Hydrodynamic Theory of Light Scattering from a Fluid in a Nonequilibrium Steady State

T. Kirkpatrick and E. G. D. Cohen
The Rockefeller University, New York, New York 10021

and

J. R. Dorfman
University of Maryland, College Park, Maryland 20742

(Received 26 November 1979)

Two new features, finite-size effects and a new hydrodynamic eigenvalue problem, are essential for a consistent discussion of the scattering of light by a fluid in a nonequilibrium steady state. The light-scattering structure factor is computed for the case of a steady thermal gradient and a steady shear flow in a fluid. The height differences found in the Brillouin peaks differ from those obtained by Ronis, Procaccia, and Oppenheim and Machta, Oppenheim, and Procaccia.

In this Letter we discuss two new theoretical aspects of the scattering of light by a fluid in a nonequilibrium steady state. The first of these deals with the required finite size of the scattering volume in a nonequilibrium steady state. Although actually present in equilibrium the effect is much more pronounced in nonequilibrium where it must be carefully taken into consideration, because gradients prevent the thermodynamic limit from being taken. The second problem deals with the change in the hydrodynamic modes caused by the spatial variation of all thermodynamic and transport coefficients appearing in the hydrodynamic equations of motion.

In our explicit calculations we consider either the case of a steady thermal gradient or the case where there is a steady shear flow in the fluid. In this Letter both the eignevalue problem and the effects due to the finite size of the scattering volume are computed by perturbation expansions. A more complete treatment will be published elsewhere.[1] Related but different results have been given by Ronis, Procaccia, and Oppenheim[2] and Machta,[3] Oppenheim, and Procaccia[3]. The difference is related to the two new theoretical aspects mentioned earlier and a precise connection will be made in the last section of this Letter.

The quantity of interest for light scattering is the nonequilibrium structure factor $S(\vec{k}, \omega)$ for wave number $\vec{k}$ and frequency ω, where $\hbar\vec{k}$ and $\hbar\omega$ are the momentum and energy transfer from the fluid to the light. In general this structure factor may be defined as[4]

$$S(\vec{k}, \omega) = T^{-1}\left[\int_V d^3R\, p^2(\vec{R})\right]^{-1} \int_V d^3R_1 \int_V d^3R_2 \int_{-T/2}^{T/2} dt_1 \int_{-T/2}^{T/2} dt_2\, p(\vec{R}_1) p(\vec{R}_2) \times \exp\{-i[\vec{k}\cdot(\vec{R}_1 - \vec{R}_2) - \omega(t_1 - t_2)]\} M_{\rho\rho}(\vec{R}_1, t_1;\ \vec{R}_2, t_2), \tag{1}$$

where V is the volume of the fluid, T is the duration of the experiment, and $M_{\rho\rho}(\vec{R}_1, t_1;\ \vec{R}_2 t_2) \equiv \langle \hat{\rho}(\vec{R}_1, t_1) \hat{\rho}(\vec{R}_2, t_2) \rangle$. Here $\hat{\rho}(\vec{R}_1, t_1) \equiv \rho(\vec{R}_1, t_1) - \langle \rho(\vec{R}_1, t_1) \rangle$, where $\rho(\vec{R}_1, t_1)$ is the microscopic fluid density at the point $\vec{R}_1$ and t_1 and the angular brackets denote an average over a nonequilibrium ensemble. The fact that usually only a small portion of the fluid is both illuminated and detected by the collection optics is taken into account by the electric field amplitude weighting function $p(\vec{R})$. This function may be used to define the scattering volume since $p(\vec{R})$ is only significantly different from zero in the scattering volume.[5] The factor $\int d^3R\, p^2(\vec{R})$ included in the definition of the structure factor is related to the power of the incident electric field in the scattering volume. To avoid effects present at the boundaries that maintain the nonequilibrium steady state, we assume that the function $p(\vec{R})$ defines a fluid region deep in the interior of the volume V. It is the spatial variation of the weighting function $p(\vec{R})$ that defines the finite-size effects and this variation *must* be taken into account, for a consistent theory, in a nonequilibrium fluid.[6]

We compute $M_{\rho\rho}(\vec{R}_1, t_1;\ \vec{R}_2, t_2)$ for a nonequilibrium steady-state fluid as follows. Using the nonequilibrium projection operator of Ernst, Hauge, and van Leeuwen[7] we construct, in a manner identical to that used by Ernst and Dorfman[8] in equilibrium, five coupled equations of motion for the variables $M_{a\rho}(\vec{R}_1, \vec{R}_2;\ t_1 - t_2 = t)$. Here a is one of the set $\{\rho, \vec{g}, \epsilon\}$ of microscopic mass, momentum, and energy densities, respectively, and $M_{a\rho}$ is defined in a similar manner as $M_{\rho\rho}$ above. For the case of a temperature gradient and no macroscopic flow, the equations are

$$\frac{\partial M_{\rho\rho}}{\partial t}+\frac{\partial M_{g_\alpha\rho}}{\partial R_{1\alpha}}=0, \tag{2}$$

$$\frac{\partial}{\partial t}M_{g_\alpha\rho}+\frac{\partial}{\partial R_{1\alpha}}\left[\left(\frac{\partial p}{\partial\rho}\right)_{\epsilon(\vec{R}_1)}M_{\rho\rho}+\left(\frac{\partial p}{\partial\epsilon}\right)_{\rho(\vec{R}_1)}M_{\epsilon\rho}\right]=\frac{\partial}{\partial R_{1\beta}}\left\{\left[\eta(\vec{R}_1)\Delta_{\alpha\beta,\gamma\nu}+\zeta(\vec{R}_1)\delta_{\alpha\beta}\delta_{\gamma\nu}\right]\frac{\partial}{\partial R_{1\gamma}}\frac{M_{g_\nu\rho}}{\rho(\vec{R}_1)}\right\}, \tag{3}$$

$$\begin{aligned}\frac{\partial}{\partial t}M_{\epsilon\rho}+\frac{\partial}{\partial R_{1\alpha}}\frac{h(\vec{R}_1)}{\rho(\vec{R}_1)}M_{g_\alpha\rho}=\frac{\partial}{\partial R_{1\alpha}}\Bigg\{&\lambda(\vec{R}_1)\frac{\partial}{\partial R_{1\alpha}}\left[\left(\frac{\partial T}{\partial\rho}\right)_{\epsilon(\vec{R}_1)}M_{\rho\rho}+\left(\frac{\partial T}{\partial\epsilon}\right)_{\epsilon(\vec{R}_1)}M_{\epsilon\rho}\right]\\ &+\left[\left(\frac{\partial\lambda}{\partial\rho}\right)_{\epsilon(\vec{R}_1)}M_{\rho\rho}+\left(\frac{\partial\lambda}{\partial\epsilon}\right)_{\rho(\vec{R}_1)}M_{\epsilon\rho}\right]\frac{\partial T}{\partial R_{1\alpha}}(\vec{R}_1)\Bigg\}.\end{aligned} \tag{4}$$

In these equations p, ρ, ϵ, h, T, η, ζ, and λ are the pressure, mass density, energy density, enthalpy density, temperature, shear viscosity, bulk viscosity, and heat conductivity, respectively, at point $\vec{R}_1$; $\Delta_{\alpha\beta,\gamma\nu}$ is given by $\delta_{\alpha\gamma}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\gamma}-\frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\nu}$; and the summation convention has been used. For the case of a shear flow a similar set of equations can be derived.[9] In equilibrium, Eqs. (2)–(4) reduce to linearized hydrodynamic equations whose eigenvalues and eigenfunctions are well known. In nonequilibrium these hydrodynamic equations define a new eigenvalue problem for the nonequilibrium hydrodynamic modes. We solve this new eigenvalue problem by a perturbation expansion around total equilibrium, i.e., we let $\langle a\rangle=a_{\text{eq}}+\Delta\delta a$ and keep terms to order Δ only. The resulting five equations for $M_{a\rho}(\vec{R}_1,\vec{R}_2,t)$ are then solved in terms of the equal-time correlation functions $M_{a\rho}(\vec{R}_1,\vec{R}_2,t=0)$. The latter can be computed by formally solving the Liouville equation for deviations from total equilibrium and then using the mode-coupling theory of Kadanoff and Swift[10] to compute the corrections to the equilibrium equal-time correlation functions. We have calculated $M_{a\rho}$ to first order in Δ and from $M_{\rho\rho}$ we obtain $S(\vec{k},\omega)$ according to Eq. (1).

We now present our results for the two cases mentioned previously.

Case 1.—The fluid is maintained in a steady state with uniform pressure but with a constant temperature gradient. We find

$$S^{(1)}(\vec{k},\omega)=\frac{\rho^2k_{\text{B}}T\chi_T}{\gamma}\left\{\frac{(\gamma-1)2D_Tk^2}{[(D_Tk^2)^2+\omega^2]}+\frac{1}{2}\sum_{\sigma=\pm1}\frac{[\Gamma_sk^2-\sigma y_\sigma^{(1)}(\vec{k},\omega)c\hat{k}\cdot\nabla T/T]}{\{(\omega-\sigma ck)^2+[(\Gamma_s/2)k^2]^2\}}\right\}. \tag{5}$$

The quantity $y_\sigma^{(1)}(\vec{k},\omega)$ is given by

$$y_\sigma^{(1)}(\vec{k},\omega)=1+\frac{[(\Gamma_sk^2/2)^2-\Delta_\sigma^2]}{[(\Gamma_sk^2/2)^2+\Delta_\sigma^2]}, \tag{6}$$

where $\Delta_\sigma=\omega-\sigma ck$. In these expressions, k_{B} is Boltzmann's constant, χ_T is the isothermal compressibility, c is the velocity of sound, $\gamma=c_p/c_v$ is the ratio of the specific heats at constant pressure and constant volume, D_T is the thermal diffusivity, Γ_s is the sound absorption coefficient, and $\hat{k}$ is the unit vector $\vec{k}/|\vec{k}|$. All thermodynamic and transport coefficients in this equation are to be interpreted as space averages (to order Δ) weighted with the function $p^2(\vec{R})/\int dRp^2(\vec{R})$. We note that to linear order in the gradients we cannot distinguish between the average of a product of functions and the product of the averages.

Case 2.—The fluid is maintained in a steady state with a constant linear shear flow, at least far from the wall, where the average local velocity of the fluid is given by $\vec{u}=Xy\hat{x}$, where $\hat{x}$ is a unit vector in the x direction. We assume that the average density and temperature in the fluid are constant in space and time (we neglect viscous heating of the fluid). The result $S^2(\vec{k},\omega)$ is given by (5) and (6) with $y_\sigma^{(1)}$ replaced by $y_\sigma^{(2)}$, given by $y_\sigma^{(1)}$ with the changes (1) $\omega\to\omega'=\omega-\vec{k}\cdot\vec{u}_{\text{av}}$, where $\vec{u}_{\text{av}}$ is the weighted spatial average of $\vec{u}$ over the scattering volume; (2) $\sigma c\hat{k}\cdot\nabla T/T\to\hat{k}_x\hat{k}_yX$.

We now comment on a number of features of these results.

(1) If we examine the function y_σ in Eq. (6), we see that there are two distinct contributions. The 1 in these equations is due to the coupling of two hydrodynamic modes in the equal-time correlation functions and represents a long-range ($\sim1/k^2$) contribution to the correlation functions. The remaining contribution arises from the new eigenvalue problem mentioned previously.

(2) In Case 1 the temperature gradient leads to unequal contributions ($\sim\sigma y_\sigma^{(1)}\hat{k}\cdot\nabla T$) to the two Brillouin lines. In Case 2 the rate of shear X leads to equal contributions ($\sim y_\sigma^{(2)}X$) to the height of the Brillouin lines.

(3) In order to obtain the results given here we

have to assume (a) that $kL \gg 1$, i.e., the wavelength of light must be much smaller than the linear dimension L of the scattering volume; (b) that $\Delta \sim L\nabla\langle a\rangle/a_{\mathrm{eq}} \ll 1$, i.e., the thermodynamic parameters do not change significantly in the scattering volume; and (c) that two dimensionless quantities $\lambda \equiv c/\Gamma_s k^2 L$ and $\epsilon \equiv L|\nabla c|k/\Gamma_s k^2$ or $\epsilon \equiv L|X|k/\Gamma_s k^2$ are small and we will discuss each in turn.

The origin of the parameter λ is the position dependence of the electric field weighting function $p(\vec{R})$, which varies over the length L. This parameter can be understood as the ratio of the uncertainty in the distance of the Brillouin lines from the central line c/L, caused by the finite size of the scattering volume, to the width of the Brillouin lines $\Gamma_s k^2$ as determined by the lifetime of a sound wave. For both equilibrium and nonequilibrium light-scattering experiments this parameter should be small in order that the width of the Brillouin peaks in $S(\vec{k}, \omega)$ be determined by the effects due to the lifetime of the sound wave rather than by the finite size of the scattering volume. For a typical light-scattering experiment in H_2O at 20 °C, with $L \approx 0.035$ cm, if $\lambda \leqslant 0.1$ then $k \geqslant 3\times10^4$ cm^{-1}.

The parameter ϵ occurs in the calculation of $S(\vec{k}, \omega)$ only when the fluid is not in equilibrium. For a fluid with a temperature gradient, $\epsilon = L|\nabla c|k/\Gamma_s k^2$, where $|\nabla c|$ is the magnitude of the gradient in the sound velocity (due to the temperature gradient), and for a fluid with a velocity gradient X, $\epsilon = L|X|k/\Gamma_s k^2$. This parameter measures the ratio of the magnitude of the broadening of the Brillouin lines due to the gradient in the scattering volume ($L|\nabla c|k$ or $L|X|k$) to the width of the Brillouin lines $\Gamma_s k^2$. The condition $\epsilon \ll 1$ is required for our expansion around total equilibrium to be valid. For H_2O at 20 °C, with $L \approx 0.035$ cm and $k \approx 3\times10^4$ cm^{-1}, if $\epsilon \leqslant 0.1$ then $|\nabla T| \leqslant 10°$/cm.

(4) Because of the required smallness of the expansion parameters λ and ϵ we can only consistently predict a change from the equilibrium structure factor that is very small. Although we cannot rule out the possibility that the height differences given by Eq. (6) will remain and become observable when λ and $\epsilon \geqslant 1$, this can only be established by a nonperturbative solution of the new eigenvalue problem mentioned previously.[1]

(5) In nonequilibrium the importance of the parameter λ is *much* more pronounced. In equilibrium the expansion parameter λ may be said to lead to boundary effects, i.e., if bulk effects are of order L^3 then the effects associated with λ are of order L^2. However, when gradients are present this assumption can break down. In that case boundary effects of the order L^2 can be multiplied by terms of order L/L_∇, representing the variation of the thermodynamic or hydrodynamic variables over the system. Here L_∇ is the characteristic length for the variation of the quantity of interest. All this can then lead to terms of order L^3 which are the same size as the bulk effects. It is terms of this type that require us to take into account the spatial variation of the $p(\vec{R})$ function, in nonequilibrium, for a consistent theory. In fact, we note that as an intermediate result one can obtain corrections to the equilibrium Landau-Placzek (LP) result that are due to the gradients which are even more singular in $1/k$ than those given by Eqs. (5) and (6). These corrections are proportional to grad$T$ or X and are of order $1/k^3$ more singular than LP and represent a change in the location of the Brillouin peaks. However, they are cancelled by terms which arise from the spatial variation of $p(\vec{R}_1)$.

(6) Terms of this type are also partially responsible for the difference between our results and those given by Ronis, Procaccia, and Oppenheim,[2] and Machta, Oppenheim, and Procaccia.[3] The nonlocality corrections discussed by Ronis, Procaccia, and Oppenheim,[2] while not imaginary,[11] as stated by the authors, are cancelled by terms which would arise from the spatial variation of the function $p(\vec{R})$.

The remaining difference between the two approaches[2,3] (those authors find $y_\sigma = 1$ for all cases) can be accounted for by the evaluation of the three-time correlation function given by Ronis, Procaccia, and Oppenheim[2] as Eq. (2.18). If one evaluates this function in a straightforward manner for low densities, using a kinetic method due to Dufty,[12] then one finds *both* the contributions to the structure factor given by Eq. (6) and discussed in (2). We believe that in evaluating this expression Ronis, Procaccia, and Oppenheim[3] treat a time-dependent projection operator introduced by them to evaluate their Eq. (2.18) in part as if it were a normal time-independent projection operator as given in Ref. (8). However, when the projection operator they define acts on a microscopic current $J\vec{k}$ then one has, for small k, an expansion of the form

$$P\vec{k}(t)J\vec{k}(t) = A\vec{k}(t)\,[C_0 + C_1 k^2 + \ldots],$$

where $A\vec{k}$ is a microscopically conserved density and, for times t longer than some microscopic decay time, the coefficients C_i in this expression may be taken as constants. When a normal time-independent projection operator acts on a current the expansion is

$$P\vec{k}J\vec{k} \simeq A\vec{k}[C_0+D_1k^2+D_2k^4+\ldots].$$

Although in the limit $k \to 0$ these two expressions become identical, for $k \neq 0$ they differ and this difference ultimately leads to terms that are the same order of magnitude as those given by Eq. (6) of this Letter.

(7) For a dilute gas the present authors[13] previously computed the structure factor, for the case of a steady thermal gradient, using a fluctuating kinetic equation. Although the formalism presented there is correct and equivalent to the one presented here, the value of the coefficient y is incorrect. The correct value, valid for all densities is given in Eq. (6) here. The bilinear term mentioned in that Letter defines, in kinectic theory, the new eigenvalue problem discussed in this paper in a hydrodynamic context.

We are much indebted to Dr. J. Dufty and Dr. Y. Kan for checking some of our calculations and to them as well as to Dr. H. Z. Cummins for stimulating discussions. This work was supported in part by the National Science Foundation.

---

[1] T. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, to be published.

[2] D. Ronis, I. Procaccia, and I. Oppenheim, Phys. Rev. A 19, 1324 (1979).

[3] J. Machta, I. Oppenheim, and I. Procaccia, Phys. Rev. Lett. 42, 1368 (1979).

[4] R. Edwards, J. Angus, M. French, and J. Dunning, J. App. Phys. 42, 837 (1971).

[5] Usually, $p(\vec{R})$ is set equal to 1 inside the scattering volume and 0 outside. However, in actual experimental situations the function $p(\vec{R})$ may be better represented by Gaussian functions (see Ref. 4), to which we restrict ourselves in this Letter.

[6] The importance of the spatial variation of $p(\vec{R})$ in nonequilibrium has been discussed previously (see Ref. 4) in a different context, i.e., the scattering of light by noninteracting Brownian particles in a fluid with a parabolic velocity field.

[7] M. H. Ernst, E. Hauge, and J. M. J. van Leeuwen, J. Stat. Phys. 15, 23 (1976).

[8] M. H. Ernst and J. R. Dorfman, J. Stat. Phys. 12, 311 (1975).

[9] We note that our Eqs. (2)–(4) can be obtained from the fluctuating hydrodynamical equations given by Keizer [J. Keizer, Phys. Fluids 21, 198 (1978)].

[10] L. Kadanoff and J. Swift, J. Phys. Rev. 166, 89 (1968).

[11] This was also noted by D. Ronis (private communication).

[12] J. Dufty, Phys. Rev. A 13, 2299 (1976).

[13] T. Kirkpatrick, E. G. D. Cohen, and J. R. Dorfman, Phys. Rev. Lett. 42, 862 (1979).

Observation of Structure Resonances in the Fluorescence Spectra from Microspheres

R. E. Benner, P. W. Barber,(a) J. F. Owen, and R. K. Chang
Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520

(Received 14 December 1979)

Sharp intensity peaks are observed in the fluorescence spectra from dye-impregnated single polystyrene microspheres which are not seen in the spectra from bulk material. The resonant peaks are shown to correspond to the natural modes of oscillation of a dielectric sphere, and excellent correlation is found between experimental and theoretically predicted spectra. The results can be applied to the interpretation of inelastic emission (fluorescence and Raman) spectra obtained for the chemical speciation of aerosols and particulates.

A dielectric sphere possesses natural modes of oscillation at characteristic frequencies corresponding to specific size-to-wavelength ratios. These structure resonances have been studied both theoretically and experimentally in the microwave range[1,2] and more recently in the optical range.[3-6] In all of these studies, the emphases have been on structure-resonance effects resulting from external excitation, usually by plane waves. The elastic absorption and scattering efficiencies and the optical levitation force are all known to be enhanced when the incident wavelength is commensurate with the natural modes of oscillation of the sphere.[3-6] Recent theoretical work[7-9] has predicted the existence of structure resonances in the inelastic emission.

We report the first experimental observation of structure resonances resulting from the internal emission of inelastic radiation by fluorescing molecules embedded in a microsphere. Sharp in-