Doppler Broadened Spectral Functions and Time Correlation Functions for a Gas in Non-Equilibrium

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Under non-equilibrium conditions, the velocity distribution function of a gas differs from the Maxwellian equilibrium distribution. The effect of this deviation from equilibrium on the time correlation function and the spectral function associated with a Doppler broadened spectral line is calculated in full generality for stationary non-equilibrium processes. As special cases the heat conduction and the viscous flow in the hydrodynamic regime are discussed.

The shape of spectral lines associated with the emission, absorption or scattering of electromagnetic radiation in gases\(^1\)\(^2\) is determined by the velocity distribution of the particles provided that their mean free path \(l\) is very large compared with \(k^{-1}\) where \(k\) is the magnitude of the relevant wave vector of the electromagnetic radiation*. The well-known Gaussian Doppler profile is obtained for the case of a Maxwellian velocity distribution. Under nonequilibrium conditions, in particular when a (stationary) transport process goes on, the velocity distribution differs from the Maxwellian. It is the purpose of this note to show how these deviations from equilibrium affect the Doppler broadening of the spectral function and the pertaining time correlation function. In these considerations, the natural line width is assumed to be small compared with the Doppler width such that it can be disregarded.

The connection between velocity distribution and Doppler broadening has recently been used to measure the deviations of the velocity distribution from its equilibrium value which are caused by a stationary heat flux\(^3\) in the hydrodynamic regime (i.e. the mean free path of the molecules was small compared with the distance \(L\) between the hot and cold plate).

This technique opens the possibility to test the kinetic theory of gases on the level of the distribution function rather than via the transport coefficients.

An experimental study of the deviations of the velocity distribution from its equilibrium state would also be of interest in connection with the effect reciprocal to flow birefringence in gases\(^4\).

In this paper, firstly the connection between the time correlation function (pertaining to a Doppler broadened spectral function) and the velocity distribution function is stated. Secondly, the most general form of the velocity distribution function for a stationary transport process is introduced. Then the time correlation function is calculated and discussed for two special cases. Finally, the spectral function is obtained from the time correlation function. Again, two special cases relevant for heat conduction and viscous flow in the hydrodynamic regime are discussed in some detail.

Spectral Function and Correlation Function

The spectral function \(S(\omega, k)\) characterizing the shape of a spectral line (\(\omega\) and \(k\) are the frequency and the wave vector) is related to a time correlation function \(C(t, k)\) by

\[
S(\omega, k) = \pi^{-1} \text{Re} \int_0^\infty \text{d}t \exp(it\omega) C(t, k) .
\]

The choice \(C(0, k) = 1\) as initial condition for the correlation function implies \(\int \text{d}\omega S(\omega, k) = 1\).

Provided that the Doppler effect is the only mechanism affecting the spectral line, the correlation function is determined by\(^1\)\(^2\)

\[
C(t, k) = \langle \exp\{-i(k \cdot v + \omega_0)t\} \rangle ,
\]

where \(v\) is the velocity of a particle and \(\omega_0\) is the frequency of the line under consideration for an unperturbed particle. The bracket \(\langle \ldots \rangle\) stands for an average to be evaluated with the velocity distribution function.

*  For light scattering, e.g. \(k\) is the difference between the wave vectors of the incident and scattered light.

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In the following it is advantageous to use the dimensionless (peculiar) velocity variable
\[ V = v_0^{-1}(v - \langle v \rangle), \quad v_0 = (2k_B T/m)^{1/2}, \] (3)
where \( T \) is the temperature of the gas and \( k_B \) is the Boltzmann constant. Notice that \( \langle V \rangle = 0 \). With the abbreviations
\[ K = v_0 k, \quad \tilde{\omega}_0 = \omega_0 + k \cdot \langle v \rangle, \] (4)
Eq. (2) can be rewritten as
\[ C(t, k) = \exp \{- i \tilde{\omega}_0 t\} \int d^3 V \exp \{- i K \cdot V t\} F(V). \] (5)
Here, \( F(V) \) is the velocity distribution function with the normalization \( \int d^3 V F(V) = 1 \). It is due to the Doppler shift caused by a uniform average velocity \( \langle v \rangle \) that the frequency \( \tilde{\omega}_0 \) instead of \( \omega_0 \) occurs in (5). Before the correlation function can be calculated from (5), the distribution function \( F(V) \) has to be considered in more detail.

**Velocity Distribution Function**

The nonequilibrium velocity distribution function is written as
\[ F(V) = F_0(V) (1 + \Phi(V)) \] (6)
where \( F_0 = \pi^{-3/2} e^{-V^2} \) is the Maxwellian equilibrium distribution and \( \Phi \) is a measure for the deviation of \( F \) from \( F_0 \). In general, \( \Phi(V) \) can be expanded with respect to a complete set of orthogonal functions. Following Reference\(^5\) basis functions are chosen which are products of irreducible Cartesian tensors constructed from the components of \( V \) and Sonine polynomials depending on \( V^2 \). More specifically, the expansion
\[ \Phi(V) = \sum_{l = 0}^{\infty} \sum_{r = 0} a_L^{(r)} q^{(r)}_{\mu_1 \ldots \mu_l} (V) \] (7)
is used with
\[ q^{(r)}_{\mu_1 \ldots \mu_l} = w_{lr} (-1)^l S_{\mu_1 \ldots \mu_l}^{l \frac{1}{2}} (V^2) V_{\mu_1} \ldots V_{\mu_l}, \] (8)
\[ w_{lr} = \frac{(2l + 1)!! r!}{l!! 2 \pi^{-1/2} (l + \frac{1}{2} + r)! 1/2}. \]
Cartesian components are denoted by Greek subscripts, the summation convention is used for them. The symbol \( \cdots \) refers to the symmetric traceless (irreducible) part of a tensor. In Eq. (8),
\[ S_{\mu}^{(r)}(x) = (r!)^{-1} c_{\mu}^{(r)} c_{\nu}^{(r)} (1 - z)^{-(1+k)} \times \exp \{z x/(z - 1)\}, \quad z \to 0, \]
is a Sonine polynomial which is identical with the generalized Laguerre polynomial \( L_r^{(k)}(x) \), cf. Ref.\(^6\).
The first few of these polynomials are \( S^{(0)}(x) = 1, \)
\[ S^{(1)}_k(x) = k + 1 - x, \]
\[ S^{(2)}_k = \frac{1}{2} (k + 1)(k + 2) - \frac{3}{2} x + \frac{1}{2} x^2. \]
The normalization coefficients \( w_{lr} \) are chosen such that
\[ \langle q^{(r)}_{\mu_1 \ldots \mu_l} q^{(r')}_{\nu_1 \ldots \nu_l} \rangle = \delta_{lr} \delta_{rr'} A^{(l)}_{\mu_1 \ldots \mu_l, \nu_1 \ldots \nu_l} \] (9)
where \( \langle \cdots \rangle \) denotes an average evaluated with the equilibrium distribution function \( F_0 \). The \( A^{(l)} \cdots \) is an isotropic tensor of rank \( 2 l \) with the property\(^7\)
\[ A^{(l)}_{\mu_1 \ldots \mu_l, \nu_1 \ldots \nu_l} = A_{\mu_1 \ldots \mu_l}, \]
where \( A \cdots \) is an arbitrary tensor of rank \( l \) and \( A \cdots \) is its irreducible (symmetric traceless) part. Relation (9) implies
\[ a^{(r)}_{\mu_1 \ldots \mu_l} = \langle q^{(r)}_{\mu_1 \ldots \mu_l} \rangle, \] (10)
i.e. the expansion coefficients \( a^{(r)} \) are the nonequilibrium averages of the expansion functions \( q^{(r)} \). Strictly speaking, the coefficients \( a^{(r)} \) have to be constant in order that Eqs. (2) and (5) are valid. However, these equations can still be used if the spatial and temporal variations of the expansion coefficients are weak over the length scale \( k^{-1} \) and the time scale \( \omega_0^{-1} \).

A remark on the physical meaning of the first few of the expansion coefficients seems to be in order. Firstly, notice that the conditions \( \langle \Phi \rangle = 0, \langle r^2 \rangle - \langle \nu \rangle^2 = \frac{3}{2} k_B T m^{-1}, \) and \( \langle V \rangle = 0 \) imply \( a^{(0)} = 0, a^{(1)} = 0, a^{(2)}_{\mu} = 0 \). The lowest order non-vanishing expansion vector and 2nd rank tensor are related to the (translational) heat flux \( q_\mu \) and to the friction pressure tensor \( p_{\mu \nu} \), respectively. More specifically, one has,
\[ a^{(1)}_{\mu} = \frac{2}{5} \left( \langle V^2 - \frac{5}{2} \rangle V_{\mu} \right) = \frac{2}{5} p_0^{-1} v_{0}^{-1} q_\mu, \]
\[ a^{(2)}_{\mu \nu} = \left[ \frac{1}{2} \langle V \rangle \langle V \rangle_{\nu} \right] = \frac{1}{2} p_0^{-1} p_{\mu \nu}, \] (11)
where \( p_0 = n k_B T \) is the equilibrium pressure, \( n \) is the number density of the gas.

For the calculation of the expansion tensors \( a^{(r)} \) from the (linearized) Boltzmann equation with the help of the moment method see References\(^5,\)\(^6\). For stationary heat conduction and viscous flow in the hydrodynamic regime, only vectors \( a^{(r)}_{\mu} \) and 2nd
rank tensors $a^{(r)}_{\mu\nu}$, respectively, occur in the expansion of $\Phi(V)$. For Maxwellian molecules the variables (11) only are needed. Higher rank tensors are of importance for transport processes in the rarefied gas regime.

**Calculation of the Correlation Function**

To calculate the correlation function $C(t, k)$, the expression (6) with the expansion (7) for $\Phi(V)$ is inserted into Equation (5). Firstly, the integration over $d^2\hat{V}$, i.e. over the direction of the velocity is performed. To this purpose, the Rayleigh expansion

$$\exp \left\{ -i \mathbf{K} \cdot \hat{V} t \right\} = \sum_{l=0}^{\infty} \left( -i \right)^l \left( 2l + 1 \right) \left( \frac{\pi}{2 K V t} \right)^{1/2} J_{l+\frac{1}{2}}(K V t) P_l(\hat{K} \cdot \hat{V})$$

is invoked where $J_{\cdot}$ is a Bessel function (the symbol $\hat{\cdot}$ refers to a unit vector, notice that $\hat{K} = \hat{k}$). Then the integration over $d^2V$ yields

$$\left( 4\pi \right)^{-1} \int d^2\hat{V} V_{\mu_1} \ldots V_{\mu_r} P_r(\hat{K} \cdot \hat{V}) = \delta_{ll'} \left( 2l + 1 \right)^{-1} V^I \hat{K}_{\mu_1} \ldots \hat{K}_{\mu_r} . \quad (12)$$

To perform the integration over the magnitude of the velocity (i.e. over $dV$), the relation (cf. Ref. 6, p. 242)

$$\int_0^\infty dV V^2 S_{l+\frac{1}{2}}^{(r)}(V^2) S_{l+\frac{1}{2}}^{(r)}(V^2) \left( \frac{\pi}{2} \right)^{1/2} (l + \frac{1}{2} + n)!^{-1} (l + \frac{1}{2} + n)!^{-1} (13)$$

is used. Due to

$$\int_0^\infty dV V^2 S_{l+\frac{1}{2}}^{(r)}(V^2) S_{l+\frac{1}{2}}^{(r)}(V^2) \delta_{rr'} \left( l + \frac{1}{2} + r \right)! (r')^{-1} ,$$

finally the result

$$C(t, k) = C_0(t, k) \left( 1 + \gamma(t, k) \right) , \quad \gamma = \sum_{l} \sum_{r} \gamma_{lr} , \quad (14)$$

is obtained with

$$C_0(t, k) = \exp \left\{ -i \omega_0 t \right\} \exp \left\{ -\frac{1}{2} K^2 t^2 \right\} , \quad (15)$$

$$\gamma_{lr}(t, k) = i^l \left( \frac{1}{2} K t \right)^{2r+1} \epsilon_{lr}(\hat{k}) . \quad (16)$$

Here

$$\epsilon_{lr}(\hat{k}) = (r')^{-1} w_{lr} a^{(r')}_{\mu_1 \ldots \mu_l} \hat{k}_{\mu_1} \ldots \hat{k}_{\mu_l} \quad (17)$$

essentially is the ,,k-component'' of the tensor $a^{(r)}_{\mu\nu}$. The quantity $C_0$ as given by (15) is the time correlation function associated with Doppler broadening in a gas under equilibrium conditions. The deviation of $C$ from $C_0$ caused by a transport process is described by $\gamma(t)$. Notice that $\gamma(0) = 0$. Furthermore, it is remarkable that a specific $\gamma_{lr}$ is proportional to a simple power of the time $t$. A directional dependence of $\gamma(t)$ on the angle between $k$ (or equivalently $K$) and directions specified by a transport process is contained in $\epsilon_{lr}$.

For heat conduction and viscous flow in the hydrodynamic regime, the terms involving $a^{(1)}_{\mu\nu}$ and $a^{(0)}_{\mu\nu}$ are the most important ones in the expansion (7).

For these special cases ($l = 1$, $r = 1$ and $l = 2$, $r = 0$), the quantities $\gamma_{lr}$ are

$$\gamma_{11} = i \left( \frac{1}{2} K t \right)^2 \epsilon_{11} , \quad \gamma_{20} = - \left( \frac{1}{2} K t \right)^2 \epsilon_{20}$$

with

$$\epsilon_{11} = \left( \frac{1}{2} p_0 v_0 \right)^{-1} q_{\mu} \hat{k}_{\mu} , \quad \epsilon_{20} = \left( p_0^{-1} - \hat{p}_{\mu\nu} \hat{k}_{\mu} \hat{k}_{\nu} \right) \quad (18)$$

where it is recalled that $q_{\mu}$ and $\hat{p}_{\mu\nu}$ are the translational heat flux and the friction pressure tensor, respectively. Notice that both $\gamma_{11}$ and $\gamma_{20}$ are inversely proportional to the pressure in the hydrodynamic regime of a dilute gas where $q_{\mu}$ and $\hat{p}_{\mu\nu}$ are independent of the pressure. Clearly, the coefficient $\epsilon_{20}$ depends on the angle between the wave vector $k$ (parallel to $K$) and the direction of the heat flux $q$. Similarly, $\epsilon_{20}$ depends on the orientation of $k$ relative to the principal axes of the friction pressure tensor.

The time correlation function for a nonequilibrium situation caused by a viscous flow and by a heat flux is discussed further in the simple approximation where all expansion coefficients associated with...
higher Sonine polynomials are disregarded. Then, the real part of \( C(t) \) (cf. 14—16) pertaining to a viscous flow is

\[
\text{Re} \, C_{20} = E_{20}(\tau) \cos(p \tau),
\]

\[
E_{20}(\tau) = e^{-\tau^2}(1 - \tau^2 z_{20})
\]  

(19)

with \( \tau = \frac{1}{2} K t \) and \( p = 2 \omega_0 K^{-1} \).

According to (19), the envelope \( E_{20}(\tau) \) of the periodic function \( \cos(p \tau) \) is modified by the viscous flow. In Figure 1, \( E_{20}(\tau) \) is plotted as function of the dimensionless time variable \( \tau \) for \( z_{20} = 0 \) (equilibrium) and \( z_{20} = \pm \frac{1}{2} \). The magnitude of \( z_{20} \) has been chosen unrealistically large in order to demonstrate the qualitative differences between the equilibrium and nonequilibrium cases more clearly.

Similarly, for heat transport the real part of the relevant time correlation function is

\[
\text{Re} \, C_{11} = e^{-\tau^2}(\cos(p \tau) + \tau^2 z_{11} \sin(p \tau)) = E_{11}(\tau) \cos(p \tau + \delta),
\]

(20)

with

\[
E_{11}(\tau) = e^{-\tau^2}(1 + \tau^2 z_{11})^{1/2},
\]

\[
\delta = -\arctan(z_{11}).
\]

(21)

In this case, both the envelope \( E_{11}(\tau) \) and the phase \( \delta \) of the periodic function \( \cos \), are affected by the transport process. In Fig. 2, \( E_{11}(\tau) \) is plotted as function of \( \tau \) for \( z_{11} = 0 \) and \( |z_{11}| = \frac{1}{2} \). The resulting correlation function \( C_{11}(\tau) \) is plotted in Fig. 3 for \( z_{11} = 0 \) (dashed curve) and \( z_{11} = \frac{1}{3} \). To demonstrate the essential features, viz. the decay of the correlation function and the phase shift caused by the heat flux, the rather small value \( p = 4 \pi \) has been chosen for the dimensionless frequency variable \( p \).

**Spectral Function**

With the correlation function determined by (14—17), the spectral function \( S(\omega) \) can now be calculated from (1). It proves convenient to introduce the dimensionless frequency variable

\[
\Omega = K^{-1}(\omega - \omega_0)
\]

(22)

and to use the dimensionless time variable \( T = K t \).

Then the spectral function \( S(\Omega) \) (related to \( S(\omega) \) by \( \int S(\Omega) \, d\Omega = \int S(\omega) \, d\omega \) is given by

\[
S(\Omega) = \pi^{-1/2} e^{-\Omega^2} \left[ T^n e^{i\Omega T} e^{-1T^2(1 + \gamma)} \right].
\]

(23)

For \( \gamma = 0 \) (equilibrium velocity distribution), the Doppler profile

\[
S_0(\Omega) = \pi^{-1/2} e^{-\Omega^2}
\]

(24)

is recovered from (23). Due to

\[
T^n e^{i\Omega T} = i^{-n} \left( \frac{\partial^n}{\partial \Omega^n} \right) e^{i\Omega T}
\]

and with the help of the relation

\[
H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}(e^{-x^2}) \text{ where } H_n(x)
\]

is a Hermite polynomial, the desired result

\[
S(\Omega) = S_0(\Omega) (1 + \sigma(\Omega)), \quad \sigma(\Omega) = \sum_i \sum_r \sigma_{ir}(\Omega),
\]

(25)
Fig. 4. The spectral function $S_{20}$ as given by Eq. (25) with (29) is plotted as function of the dimensionless frequency variable $\Omega$, cf. Equation (22). The labelling of the curves has the same meaning as in Figure 1.

with

$$\sigma_{1r}(\Omega) = (-1)^{r+1} 2^{-\frac{1}{2}} \gamma \alpha^{r+1} H_{2r+1}(\Omega)$$

(26)

is found for the spectral function under nonequilibrium conditions. Due to \( \gamma(0) = 0 \) one has \( \int S_0(\Omega) \sigma(\Omega) d\Omega = 0 \) and consequently

$$\int S(\Omega) d\Omega = \int S_0(\Omega) d\Omega.$$

The Hermite polynomials occurring in (26) can also be expressed in terms of Sonine polynomials, (cf. Ref. 6, p. 240) i.e. Eq. (26) is equivalent to

$$\sigma_{1r}(\Omega) = (-1)^{l/2} \left( r + \frac{l}{2} \right) \alpha^{l+1} H_{l+1}(\Omega^2)$$

(27)

for \( l = 0, 2, 4, \ldots \) and to

$$\sigma_{1r}(\Omega) = (-1)^{(l+1)/2} \left( r + \frac{l-1}{2} \right) \alpha^{l+1} H_{l+1}(\Omega^2)$$

(28)

for \( l = 1, 3, 5, \ldots \).

It is recalled that the cases \( l = 1 \) and \( l = 2 \) are relevant for heat conduction and viscous flow in the hydrodynamic regime. For the special cases \( l = 1, r = 1, 2 \) and \( l = 2, r = 0 \), expressions essentially equivalent to (25) with (27) and (28) have previously been stated in Ref. 3 and in Reference 4.

For the special cases considered in the previous section where only the translational heat flux \( q \) and the friction pressure tensor \( \mathbf{F} \) have been taken into consideration, the relevant \( \sigma_{1r} \) are

$$\sigma_{11} = \alpha_{11} (\Omega^2 - \frac{1}{2})$$

and

$$\sigma_{20} = \alpha_{20} (\Omega^2 - \frac{1}{2}).$$

(29)

In Figure 4, the spectral function pertaining to viscous flow, \( S_{20} = S_0(1 + \sigma_{20}) \) is plotted as function of the dimensionless frequency variable $\Omega$ for \( \alpha_{20} = 0 \) (equilibrium) and \( \alpha_{20} = \pm \frac{1}{2} \). Again, the magnitude of \( \alpha_{20} \) has been chosen unrealistically large in order to show the difference between equilibrium and nonequilibrium situation more clearly. The spectral function associated with heat conduction (for \( \alpha_{11} = 0, r > 1 \)), \( S_{11} = S_0(1 + \sigma_{11}) \) is plotted in Fig. 5 as function of for \( \alpha_{11} = 0 \) and \( \alpha_{11} = 0 \). Clearly, a heat flux renders the spectral function asymmetric.

Furthermore, notice that the $\Omega$ where the spectral functions become negative (cf. Figs. 4, 5) are very large for the small values of \( \alpha_{20} \) and \( \alpha_{11} \) which can be obtained in reality. Hence this unphysical behavior of the spectral functions can be disregarded because the factor $e^{-\Omega^2}$ occurring in the spectral function becomes extremely small in this frequency range.

Concluding Remarks

In this note, the time correlation function and the spectral function associated with a Doppler broadened spectral line have been calculated for the most general (stationary) nonequilibrium velocity distribution as given by Equations (6, 7). Two special cases of interest, viz. heat conduction and viscous flow in the hydrodynamic regime have been discussed. The effect of a heat flux on the spectral function has already been investigated experimentally, cf. Reference 3. Similar experiments for a viscous flow are desirable.
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3 F. Baas, P. Oudeman, and J. J. M. Beenakker, Phys. Letters 55 A, 81 [1975];