Kinetic Theory of Light Scattering from a Fluid Not in Equilibrium

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The kinetic theory of the fluctuations of a gas not in equilibrium is given and applied to light scattering. Unequal heights of the Brillouin lines are found in the presence of a temperature gradient.

As part of a systematic theory of fluctuations in a fluid near equilibrium, which will be published elsewhere,[1] we have computed the scattering of light by such a fluid. Contrary to the case of a fluid in equilibrium, we find that when there is a thermal gradient in the fluid, the intensities of the two Brillouin lines differ by an amount proportional to the temperature gradient. The same effect was found by Procaccia, Ronis, and Oppenheim[2] on the basis of a different theory, but their expression differs from ours in that we find an important additional contribution to light scattering not present in their theory. We will now outline our calculations based on the kinetic theory of gases explicitly for a gas of hard spheres. However, the results are also valid for more realistic interparticle potentials.

The kinetic theory starts from a nonlinear fluctuating Boltzmann equation for the deviation $n_0\varphi_0(V_1)\psi(X_1;t)$ of the actual single-particle distribution function

$$\tilde{F}(X_1;t)=\sum_{i=1}^{N}\delta(X_1-x_i(t))$$

from its equilibrium average value

$$n_0\varphi_0(V_1)=n_0(m/2\pi k_BT_0)^{3/2}\exp(-\beta_0 mV_1^2/2)$$

so that

$$\tilde{F}(X_1;t)=n_0\varphi_0(V_1)[1+\psi(X_1;t)] \tag{1}$$

and

$$[\partial/\partial t+L(X_1)]\psi(X_1;t)=n_0\int dX_2\,\varphi_0(V_2)\overline{T}(X_1,X_2)\psi(X_1;t)\psi(X_2;t)+\tilde{S}(X_1;t). \tag{2}$$

Here x_i $(=\vec{r}_i,\vec{v}_i)$ denotes collectively the phase-space variables of molecule i. X_i refers to a particular position $\vec{R}_i$ and velocity $\vec{V}_i$ $(i=1,2)$ in phase space; $\beta_0=1/k_BT_0$; and n_0 and T_0 are the equilibrium number density and temperature, respectively; $L(X_1)=\vec{V}_1\cdot\partial/\partial\vec{R}_1-n_0\Lambda_0(\vec{V}_1)$, where $\Lambda_0(\vec{V}_1)$ is the linear Boltzmann collision operator[3]; $\overline{T}(X_1,X_2)$ a binary-collision operator defined elsewhere[4] with $\Lambda_0(\vec{V}_1)=n_0\int dX_2\,\varphi_0(V_2)\overline{T}(X_1,X_2)(1+P_{12})$, where P_{12} is an operator that permutes particles 1 and 2; m is the mass of a particle; N is the number of particles; k_B is Boltzmann's constant; and t is the time.

$\tilde{S}(X_1;t)$ is a fluctuating force, whose properties are determined by the procedure outlined below. Setting

$$\psi=\langle\psi\rangle+\delta\tilde{\psi}, \tag{3}$$

where angular brackets indicate a phase-space average over an initial nonequilibrium ensemble describing the fluid, one obtains from (2) two coupled equations, where the equation for $\langle\psi\rangle$ is the average of Eq. (2), and that for $\delta\tilde{\psi}$ is given by the difference between Eq. (2) and its average. Expanding $\langle\psi\rangle$ and $\delta\tilde{\psi}$ as $\langle\psi\rangle=\Delta\langle\psi_1\rangle+\ldots$, $\delta\tilde{\psi}=\epsilon\delta\tilde{\psi}_1+\ldots$, where Δ and ϵ characterize the magnitude of the deviations from equilibrium and of the size of the fluctuations, respectively, and keeping only terms to first order in the expansion parameters Δ and ϵ, one obtains the following coupled equations:

$$[\partial/\partial t+L(X_1)]\langle\psi_1(X_1;t)\rangle=0, \tag{4}$$

$$[\partial/\partial t+L(X_1)]\delta\tilde{\psi}_1(X_1;t)=n_0\int dX_2\,\varphi_0(V_2)\overline{T}(X_1,X_2)(1+P_{12})\langle\psi_1(X_1;t)\rangle\delta\tilde{\psi}_1(X_2;t)+\tilde{S}(X_1;t), \tag{5}$$

where $\tilde{S}(X_1;t)$ has been assumed to be of order ϵ, and the term involving $\langle\psi_1(X_1;t)\rangle\delta\tilde{\psi}_1(X_1;t)$ is of order $\epsilon\Delta$.

Assuming that

$$\langle\tilde{S}(X_1;t_1)\tilde{S}(X_2;t_2)\rangle = A(X_1,X_2;t_1)\delta(t_1-t_2), \tag{6}$$

and that

$$\langle\tilde{S}(X_i;t)\rangle = 0 \text{ and } \langle\tilde{S}(X_1;t)\delta\tilde{\psi}(X_2;0)\rangle = 0 \tag{7}$$

for all $t>0$, and using the formal solution of (5) for $\delta\tilde{\psi}_1(X_i;t)$ $(i=1,2)$, one can determine $A(X_1,X_2;t)$ in terms of the known equal-time correlation function $\langle\delta\tilde{\psi}(X_1;t)\delta\tilde{\psi}(X_2;t)\rangle$, with the help of (1) and (3). First, one has

$$\langle\delta\tilde{\psi}(X_1;t)\delta\tilde{\psi}(X_2;t)\rangle = \frac{\delta(X_1-X_2)}{n_0\varphi_0(V_1)}[1+\langle\psi(X_1;t)\rangle] + g_2(X_1,X_2;t), \tag{8}$$

where

$$g_2(X_1,X_2;t) = [F_2(X_1,X_2;t) - F_1(X_1;t)F_1(X_2;t)]/n_0^2\varphi_0(V_1)\varphi_0(V_2)$$

with

$$F_1(X_1;t) = \langle\tilde{F}(X_1;t)\rangle \text{ and } F_2(X_1,X_2;t) = \langle\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\delta(X_1-x_i(t))\delta(X_2-x_j(t))\rangle.$$

Now $\langle\delta\tilde{\psi}_1(X_1;t)\delta\tilde{\psi}_1(X_2;t)\rangle$ is given by the right-hand side of Eq. (8) including $O(\Delta)$. Here g_2 satisfies the equation[5]

$$[\partial/\partial t + L(X_1) + L(X_2)]g_2 = \overline{T}(X_1,X_2)(1+P_{12})\langle\psi_1\rangle \tag{9}$$

while $\langle\psi_1\rangle$ is a solution of (4) to first order in the gradients:

$$\begin{aligned}\langle\psi_1(X_1;t)\rangle = {}& \frac{\delta n(\vec{R}_1;t)}{n_0} + \beta_0 m V_{1\alpha}\delta u_\alpha(\vec{R}_1;t) + [\tfrac{1}{2}\beta_0 m V_1^2 - \tfrac{3}{2}]\frac{\delta T(\vec{R}_1;t)}{T_0} \\ & + \frac{\beta_0 m}{n_0\Lambda_0}[V_{1\alpha}V_{1\beta} - \tfrac{1}{3}\delta_{\alpha\beta}V_1^2]D_{\alpha\beta}(\vec{R}_1;t) + \frac{1}{n_0\Lambda_0}[\tfrac{1}{2}\beta_0 m V_1^2 - \tfrac{5}{2}]\frac{V_\alpha}{T_0}\frac{\partial\delta T(\vec{R}_1;t)}{\partial R_{1\alpha}}.\end{aligned} \tag{10}$$

Here δn, $\delta\vec{u}$, and δT are the average deviations, respectively, of the density $n(\vec{R}_1;t)$, the flow velocity $\vec{u}(\vec{R}_1;t)$, and the temperature $T(\vec{R}_1;t)$ from their equilibrium values; $D_{ij}(\vec{R}_1;t) = \frac{1}{2}[\partial u_i/\partial R_{1j} + \partial u_j/\partial R_{1i}]$, repeated Greek symbols imply summation convention, and δ_{ij} is Kronecker's δ function. This leads to

$$\begin{aligned}A(X_1,X_2;t) = {}& \left[\frac{\partial}{\partial t} + L(1) + L(2)\right]\frac{\delta(X_1-X_2)}{n_0\varphi_0(V_1)}[1+\langle\psi_1(X_1;t)\rangle] + \overline{T}(X_1,X_2)(1+P_{12})\langle\psi(X_1;t)\rangle \\ & - n_0(1+P_{12})\int dX_3\,\varphi_0(V_3)\overline{T}(X_1,X_3)(1+P_{13})\langle\psi_1(X_1;t)\rangle\frac{\delta(X_2-X_3)}{n_0\varphi_0(V_3)}.\end{aligned} \tag{11}$$

This expression for $A(X_1,X_2;t)$ is a generalization to a nonequilibrium system of one given before by Bixon and Zwanzig[6] and also by Hinton[7] and by Fox and Uhlenbeck[8] for fluids in equilibrium. As will be discussed below (cf. remarks 2 and 3), the equations (4)–(11) with the bilinear term form a consistent set.[9]

The light-scattering intensity can be expressed in terms of the unequal-time density-density correlation function:

$$S(\vec{k},\omega) = (VT)^{-1}\int_V d^3R_1\int_V d^3R_2\int_{-T/2}^{T/2}dt_1\int_{-T/2}^{T/2}dt_2\exp\{-i[\vec{k}\cdot(\vec{R}_1-\vec{R}_2) - \omega(t_1-t_2)]\}\langle\delta\tilde{\rho}(\vec{R}_1;t_1)\delta\tilde{\rho}(\vec{R}_2;t_2)\rangle, \tag{12}$$

where

$$\delta\tilde{\rho}(\vec{R}_1;t_i) = n_0 m\int d^3V_1\,\varphi_0(V_1)\delta\tilde{\psi}(X_1;t_i) \tag{13}$$

is the local density fluctuation at $\vec{R}_1$ at t_i, and T the time of observation. Equation (12) is a generalization to nonequilibrium of the usual expression for $S(\vec{k},\omega)$ for a fluid in equilibrium.[10] $\langle\delta\tilde{\rho}(\vec{R}_1;t_1)\delta\tilde{\rho}(\vec{R}_2;t_2)\rangle$

can be computed with Eq. (13) from the unequal-time correlation function $\langle \delta\bar{\psi}_1(X_1;t_1)\delta\bar{\psi}_1(X_2;t_2)\rangle$ which in turn can be obtained by first solving Eq. (5) for $\delta\bar{\psi}_1(X_1;t_1)$ and $\delta\bar{\psi}_1(X_2;t_2)$, multiplying these solutions, and then averaging over fluctuations using Eqs. (6) and (7). Inserting hydrodynamic modes[3,11] to calculate evolution operators involving $L(1)$ and $L(1)+L(2)$, one finds that for a stationary state with $\delta\vec{u}=0$, that is, a state with a constant temperature gradient and no pressure gradient,

$$S(\vec{k},\omega)=\rho^2 k_B T\chi_T\left\{\frac{c_p-c_v}{c_p}\,\frac{2D_T k^2}{\omega^2+(D_T k^2)^2}\right.$$
$$\left.+\frac{c_v}{2c_p}\left[\frac{\Gamma_s k^2-y_+(\vec{k},\omega)cT^{-1}\hat{k}\cdot\nabla\delta T}{(\omega-ck)^2+(\frac{1}{2}\Gamma_s k^2)^2}+\frac{\Gamma_s k^2+y_-(\vec{k},\omega)cT^{-1}\hat{k}\cdot\nabla\delta T}{(\omega+ck)^2+(\frac{1}{2}\Gamma_s k^2)^2}\right]\right\}. \qquad (14)$$

The qunatities $y_\pm(\vec{k},\omega)$ are functions of $\vec{k}$ and ω, whose explicit form will be given elsewhere.[12] As functions of ω, $y_+(\vec{k},\omega)$ and $y_-(\vec{k},\omega)$ have extrema at $\omega=kc$ and $\omega=kc$, respectively, and the value of $y_\pm$ at these points is given by

$$y_+(\vec{k},\omega=kc)=y_-(\vec{k},\omega=-kc)=y,$$

where

$$y=1-\left[\frac{2T}{\Gamma_s}\left(\frac{\partial\Gamma_s}{\partial T}\right)_\rho+\frac{1}{2}-\frac{4}{3}\frac{D_T}{\Gamma_s}+2\alpha T\right]. \qquad (15)$$

In the above expressions, $\rho=mn$, D_T is the thermal diffusivity, Γ_s is the sound-absorption coefficient, c is the velocity of sound, α is the coefficient of thermal expansion, χ_T is the isothermal compressibility, and c_p and c_v are the specific heats at constant pressure and volume, respectively. All thermodynamic quantities and transport coefficients as well as $\nabla\delta T$ in Eqs. (14) and (15) are to be interpreted as space averages over the scattering volume. In Eq. (15) the first term, 1, is due to $g_2(X_1,X_2;t)$ while the other terms (between square brackets) are due to the bilinear term containing $\langle\psi\rangle\delta\bar{\psi}$ in Eq. (2); the last term in Eq. (15) stems from the condition $\text{grad}p=0$. We make the following remarks:

1. A temperature gradient leads in our approximation to unequal contributions $\sim\pm y\,\text{grad}T$ to the Brillouin lines that do not occur in equilibrium when $\text{grad}T=0$. In contrast to our results, Procaccia, Ronis, and Oppenheim[2] find that $y=1$. We remark that a velocity gradient leads to equal contributions of $\sim\text{grad}\,\vec{u}$ to the Brillouin lines.

2. Without inclusion of the bilinear term, $S(\vec{k},\omega)$ will depend on the particular equilibrium state $n_0\varphi_0(V_1)$ chosen in Eq. (1).

3. The contribution to y from g_2 is caused by long-range correlations $\sim 1/k^2$ between two particles that have previously collided. These correlations in g_2 only exist in a fluid not in equilibrium and have been discussed before by Kirtz, Ramanathan, and Sandri,[13] by Blatt and co-workers,[14] and by Procaccia, Ronis, and Oppenheim.[2] We find that they as well as the bilinear term in Eq. (5) have to be included if spurious fluctuations in the Euler equations on the hydrodynamic level are to be avoided.

4. All thermodynamic quantities and transport coefficients in Eqs. (14) and (15) should be taken at their low-density values. Then the contributions to y from the bilinear term exceed that of g_2, leading to a value for y of about -1.6. To obtain an effect of a few percent, k values of the order of 1000 cm^{-1} have to be used.

5. A generalization of the formula, Eq. (14), for $S(\vec{k},\omega)$ to dense gases and liquids on the basis of a hydrodynamic calculation will be published elsewhere.[12] It appears that for k values of the order of 10^4, i.e., for light in the visible range and for small scattering angles, one has an effect of a few percent.

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