Kinetic Theory for the Broadening of the Depolarized Rayleigh Line

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Collisional and diffusional broadening of the depolarized Rayleigh light scattered by a gas of linear molecules are studied by a kinetic theory approach based on the Waldmann-Snider equation.

The spectrum of the depolarized Rayleigh light has recently been measured [1] for some gases (H_2, N_2, CO_2) in the pressure region where the width of the line is due to collisional broadening (pressure broadening). This note is concerned with the kinetic theory of the collisional and diffusional broadening of the depolarized Rayleigh light scattered by a gas of linear molecules. The possibility of treating this line width problem by a kinetic theory approach based on the WALDMANN-SNIDER equation [2] has already been mentioned earlier in connection with an investigation of the influence of a magnetic field on the depolarized Rayleigh light [3]. Previously, collisional broadening of the depolarized Rayleigh line has been studied qualitatively by GORDON [4].

For a gas of linear molecules the spectrum of the depolarized Rayleigh light is determined by the spectral function $S(\omega \mid \boldsymbol{k})$ of the (2nd rank) tensor polarization $\mathbf{a}$ of the rotational angular momenta of the molecules if ω and $\boldsymbol{k}$ are put equal to the differences between the frequencies $\omega_1-\omega_0$ and the wave vectors $\boldsymbol{k}_1-\boldsymbol{k}_0$, respectively, of the incident and the detected scattered light [5]. The tensor polarization $\mathbf{a}(t,\boldsymbol{x})$ is proportional to $\langle J^{-2}\,\overline{\boldsymbol{J}\boldsymbol{J}}\rangle$ where $\boldsymbol{J}$ is the rotational angular momentum operator, the sign $\overline{\ldots}$ denotes the irreducible (symmetric, traceless) part of a tensor and the bracket $\langle\ldots\rangle$ refers to an average over the one-particle distribution operator of the gas. For the light scattering problem the initial condition imposed on $\mathbf{a}(t,\boldsymbol{x})$ is $\mathbf{a}(0,\boldsymbol{x})=\delta(\boldsymbol{x})$. The spectral function is determined by [5]

$$S(\omega \mid \boldsymbol{k}) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty e^{i\omega t}\,A(t \mid \boldsymbol{k})\,\mathrm{d}t \qquad (1)$$

where the function $A(t \mid \boldsymbol{k})$ is defined by [6]

$$\hat{\mathbf{a}}(t,\boldsymbol{k}) = A(t \mid \boldsymbol{k})\,\hat{\mathbf{a}}(0,\boldsymbol{k})\,;\quad t \geqq 0. \qquad (2)$$

In Eq. (2) $\hat{\mathbf{a}}(t,\boldsymbol{k}) = \int e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}\,\mathbf{a}(t,\boldsymbol{x})\,\mathrm{d}^3x$ is the spatial Fourier transform of the tensor polarization $\mathbf{a}$.

The time dependence of the spatial Fourier components of the tensor polarization needed for the calculation of $S(\omega \mid \boldsymbol{k})$ can be obtained from the relevant transport-relaxation equations which, in turn, can be derived from the linearized WALDMANN-SNIDER equation by application of the moment method [7]. In a simple description where only two moments, viz., the tensor polarization $\mathbf{a}$ and the "tensor polarization flux" $\mathbf{b} \propto \langle \boldsymbol{v} J^{-2}\,\overline{\boldsymbol{J}\boldsymbol{J}}\rangle$ ($\boldsymbol{v}$ is the particle velocity) are taken into account the following set of equations is found

$$\dot{\mathbf{a}} + \sqrt{\frac{k_B\,T}{m}}\,\nabla\cdot\underline{\mathbf{b}} + \omega_T\,\mathbf{a} = 0, \qquad (3)$$

$$\dot{\underline{\mathbf{b}}} + \sqrt{\frac{m}{k_B\,T}}\,\nabla\,\mathbf{a} + \omega_{TF}\,\mathbf{b} = 0. \qquad (4)$$

In Eqs. (3, 4) k_B, T, and m are Boltzmann's constant, the temperature of the gas and the mass of a molecule, respectively. The dot denotes differentiation with respec to time and ∇ is the Nabla operator. The relaxation coefficients ω_T and ω_{TF} can be expressed in terms of collision brackets obtained from the linearized WALDMANN-SNIDER collision operator. They can be written as

$$\omega_T = n\,c\,\sigma_T\,,\quad \omega_{TF} = n\,c\,\sigma_{TF}\,, \qquad (5)$$

where n is the number density of the gas, c is an average thermal velocity, and σ_T and σ_{TF} are effective cross sections. In Eq. (4) it has been assumed that the three relaxation coefficients of the irreducible parts of the 3rd rank tensor $\underline{\mathbf{b}}$ are approximately equal to each other ("spherical approximation" [8]).

To calculate the spectral function of $\mathbf{a}$ from Eqs. (3, 4) it is assumed that the term $\dot{\underline{\mathbf{b}}}$ can be neglected in Eq. (4). This approximation leads to following closed aquation for $\mathbf{a}$:

$$\dot{\mathbf{a}} - D_T\,\Delta\,\mathbf{a} + \omega_T\,\mathbf{a} = 0\,, \qquad (6)$$

where

$$D_T = \frac{k_B\,T}{m}\,\frac{1}{\omega_{TF}} \qquad (7)$$

is the diffusion coefficient of the tensor polarization and Δ is the Laplacian. Notice that D_T, in general, differs from the self-diffusion coefficient. Eq. (6) yields $A(t \mid \boldsymbol{k}) = \exp\{-(\omega_T + k^2 D_T)\,t\}$ and hence, according to Eq. (1), the following spectral function is found

$$S(\omega \mid \boldsymbol{k}) = \frac{1}{\pi}\,\frac{\omega_T + k^2 D_T}{\omega^2 + (\omega_T + k^2 D_T)^2}\,. \qquad (8)$$

The half of the width at half height is given by

$$(\Delta\omega)_{1/2} = \omega_T + k^2 D_T\,. \qquad (9)$$

Clearly, the line width is determined by two additive contributions. Collisional broadening is characterized by the relaxation coefficient $\omega_T \propto n$ for the tensor

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polarization. Diffusional broadening is determined by $k^2 D_T \propto n^{-1}$. The latter contribution depends on the scattering angle between the wave vectors of the incident and the detected scattered light. For scattering under 90° where k is of the order of λ^{-1} collisional broadening dominates if the pressure is high enough that the mean free path of a molecule is very short compared with the wave length λ of the light.

The derivation of Eqs. (3, 4) from the WALDMANN-SNIDER equation, the calculation of the spectral function S from the full Eqs. (3, 4), and a discussion of the approximations involved in Eq. (6) are given in a forthcoming publication [9]. Also in Ref. [9], the relaxation coefficients ω_T and ω_{TF} are expressed in terms of collision brackets obtained from the WALDMANN-SNIDER collision term which contains the binary molecular scattering amplitude operator and its adjoint. This point is of particular interest for ω_T which is especially sensitive to the nonspherical part of scattering amplitude. Furthermore, it will be discussed under which conditions ω_T obtained from the light scattering experiment can be compared with data obtained from the Senftleben-Beenakker effect on the viscosity and from nuclear spin relaxation and when ω_{TF} can be compared with Senftleben-Beenakker effect measurements of the heat conductivity.

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Zur Begründung der Lorentz-Gruppe von Süßmann

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SÜSSMANN's *deduction of the Lorentz group is mathematized. It is shown that it depends mainly on the notion of velocity transformation.*

Diese Arbeit stellt im wesentlichen eine Analyse des Artikels von SÜSSMANN [1] dar. Es stellt sich heraus, daß für die Begründung der Lorentz-Gruppe in Süßmanns Form der Begriff der „reinen Geschwindigkeitstransformation" wesentlich ist. Der Aufbau der Arbeit ist synthetisch.

Das physikalische Geschehen spiele sich im $\mathbf{R}^4$, der Raum-Zeit, ab. Jedes physikalische System soll eine durchgehende zeitliche Entwicklung haben, d. h. in allen Zeitpunkten definiert sein. Wir postulieren die Existenz von freien Systemen, die durch Geraden beschrieben werden. Sei $(t, \boldsymbol{x}) \in \mathbf{R}^4$, so nennen wir $T(t, \boldsymbol{x})$ die Menge aller Geraden durch $(t, \boldsymbol{x})$, die freie Systeme beschreiben. Diese Geraden müssen von der Form

$$\{(t+\tau, \boldsymbol{x}+\tau \boldsymbol{v}) \in \mathbf{R}^4 : \tau \in \mathbf{R}\}$$

sein, und $T'(t, \boldsymbol{x})$ sei die Menge der so definierten „Geschwindigkeiten" $\boldsymbol{v}$; die Abbildung

$$T'(t, \boldsymbol{x}) \ni \boldsymbol{v} \to \{(t+\tau, \boldsymbol{x}+\tau \boldsymbol{v}) \in \mathbf{R}^4 : \tau \in \mathbf{R}\} \in T(t, \boldsymbol{x})$$

ist also eine Bijektion.

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[1] G. SÜSSMANN, Z. Naturforsch. **24 a**, 495 [1969].

Als Symmetrien bezeichnen wir bestimmte Bijektionen des $\mathbf{R}^4$. Jede Bijektion des $\mathbf{R}^4$ definiert eine Abbildung von $T(t, \boldsymbol{x})$ in eine Menge von Punktmengen im $\mathbf{R}^4$: sei b die Bijektion, so definieren wir

$$b'_{(t,\boldsymbol{x})} : T(t, \boldsymbol{x}) \to b'_{(t,\boldsymbol{x})}(T(t, \boldsymbol{x})),$$

$$b'_{(t,\boldsymbol{x})}(\{(t+\tau, \boldsymbol{x}+\tau \boldsymbol{v}) \in \mathbf{R}^4 : \tau \in \mathbf{R}\}) := \{b(t+\tau, \boldsymbol{x}+\tau \boldsymbol{v}) \in \mathbf{R}^4 : \tau \in \mathbf{R}\}.$$

So kommen wir zu

A 1 Ist S eine Symmetrie, so gilt: für alle $(t, \boldsymbol{x}) \in \mathbf{R}^4$ und alle $g \in T(t, \boldsymbol{x})$ ist $S'_{(t,\boldsymbol{x})}(g)$ eine Gerade durch $S(t, \boldsymbol{x})$, die ein freies physikalisches System beschreibt.

Also definiert dann $S'_{(t,\boldsymbol{x})}$ eine Abbildung von $T(t, \boldsymbol{x})$ in $T(S(t, \boldsymbol{x}))$; wir fordern:

A 2: Die durch eine Symmetrie S definierte Abbildung von $T(t, \boldsymbol{x})$ in $T(S(t, \boldsymbol{x}))$ ist eine Bijektion.

Diese Bijektion definiert dann wiederum eine Bijektion von $T'(t, \boldsymbol{x})$ auf $T'(S(t, \boldsymbol{x}))$. Weiter fordern wir:

B 1 Die Abbildungen $(t, \boldsymbol{x}) \to (t+\mathring{a}, D\boldsymbol{x}+\boldsymbol{a})$ sind für alle $(\mathring{a}, \boldsymbol{a}) \in \mathbf{R}^4$ und für alle $D \in SO(3)$ Symmetrien.

Unter Benutzung der Translation

$$(t, \boldsymbol{x}) \to (t+\mathring{a}, \boldsymbol{x}+\boldsymbol{a})$$

sieht man sofort, daß dann $T'(t, \boldsymbol{x})$ nicht von $(t, \boldsymbol{x})$ abhängt, so daß wir $T'(t, \boldsymbol{x})$ durch T abkürzen. T soll den Nullvektor und ein von ihm verschiedenes Element enthalten. Weiter folgt aus der Invarianz unter $SO(3)$: ist $\boldsymbol{v} \in T$, so auch $D\boldsymbol{v} \in T$ für alle $D \in SO(3)$, d. h. mit $\boldsymbol{v}$ ist jede Geschwindigkeit vom gleichen Betrag physikalisch. Ist S eine Sym-