rangle_{\mathrm{av}}$ are multiplied by $e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}$ and integrated over $\vec{r}$ and $\vec{r}\,'$ in calculating a light scattering spectrum. A major complication arises in light scattering from NESS because, according to the localization scheme, we should use a different localization for each $\vec{r}$. Although more work may be needed on this problem, we will now assume, as have Oppenheim *et al.*, that we may simple localize the correlation functions about the center of V and proceed with the result for V centered at $\vec{y}$,

$$\langle B_{\vec{k}}(t)C_{-\vec{k}}(\vec{y})\rangle_{\rm av} = \langle B_{\vec{k}}(t)C_{-\vec{k}}\rangle^{1}_{\rm Hom}(\vec{y}) + \langle B_{\vec{k}}(t)C_{-\vec{k}}\rangle^{1}_{\rm NL}(\vec{y}) + \tfrac{1}{2}\int_{-\infty}^{\infty} d\tau [\langle B_{\vec{k}}(t+\tau)C_{-\vec{k}}(\tau)\underline{I}^{D}_{\rm tot}\rangle \cdot \vec{\nabla}\vec{\phi}(\vec{y}) - \langle B_{\vec{k}}(t+\tau)C_{-\vec{k}}(\tau)\dot{\underline{Q}}^{D}_{\rm tot}\rangle \cdot \underline{\phi}_{Q}(\vec{y})] . \tag{19}$$

Oppenheim has given[6] a mode coupling method for evaluation of the dissipative terms in Eq. (19). The quantities $\underline{I}^{D}_{\rm tot}$ and $\dot{\underline{Q}}^{D}_{\rm tot}$ are projected onto bilinear products of the $\vec{A}$'s using Mori's[11] projection operator, and the hydrodynamic timescale behavior of the resulting four-A correlation functions is evaluated with the M matrix. Borrowing Oppenehim's result, we finally obtain

$$\begin{aligned}\langle B_{\vec{k}}(t)C_{-\vec{k}}(\vec{y})\rangle_{\rm av} &= \langle B_{\vec{k}}(t)C_{-\vec{k}}\rangle^{1}_{\rm Hom}(\vec{y}) + \langle B_{\vec{k}}(t)C_{-\vec{k}}\rangle^{1}_{\rm NL}(\vec{y}) \\ &\quad + \int_{0}^{\infty} d\tau\, e^{M_{\vec{k}}(t+\tau)}_{B\alpha}\, e^{M_{-\vec{k}}(\tau)}_{C\gamma} [\langle A_{\alpha\vec{k}}A_{\gamma-\vec{k}}\underline{I}^{D}_{\rm tot}\rangle \cdot \vec{\nabla}\vec{\phi}(\vec{y}) - \langle A_{\alpha\vec{k}}A_{\gamma-\vec{k}}\dot{\underline{Q}}^{D}_{\rm tot}\rangle \cdot \underline{\phi}_{Q}(\vec{y})] \\ &\quad + \tfrac{1}{2}\int_{-t}^{0} d\tau\, e^{M_{\vec{k}}(t+\tau)}_{B\alpha}\, e^{-M_{-\vec{k}}(\tau)}_{C\gamma} [\langle A_{\alpha\vec{k}}A_{\gamma-\vec{k}}\underline{I}^{D}_{\rm tot}\rangle \cdot \vec{\nabla}\vec{\phi}(\vec{y}) - \langle A_{\alpha\vec{k}}A_{\gamma-\vec{k}}\dot{\underline{Q}}^{D}_{\rm tot}\rangle \cdot \underline{\phi}_{Q}(\vec{y})] ,\end{aligned} \tag{20}$$

with a sum over repeated indices. Equation (20) is our starting point for calculation of correlation functions which appear in NESS light scattering.

As mentioned in the Introduction, we will next discuss two possible experiments. Of course, for each light scattering experiment there are also different possible steady states. The simplest states are those with constant temperature gradients,

$$\vec{\nabla}T = \text{const}, \quad \text{other } \vec{\nabla}\phi = 0 ,$$

$$\vec{\nabla}\phi_{E} = \frac{1}{kT^{2}}\vec{\nabla}T , \quad \underline{\phi}_{Q} = 0 ,$$

and those with constant velocity gradients,

$$(\vec{\nabla}\vec{v}) = \text{const} , \quad \phi_{Q} \neq 0 ,$$

$$\text{other } \vec{\nabla}\phi = 0 .$$

The latter case requires more comment. In a true steady state, diagonal elements of $(\vec{\nabla}\vec{v})$ vanish, as these are proportional to $\partial N/\partial t$. However, the NESS theory is applicable to nonsteady states which vary slowly on the timescale of the process being studied. So, a low-frequency sound wave could provide $(\nabla v)_{ii}$ which could be used, under appropriate conditions, as a steady-state quantity. Also, $\underline{\phi}_{Q}$ will be nonzero in this case due to[12] the usual shear induced or[13] accoustically induced [for $(\vec{\nabla}\vec{v})_{ii}$] molecular orientational ordering, which causes birefringence.

In their consideration of density fluctuations, Oppenheim *et al.* found new contributions to hydrodynamic correlation functions with amplitudes of order k^{0}, k^{-1}, and k^{-2}. Although k is "small," only the k^{-2} terms turned out to be important. Thus, for a given scattering experiment, we will choose a steady state so as to obtain the largest possible inverse power of k.

III. VH scattering

Let the incident and scattered light lie in the xy plane, with $\vec{k}$ along the x axis. For $\hat{n} \parallel \hat{z}$ (out of plane or "vertical") and $\hat{n}_{f} \perp \hat{z}$ (in plane or "horizontal") we have "VH" scattering, and[8]

$$S^{VH}_{k} = \left(\frac{\epsilon+2}{3}\right)^{2} \Delta\alpha^{e} [\cos\tfrac{1}{2}\theta Q^{xz}_{k} + \sin\tfrac{1}{2}\theta Q^{yz}_{k}] \tag{21}$$

or

$$I^{VH}(k,t;y) = \frac{1}{V}(\Delta\alpha^{e})^{2}\left(\frac{\epsilon+2}{3}\right)^{4}\{\cos^{2}\tfrac{1}{2}\theta\langle Q^{xz}_{k}(t)Q^{xz}_{-k}(y)\rangle_{\rm av} + \cos\tfrac{1}{2}\theta\sin\tfrac{1}{2}\theta\langle[Q^{xz}_{k}(t)Q^{yz}_{-k}(y)\rangle_{\rm av} + \langle Q^{yz}_{k}(t)Q^{xz}_{-k}(y)\rangle_{\rm av}] + \sin^{2}(\tfrac{1}{2}\theta)\langle Q^{yz}_{k}(t)Q^{yz}_{-k}(t)Q^{yz}_{-k}(y)\rangle_{\rm av}\} . \tag{22}$$

Equation (22) has been extensively analyzed[14] for equilibrium. There, of course, no y dependence exists, the cross correlations canish, and the M matrices, Eqs. (6) and (7), give the curly bracket,

$$\{\,\} = Ng^{(2)}\left(e^{-\Gamma t} - \cos^{2}\tfrac{1}{2}\theta\frac{k^{2}\eta}{\Gamma}R\, e^{-k^{2}\eta t}\right) , \tag{23}$$

where we have ignored k^{2} terms with respect to k^{0} terms. The hydrodynamic subtraction in Eq. (23), which comes from the coupling of Q^{xz} to g^{z}, gives rise to a "dip" or minimum in the low-frequency VH spectrum.

Let us now consider which steady state will give the most important new hydrodynamic features in VH scattering. Oppenheim *et al.* found, and we shall see shortly, that the dominant contributions come from the dissipative terms in Eq. (20). The order in k of these terms is determined by any k's which appear as multiplicative constants in the e^{M}'s and the order of the time integrals. If the product of e^{M}'s has a contribution of form e^{-k^2}, a "pure hydrodynamic" contribution, the time integral gives k^{-2}, while a time integral of $e^{-\Gamma t}$ or $e^{-(\Gamma+k^2)t}$ gives k^0, k being negligible with respect to Γ at small k. Equations (6) and (7) easily give

$$e^{M_{\vec{k}}t}_{Q^{yz}Q^{yz}}=e^{-\Gamma t}\,, \tag{24}$$

$$e^{M_{\vec{k}}t}_{Q^{xz}Q^{xz}}=\left(1+\frac{k^2\eta}{\Gamma}R\right)e^{-(\Gamma-k^2\eta_R)t}-\frac{k^2\eta}{\Gamma}Re^{-k^2\eta t}\,, \tag{25}$$

$$e^{M_k t}_{Q^{xz}g^z}=\frac{ika}{\Gamma}\left(e^{-(\Gamma-k^2\eta_R)t}-e^{-k^2\eta t}\right). \tag{26}$$

Consequently, $\langle Q^{xz}_k(t)Q^{xz}_{-k}\rangle$ has a contribution of order k^0 which arises from $\alpha=\gamma$ [in Eq. (20)] $=g^z$; two e^{M}_{Qg}'s produce k^2 times a pure hydrodynamic time integral $O(k^{-2})$; no other k^0 contribution exists. Since the equilibrium hydrodynamic part of I^{VH} has amplitude $O(k^2)$, our new term has the same relative magnitude in k as do the k^{-2} terms in density fluctuations.

Thus, NESS effects in VH scattering will be best observed if $\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\underline{I}^D_{\mathrm{tot}}\rangle$ or/and $\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\dot{\underline{Q}}^D_{\mathrm{tot}}\rangle$ are nonzero. It is immediately obvious[15] that, to lowest order in k,

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}I^D_{E,\mathrm{tot}}\rangle=0 \text{ (tensorial symmetry; the energy flux is a vector)}. \tag{27}$$

So the VH experiment must be done with a velocity gradient; symmetry further requires zz longitudinal stress, $v_z=fn(z)$, i.e., a sound wave. Machta and Oppenheim have shown[5] that

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}I^{D,zz}_{g,\mathrm{tot}}\rangle=2(k_BT)^2mN\,. \tag{28}$$

Now, the dissipative fluxes are determined by the relation

$$\vec{\mathrm{A}}^D_{\vec{k}}=\vec{\mathrm{A}}_{\vec{k}}-\underline{M}_{\vec{k}}\cdot\vec{\mathrm{A}}_{\vec{k}}\,. \tag{29}$$

Our hydrodynamics has more variables, the Q's, than does that of Machta and Oppenheim, so our $I^{D,zz}_{g,\mathrm{tot}}$ has some extra subtractions, proportional to $\underline{Q}$. However,

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\underline{Q}_{\mathrm{tot}}\rangle=0 \tag{30}$$

so we can use Eq. (28).

In the presence of a sound wave $\underline{\phi}_Q$ will be nonzero, so we also need $\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\dot{\underline{Q}}^D_{\mathrm{tot}}\rangle$. The independence of linear and angular momenta gives

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\dot{\underline{Q}}_{\mathrm{tot}}\rangle=0 \tag{31}$$

and, it is also true that

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\vec{\mathrm{A}}_{\mathrm{tot}}\rangle=0\,, \tag{32}$$

so

$$\langle g^{z}_{\vec{k}}g^{z}_{-\vec{k}}\dot{\underline{Q}}^D_{\mathrm{tot}}\rangle=0\,. \tag{33}$$

Although we have selected the experiment based on consideration of the largest hydrodynamic term, we will give all the contributions to I^{VH} which are $O(k^{-1})$ and $O(k^{-2})$ with respect to a term of the same form which exists in equilibrium. It is now easy to run quickly through all possible dissipative contributions:

(a) yz, yz correlation; $\alpha=\gamma=Q^{yz}$, possible nonhydrodynamic part of same $O(k)$ as equilibrium nonhydrodynamic part—hence can be ignored,

(b) $\left\{{xz,yz \atop yz,xz}\right\}$ correlation; identically zero,

(c) xz, xz; $\alpha=\gamma=Q^{xz}$, both hydrodynamic and nonhydrodynamic parts of at most same order as in Eq. (23); therefore can be ignored:

$\alpha=Q^{xz}$, $\gamma=g^z$ and vice versa are identically zero but

$\alpha=\gamma=g^z$ is the dominant term and should be retained.

We may therefore use Eqs. (28), (26), (20), (12), (10), (9), and (8) to write down the only surviving dissipative part of I^{VH},

$$I^{\mathrm{VH}}_D(k,t;y)\simeq(\Delta\alpha^e)^2\left(\frac{\epsilon+2}{3}\right)^4\cos^2\tfrac{1}{2}\theta\, n g^{(2)}\left(\frac{k^2\eta}{\Gamma}\right)R \times e^{-k^2\eta t}\left(\frac{1}{k^2\eta}+t\right)\nabla v(y)\,, \tag{34}$$

where n is the number density.

The "Hom" term is just the spectrum in a moving system. Carrying out[5] a Gallilean transform, it is easy to show that

$$I^{VH}_{\mathrm{Hom}}(k,t;y)=e^{-\vec{k}\cdot\vec{v}(y)t}I^{\mathrm{VH}}_{\mathrm{eq}}(k,t)\,. \tag{35}$$

This is nothing but the Doppler shifted spectrum which one expects in a moving system. Our theory contains the Hom average to first order in $\vec{\phi}$, so for our purposes

$$I^{VH}_{\mathrm{Hom}}(k,t;y)\simeq I^{\mathrm{VH}}_{\mathrm{eq}}(k,t)[1-i\vec{k}\cdot\vec{v}(y)t]\,. \tag{36}$$

However, for a $\hat{z}$ sound wave in VH scattering, $\vec{k}\cdot\vec{v}=0$, and the Hom term is just the equilibrium term. For the same reason, Eq. (17) shows that the NL term vanishes [note that we are now treating the source as a single entity, not as a sum of terms to be obtained separately, so Eq. (11), derived for autocorrelation functions, holds] and we finally obtain

$$I^{VH}(k,t;y)\simeq(\Delta\alpha^{e})^{2}\left(\frac{\epsilon+2}{3}\right)^{4}ng^{(2)}\times\left\{e^{-\Gamma t}-\cos^{2}\tfrac{1}{2}\theta\frac{k^{2}\eta}{\Gamma}R\times\left[1-\left(\frac{1}{k^{2}\eta}+t\right)\nabla v(y)\right]\right\}. \quad (37)$$

Equation (37) is our principal result for *VH* scattering. It clearly shows that a sound wave propagating along the z axis can make an important change in I^{VH}. The value of ∇v is comparable to the sound frequency ν_s, so the importance of the new term is of order $\nu_s/k^2\eta$. However, the condition for validity of NESS theory for the nonsteady state is $\nu_s \ll k^2\eta$, so Eq. (37) cannot be used in the indicated regime of greatest interest, $\nu_s \sim k^2\eta$. We conclude that we have probably found an important effect in *VH* scattering, which cannot be properly evaluated until the existing formalism is extended to nonsteady states; we plan to do this in a future article.

IV. VH-VV scattering

We now turn to a phenomenon which does not exist at all in equilibrium—correlation between light scattered at VV and as VH. We envision the following experiment. The geometry is as in VH scattering, but the scattered beam is split; the V component of one beam and the H component of the other are selected. The beams are then detected in such a way as to yield $\langle S^{\mathrm{VH}}_{\vec{k}}(t)S^{\mathrm{VV}}_{-\vec{k}}\rangle$. The best way to carry out the latter step is by no means obvious to us, but it surely seems possible. For example, one could simply detect the beams on the surface of two separate phototubes and find the correlations of the two photocurrents. One attractive feature of the experiment is that it is a null experiment; all the optics must be adjusted to give zero correlation in equilibrium, and one only measures the change when $\vec{\nabla}\vec{\phi}$ is made nonzero.

Equation (21) gives S^{VH}, and, for the chosen geometry,

$$S^{VV}_{\vec{k}}=\left(\frac{\epsilon+2}{3}\right)^{4}(\alpha^{e}_{0}N_{\vec{k}}+\Delta\alpha^{e}Q^{zz}_{\vec{k}}), \quad (38)$$

since $N_{\vec{k}}=\delta N_{\vec{k}}$, $k\neq 0$. We shall calculate the symmetrized cross correlation, defined as C_s

$$C_s(k,t;y)\equiv\frac{1}{V}\{S^{VV}_{\vec{k}}(t)S^{\mathrm{VH}}_{-\vec{k}}\rangle_{\mathrm{av}}+\langle S^{\mathrm{VH}}_{\vec{k}}(t)S^{\mathrm{VV}}_{-\vec{k}}\rangle_{\mathrm{av}}\}. \quad (39)$$

In this paper, we examine C_s on the hydrodynamic timescale.

Now, $Q^{zz}_{\vec{k}}$, $k\parallel x$, does not couple to any hydrodynamic variables, nor, as we have seen, does $Q^{yz}_{\vec{k}}$. So, on the hydrodynamic timescale, the dissipative part of C_s is

$$C^{D}_{s}(k,t;y)\simeq\frac{1}{V}\alpha^{e}_{0}\Delta\alpha^{e}\left(\frac{\epsilon+2}{3}\right)^{4}\times\cos\tfrac{1}{2}\theta[\langle N_{\vec{k}}(t)Q^{xz}_{-\vec{k}}\rangle_{\mathrm{av}}+\langle Q^{xz}_{\vec{k}}(t)N_{-\vec{k}}\rangle_{\mathrm{av}}]. \quad (40)$$

We follow the same logic as in the last section. The only possibility of a k^{-2} term comes from C^{D}_{s}, so we choose a NESS which best produces that term. Then we evaluate all contributions to C_s which might be important in the chosen NESS.

Evaluation of C^{D}_{s} requires $e^{Mt}_{N\gamma}$, i.e., we need that block of M which contains N and, as it turns out, also contains g^x, E, and $(Q^{xx}-Q^{yy})$. Since we study the hydrodynamic timescale, however, N need not be coupled to Q, and we can use the usual M, as well as the usual $e^{Mt}_{N\gamma}$, which have been given[3,5] by Oppenheim *et al*. All the elements of $e^{Mt}_{N\gamma}$ have amplitude $O(k^0)$.

The hydrodynamic part of $e^{Mt}_{Q^{xz}Q^{xz}}$ is $O(k^2)$, so this can at best produce C^{D}_{S} of $O(k^0)$. The hydrodynamic part of $e^{Mt}_{Q^{xz}g^{z}}$ is $O(ik)$, so an $O(k^{-1})$ term is possible here if

$$\left\langle g^{z}_{\vec{k}}A_{-\vec{k}\gamma}\left\{\begin{matrix}\underline{I}^{D}_{\mathrm{tot}}\\ \dot{\underline{Q}}^{D}_{\mathrm{tot}}\end{matrix}\right\}\right\rangle\neq 0.$$

There are two ways to make the average nonzero. For a temperature gradient along z, we need $\langle g^{z}_{\vec{k}}A_{-\vec{k},\gamma}I^{D}_{E,\mathrm{tot}}\rangle$, which is nonzero for $\gamma=N$, E and has been evaluated[3] by Oppenheim *et al*. Also, when $\gamma=g^x$, the average will be nonzero for xz shear flow. Machta and Oppenheim have shown[5] that NESS shear states are harder to observe than $\vec{\nabla}T$ states, so we now focus on a state with a temperature gradient along $\hat{z}$.

The "Hom" term is zero, since the Hom state is just an equilibrium state with a different temperature, and $C_s=0$ in equilibrium. The NL term is also zero. Although C_s is not an autocorrelation function, it is a combination of them:

$$C_s(k,t)\alpha[\langle\Delta\alpha^{e}Q^{xz}_{\vec{k}}(t)+\alpha^{e}_{0}N_{\vec{k}}(t)(\Delta\alpha^{e}Q^{xz}_{-\vec{k}}+\alpha^{e}_{0}N_{-\vec{k}})\rangle_{\mathrm{av}}-(\Delta\alpha^{e})^{2}\langle Q^{xz}_{\vec{k}}(t)Q^{xz}_{-\vec{k}}\rangle_{\mathrm{av}}-(\alpha^{e}_{0})^{2}\langle N_{\vec{k}}(t)N_{-\vec{k}}\rangle_{\mathrm{av}}]; \quad (41)$$

the total NL term comes from the three separate NL terms. However, the Hom part of the first term in Eq. (41) is, due to vanishing of Hom cross correlations, equal to the sum of the two subtractions, and so the combination of the three NL terms obtained from Eq. (17) vanishes.

We therefore obtain

$$C_s^D(k,t;y)=\frac{1}{V}\,\alpha_0^e\Delta\alpha^e\left(\frac{\epsilon+2}{3}\right)^4\cos\tfrac{1}{2}\theta\frac{\nabla T(y)}{k_BT^2}$$
$$\times\sum_{\gamma=N,E}\Bigg[\int_0^\infty d\tau\left(e^{M_{\vec{k}}(t+\tau)}_{Q^{xz}g^{z}}\,e^{M_{-\vec{k}}(\tau)}_{N\gamma}+e^{M_{\vec{k}}(t+\tau)}_{N\gamma}\,e^{M_{-\vec{k}}(\tau)}_{Q^{xz}g^{z}}\right)$$
$$+\tfrac{1}{2}\int_{-t}^0 d\tau\left(e^{M_{\vec{k}}(t+\tau)}_{Q^{xz}g^{z}}\,e^{-M_{-\vec{k}}(\tau)}_{N\gamma}+e^{M_{\vec{k}}(t+\tau)}_{N\gamma}\,e^{-M_{-\vec{k}}(\tau)}_{Q^{xz}}\right)\Big)\langle g^z_{\vec{k}}A_{-\vec{k}\gamma}I^{D,z}_{E,\mathrm{tot}}\rangle\Bigg] \qquad (42)$$

In the Appendix of Ref. 3 we find

$$e^{Mt}_{NN}=\frac{1}{2c^2}\left((e^{\xi_+t}+e^{\xi_-t})\chi_n/m+2e^{\xi_Tt}\,\frac{\chi_eh}{mn}\right), \qquad (43)$$

$$e^{Mt}_{NE}=\frac{1}{2c^2}\,\frac{\chi_e}{m}\,(e^{\xi_+t}+e^{\xi_-t}-2e^{\xi_Tt}), \qquad (44)$$

where

$$\xi_\pm=\pm ikc-k^2[(C_p/C_V-1)\Gamma_T+\nu_l]\equiv\pm ikc-k^2\Gamma_l\,, \qquad (45)$$

$$\xi_T=-k^2\Gamma_T\,, \qquad (46)$$

h is the enthalpy density, c is the adiabatic sound velocity, C_p and C_v the constant pressure and volume heat capacities, Γ_T the thermal diffusivity, ν_l the longitudinal viscosity,

$$\chi_n=\left(\frac{\partial P}{\partial n}\right)_e, \qquad (47)$$

$$\chi_e=\left(\frac{\partial P}{\partial e}\right)_n, \qquad (48)$$

P is the pressure, and e is the usual thermodynamic energy density. We also find, in Ref. 3,

$$\theta_N\equiv\langle g^z_{\vec{k}}N_{-\vec{k}}I^{D;z}_{E,\mathrm{tot}}\rangle=Nk_BT\left(\frac{\partial h/n}{\partial\beta\mu}\right)_{\beta,V}, \qquad (49)$$

$$\theta_E\equiv\langle g^z_{\vec{k}}E_{-\vec{k}}I^{D;z}_{E,\mathrm{tot}}\rangle=Nk_BT\left(\frac{\partial h/n}{\partial\beta}\right)_{\beta\mu,V}. \qquad (50)$$

Since we are interested in the hydrodynamic timescale, we substitute the hydrodynamic part of Eq. (26), and Eqs. (43)–(50), into Eq. (42), the result for the sum in Eq. (42) being

$$\Sigma=\frac{1}{c^2}\,\frac{ika}{\Gamma}\Bigg\{-e^{-k^2\eta t}\left[\frac{k^2(\eta+\Gamma_l)}{[k^2(\eta+\Gamma_l)]^2+k^2c^2}\left(\frac{\chi_n}{m}\,\theta_N+\frac{\chi_e}{m}\,\theta_E\right)+\frac{1}{k^2(\eta+\Gamma_T)}\left(\frac{\chi_eh}{nm}\,\theta_N-\frac{\chi_e}{m}\,\theta_E\right)\right]$$
$$+e^{-k^2\Gamma_Tt}\left[\frac{1}{k^2(\eta+\Gamma_T)}\left(\frac{\chi_eh}{nm}\,\theta_N-\frac{\chi_e}{m}\,\theta_E\right)\right]+e^{-k^2\Gamma_lt}\left[\frac{k^2(\eta+\Gamma_l)\cos kct-kc\sin kct}{[k^2(\eta+\Gamma_l)]^2+k^2c^2}\left(\frac{\chi_n}{m}\,\theta_N+\frac{\chi_e}{m}\,\theta_E\right)\right]\Bigg\}. \qquad (51)$$

Equation (51) may be further simplified with results taken from the Appendix of Ref. 3,

$$\left(\frac{\chi_n}{m}\,\theta_N+\frac{\chi_e}{m}\,\theta_E\right)=N(k_BTc)^2, \qquad (52)$$

$$\left(\frac{\chi_e}{m}\,\frac{h}{n}\,\theta_N-\theta_E\right)=-N\chi_e\,\frac{k_B^2T^3C_P}{m}. \qquad (53)$$

We also use Eqs. (8) and (9) and the fact that $kc\gg$ any other hydrodynamic frequency, and Eq. (42) becomes

$$C_s(k,t;y)=\eta\alpha_0^e\Delta\alpha^e\left(\frac{\epsilon+2}{3}\right)^4\cos\tfrac{1}{2}\theta[\nabla k_BT(y)]\,i\left(\frac{k^2\eta}{\Gamma}R\right)^{1/2}\left(\frac{g^{(2)}}{mk_BT}\right)^{1/2}$$
$$\times\left(\frac{1}{k^2(\eta+\Gamma_T)}\,\frac{C_PT}{mc^2}\,\chi_e(e^{-k^2\eta t}-e^{-k^2\Gamma_Tt})-\frac{\sin kct}{kc}\,e^{-k^2\Gamma_lt}\right), \qquad (54)$$

our final result for VV–VH scattering.

There is no reason why C_s should be small compared to correlations ordinarily observed in light scattering. Reading the right-hand side from left to right, all the factors up to $\cos\frac{1}{2}\theta$ are typical of any light scattering experiment. For $\nabla T \simeq 0.1^\circ/$cm, a fairly conservative gradient, the rest of the term before $\{\,\}$ may, typically, be $\lesssim 1$. For a perfect gas, $(C_P T/mc^2)\chi_e \sim 1$ and, in a liquid, might be $\sim 10^{-3}$. Upon Fourier transformation and taking the real part, an $e^{-k^2\Lambda t}$ decay gives a contribution $\omega/[\omega^2+(k^2\Lambda)]$; the amplitude of the resulting spectrum is quite substantial. We think that VH–VV scattering would be an interesting experiment to try.

V. SUMMARY

We have shown that light scattering experiments on liquids of nonspherical molecules in NESS show a rich collection of phenomena, much of which is missed if one simply focuses on density fluctuations. Particularly intriguing is the possibility of observing phenomena which vanish identically in equilibrium, a feature which is attractive both theoretically and experimentally. We have surely not given all the possible new experiments here. For example, an "HH–HV" experiment also seems possible. It appears that NESS could open an entire new area of light scattering experiments.

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