Sound absorption and dispersion in
dilute polyatomic gases: a generalized
kinetic approach

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Abstract. A generalized kinetic model equation which takes into account the
frequency dependence of the thermal conductivity is used to analyze the problem
of sound propagation in dilute polyatomic gases. By comparing the theoretical
results with some available experimental data we infer that our model equation
provides a precise transition between low- and high-frequency limits.

Keywords: kinetic theory of gases and liquids, Boltzmann equation, heat
conduction, rarefied gas dynamics

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1. Introduction

Essentially, there are two different approaches to solve the problem concerning the propagation of plane harmonic waves in gases, namely: macroscopic and microscopic approaches. The macroscopic approach is based on conservation equations of mass, momentum and energy, and on the laws of Navier–Stokes and Fourier. Sound propagation predictions derived from this macroscopic approach are valid as long as the oscillation frequency of the acoustic wave is smaller than the mean molecular collision frequency [1]. In this case, sound dispersion is negligible, while the absorption per wavelength is proportional to the oscillation frequency and can be written as a sum of contributions due to viscous and thermal effects. Different generalizations of the usual macroscopic approach—trying to extend its validity to the high-frequency region—are reported in the literature [2]–[4]. Among them, the most popular are those that take into account the frequency dependence of the transport coefficients. However, the sound propagation results derived from this approach give good agreement with the experimental data only for the phase velocity of the sound waves. When the oscillation frequency is comparable to the molecular collision frequency, one has no recourse except to turn to a microscopic approach, i.e., one has to use the Boltzmann equation. One of the earliest attempts to solve the problem of sound propagation in polyatomic gases based on a kinetic equation was made by Hanson et al [5]. By employing the method of Sirovich and Thurber for polyatomic kinetic models—which is based on a generalization of the Gross–Jackson procedure for monatomic gases—they derived dispersion relations for the four-moment and seven-moment approximations. Calculations performed by Hanson, Morse and Sirovich for nitrogen and oxygen show that their results are in some agreement with the experimental results of Greenspan [6].

Our purpose in this paper is to study the propagation of sound waves in dilute polyatomic gases using a kinetic model equation which replaces the collision operator of the Boltzmann equation by a single relaxation time term [7] and generalizes the classical...
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hydrodynamic description by considering a frequency-dependent thermal conductivity. In particular, our expression for the generalized thermal conductivity follows from the Maxwell–Cattaneo law of heat conduction which can be written as a constitutive equation for the heat flux vector with an exponential memory kernel. By applying the normal mode method to our generalized model equation, it is possible to derive a dispersion relation which can be used to determine the phase velocity and the attenuation coefficient of the acoustic mode. Comparison of the theoretical results with the acoustic measurements performed by Greenspan in oxygen and nitrogen shows that our generalized kinetic model equation for dilute polyatomic gases provides a precise transition between low- and high-frequency limits.

We organize the paper as follows: in section 2 we derive a generalized kinetic model equation for dilute polyatomic gases which takes into account the frequency dependence of the thermal conductivity. The sound wave propagation problem is analyzed in section 3, while in section 4 we compare the theoretical results with some available experimental data. Finally, in section 5, we finish with some concluding remarks.

Cartesian notation for tensors with the usual summation convention is used. Furthermore, angular parentheses around indices denote traceless symmetrization.

2. Generalized model equation

In the classical kinetic theory developed by Taxman [8] for dilute polyatomic gases, the one-particle distribution function \( f(\mathbf{x}, \mathbf{c}, t, s) \) is defined in such a way that \( f(\mathbf{x}, \mathbf{c}, t, s) \, d\mathbf{c} \, ds \) gives the number of molecules at position \( \mathbf{x} \) and time \( t \) with molecular velocities between \( \mathbf{c} \) and \( \mathbf{c} + d\mathbf{c} \) and with internal degrees of freedom between \( s \) and \( s + ds \). By neglecting external forces, the one-particle distribution function satisfies the Boltzmann equation [9]

\[
\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = \mathcal{C}(f, f),
\]

where \( \mathcal{C}(f, f) \) is the Boltzmann collision operator. The collision operator describes the rate of change of the distribution function due to molecular collisions and obeys the following collisional invariant conditions [10]:

\[
\int m \mathcal{C}(f, f) \, d\mathbf{c} \, ds = 0,
\]

\[
\int mc \mathcal{C}(f, f) \, d\mathbf{c} \, ds = 0,
\]

\[
\int \left( \frac{mc^2}{2} + E_s \right) \mathcal{C}(f, f) \, d\mathbf{c} \, ds = 0,
\]

where \( m \) is the molecular mass and \( E_s \) denotes the energy associated with the internal degrees of freedom. Conditions (2)–(4) correspond to the conservation of mass, momentum and energy during collisions, respectively.

The mathematical complexity of the collision operator \( \mathcal{C}(f, f) \) to analyze time-dependent problems like sound propagation and light scattering in dilute polyatomic gases
is usually avoided by replacing it by a single relaxation time term of the form

\[ C(f, f) = -\frac{(f - f_r)}{\tau}, \]  

(5)

where \( \tau \) is an effective relaxation time and \( f_r \) is a reference distribution function which satisfies the main physical properties of the Boltzmann collision operator. Recently, an expression for the reference distribution function was obtained by Marques [11] by requiring the Chapman–Enskog solution of the kinetic model equation to be consistent with the classical Navier–Stokes–Fourier description.

In the usual Navier–Stokes–Fourier theory a macroscopic state of a dilute polyatomic gas is characterized by the fields of mass density

\[ \rho = \int mf \, dc \, ds, \]  

(6)

flow velocity

\[ v_i = \rho^{-1} \int mc_i f \, dc \, ds, \]  

(7)

and temperature

\[ T = (\rho c_v)^{-1} \int \left( \frac{mC_i^2}{2} + \mathcal{E}_s \right) f \, dc \, ds, \]  

(8)

while the pressure tensor

\[ p_{ij} = \int mC_i C_j f \, dc \, ds \]  

(9)

and the heat flux vector

\[ q_i = \int \left( \frac{mC_i^2}{2} + \mathcal{E}_s \right) C_i f \, dc \, ds \]  

(10)

are given, respectively, by the following constitutive relations [12]

\[ p_{ij} = \left( p - \eta_0 \frac{\partial v_i}{\partial x_r} \right) \delta_{ij} - 2\mu_0 \frac{\partial v_{ij}}{\partial x_j} \]  

(11)

and

\[ q_i = -\lambda_0 \frac{\partial T}{\partial x_i}, \]  

(12)

where \( c_v \) is the total specific heat at constant volume, \( C_i = c_i - v_i \) is the peculiar velocity, \( p \) is the gas pressure, \( \mu_0 \) is the shear viscosity, \( \eta_0 \) is the bulk viscosity and \( \lambda_0 \) is the thermal conductivity. By taking the effective relaxation time \( \tau \) equal to the stress relaxation time \( \tau_s = \mu_0 / p \), the reference distribution function for dilute polyatomic gases which is compatible with the classical Navier–Stokes–Fourier theory reads

\[ f_r = f^{(0)} \left\{ 1 + \tau \left( 1 - \frac{\delta_0}{\gamma} \right) \left[ \left( \frac{mC_i^2}{2kT} - \frac{5}{2} \right) + \left( \frac{\mathcal{E}_s}{kT} - \frac{\mathcal{E}}{kT} \right) \right] \frac{C_i \, \partial T}{T} \frac{\partial x_i}{\partial x_r}, \right. \]

\[ + \tau (1 - Z_0) \left[ \left( \frac{5}{3} - \gamma \right) \left( \frac{mC_i^2}{2kT} - \frac{3}{2} \right) - (\gamma - 1) \left( \frac{\mathcal{E}_s}{kT} - \frac{\mathcal{E}}{kT} \right) \right] \frac{\partial v_r}{\partial x_r} \right\}, \]  

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where

\[ f^{(0)} = \frac{\rho}{m} \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{mC^2}{2kT} \right) \exp \left( -\frac{E_s}{kT} \right) Z \]  

is the local equilibrium distribution function and

\[ Z = \int \exp \left( -\frac{E_s}{kT} \right) ds \]

is the partition function associated with the internal degrees of freedom. Moreover, \( \gamma \) is the specific heat ratio, \( f_0 = \lambda_0/\mu_0 c_v \) is the Eucken factor, \( Z_0 = (\eta_0/\mu_0)/(5/3 - \gamma) \) is the internal relaxation number (i.e., the mean number of molecular collisions required for the translational and internal degrees of freedom to come to thermal equilibrium [13]) and

\[ \mathcal{E} = \frac{1}{Z} \int E_s \exp \left( -\frac{E_s}{kT} \right) ds \]

is the mean internal energy.

By analyzing time-dependent problems like sound propagation and light scattering in dilute polyatomic gases, Marques [11] was able to determine the range of applicability of his kinetic model equation. Comparison of theoretical results with available experimental data in nitrogen, oxygen, carbon dioxide and methane shows that the reference distribution function equation (13) is valid as long as the external oscillation frequency is smaller than the relaxation frequency for internal and translational degrees of freedom to come to thermal equilibrium.

It is possible to extend the validity of the kinetic model equation to the high-frequency region by considering a generalization of the classical hydrodynamic description. Certainly, the most popular approach that generalizes the hydrodynamic behavior of simple fluids is based on the Maxwell–Cattaneo law of heat conduction [3]

\[ \tau_q \frac{\partial q_i}{\partial t} + q_i = -\lambda_0 \frac{\partial T}{\partial x_i}, \]

where the relaxation time \( \tau_q \) gives us a measure of the time interval spent by the heat flux vector to achieve a stationary value. It is well known [14, 15] that the Maxwell–Cattaneo equation (17) can be written as

\[ q_i = -\int_0^t \frac{\lambda_0}{\tau_q} \exp \left( -\frac{t - t'}{\tau_q} \right) \frac{\partial T(x, t')}{\partial x_i} \, dt', \]

i.e., as a constitutive equation with an exponential memory kernel in such a way that a generalized thermal conductivity can be defined as

\[ \lambda(t - t') = \frac{\lambda_0}{\tau_q} \exp \left( -\frac{t - t'}{\tau_q} \right). \]

Since sound wave and light scattering solutions are found by Fourier transformation in space and time, we verify from (19) that this generalization introduces a frequency-dependent thermal conductivity

\[ \lambda(\omega) = \frac{\lambda_0}{1 + \omega \tau_q}. \]

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Furthermore, based on the work of Zwanzig [4], it is possible to modify the constitutive relation equation (11) for the pressure tensor to take into account the frequency dependence of the bulk viscosity. Aiming to calculate the spectral distribution of scattered light in a one-component fluid whose molecules have internal degrees of freedom weakly coupled to their translational degrees of freedom by a single relaxation time process, Mountain wrote the pressure tensor as [16]

\[
p_{ij} = \left( p - \eta_0 \frac{\partial v_r}{\partial x_r} - \int_0^t \frac{\eta_0}{\tau_s} \exp \left( -\frac{t - t'}{\tau_s} \right) \frac{\partial v_r(x, t')}{\partial x_r} \, dt' \right) \delta_{ij} - 2\mu_0 \frac{\partial v_i}{\partial x_j},
\]

(21)

where \( \tau_s \) is the relaxation time. Expression (21) shows that in the so-called weak coupling limit the bulk viscosity consists of two parts, a frequency independent one due to translational motions and a frequency-dependent one which is related to the exponential decay of the energy in internal modes as a result of interactions with translational modes. Comparison between theory and experiments shows that the generalized hydrodynamical model proposed by Mountain does not always apply since in some fluids the relaxation of the internal degrees of freedom involves more than one relaxation time.

Based on these facts we construct in this work a generalized kinetic model equation for dilute polyatomic gases which takes into account the frequency dependence of the thermal conductivity via the Maxwell–Cattaneo law, but disregards the frequency-dependent part of the bulk viscosity. In addition, we can neglect the frequency dependence of the shear viscosity since (as pointed out by Zwanzig [4]) the shear tensor is related to the transport of momentum, not to the transport of energy and, therefore, the internal degrees of freedom of the molecules do not contribute to the shear viscosity. For the construction of our generalized kinetic model equation we start by assuming that the reference distribution function is given by the expression

\[
f_{r} = f^{(0)} \left\{ 1 + A \left( \frac{\mathcal{E}_s}{kT} - \frac{\mathcal{E}}{kT} \right) + A_i C_i + A_{rr} \left( \frac{mC_r^2}{2kT} - \frac{3}{2} \right) \right. \\
+ \left. A_{(ij)} C_i C_j + A_{irr} \left( \frac{mC_r^2}{2kT} + \frac{\mathcal{E}_s}{kT} \right) C_i \right\},
\]

(22)

where \( A, A_i, A_{rr}, A_{(ij)} \) and \( A_{irr} \) are expansion coefficients that depend on position and time through the basic fields. As described in detail by Marques [11], the application of the Chapman–Enskog method [9] to solve the kinetic model equation allows the determination of the expansion coefficients appearing in the above reference distribution function. Hence, by considering the constitutive relations (11) and (18) we get

\[
\frac{5}{3} - \gamma A + (\gamma - 1) A_{rr} = 0, \\
A_i + \frac{5}{2} + \frac{\mathcal{E}}{kT} A_{rr} = 0, \\
A_{(ij)} = 0, \\
A_{rr} = \frac{\mu_0}{p} \left( \frac{5}{3} - \gamma \right) (1 - Z_0) \frac{\partial v_r}{\partial x_r}, \\
A_{irr} = \frac{\mu_0}{pT} \left[ \frac{\partial T}{\partial x_i} - \frac{1}{\tau_q} \int_0^t \frac{\mathcal{F}_0}{\gamma} \exp \left( \frac{-t - t'}{\tau_q} \right) \frac{\partial T(x, t')}{\partial x_i} \, dt' \right].
\]

(23)

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Finally, by combining expressions (1), (5), (22) and (23) we can write our generalized kinetic model equation for dilute polyatomic gases as

\[
\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = -p_{\mu_0} \left( f - f^{(0)} \right) + f^{(0)} (1 - Z_0) \left[ \left( \frac{mC_2^2}{2kT} - \frac{3}{2} \right) \left( \frac{5}{3} - \gamma \right) \left( \frac{mC_2^2}{2kT} - \frac{5}{2} \right) + \left( \frac{\mathcal{E}_s}{kT} - \frac{\mathcal{E}}{kT} \right) \right]
\]

\[
\times C_i \frac{\partial T}{T} \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \right],
\]

where

\[
f(t - t') = \frac{f_0}{\tau_q} \exp \left( - \frac{t - t'}{\tau_q} \right)
\]

is the generalized Eucken factor. Being an approximation to the Boltzmann equation for dilute polyatomic gases, equation (24) must fulfill two basic properties of the true collision term of the Boltzmann equation, namely: (i) for all summation invariants the collision term (5) must satisfy the conditions (2)–(4) and (ii) the tendency of the distribution function to equilibrium (or equivalently the H-theorem) must hold, i.e., \( \int \ln f \mathcal{C}(f, f) \, dc \, ds \leq 0 \). Because the construction of our model equation is based on constrains (2)–(4), the first property is verified. Concerning the H-theorem, we show in appendix A that our model equation also satisfies this requirement.

Closing this section, we call attention to the fact that the application of the above generalized kinetic model equation to study time-dependent problems in dilute polyatomic gases only requires the specification of the ratio of the specific heats \( \gamma \), the Eucken factor \( f_0 \) and the internal relaxation number \( Z_0 \).

### 3. Absorption and dispersion of sound

As an application of the generalized kinetic model equation derived in the previous section, we study the problem concerning the propagation of a plane harmonic wave in dilute polyatomic gases. To simplify this study we consider the sound propagation process in the linear regime near equilibrium and assume that the sound wave moves along the \( x \)-axis. Hence, we write the distribution function as

\[
f = f_0 \{ 1 + \psi \exp [i(\kappa x - \omega t)] \},
\]

where \( f_0 \) is the absolute equilibrium distribution function, \( \kappa = \omega/v + i\alpha \) is the complex wavenumber, \( \omega \) is the angular oscillation frequency, \( v \) is the phase velocity, \( \alpha \) is the attenuation coefficient and \( \psi = \psi(c) \) is a function that depends only on the molecular velocity. In sound propagation problems the complex wavenumber \( \kappa \) is determined as a function of the oscillation frequency \( \omega \) via solution of the dispersion relation (for details see [11, 17, 18])

\[
\det(RM^{(0)} - i(\kappa v_0/\omega)(I - M^{(1)})) = 0,
\]

where \( R = p_0/\mu_0 \omega \) is the rarefaction parameter, \( v_0 = \sqrt{2kT_0/m} \) is the equilibrium thermal velocity and \( I \) is the identity matrix. Moreover, \( M^{(0)} \) and \( M^{(1)} \) are \( 3 \times 3 \) matrices whose elements—given in appendix B—depend on the dimensionless parameter

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\[ z = \left( \frac{\omega}{\kappa v_0} \right)(1 + iR) \]

and on the plasma dispersion function [19]

\[ W(z) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)}{t - z} \, dt. \tag{28} \]

The acoustic solution of the dispersion relation (27) in the low-frequency limit can be determined by expanding the dimensionless wave number \( \kappa v_0/\omega \) in powers of \( 1/R \). By retaining terms up to first order we obtain

\[
\frac{\kappa c_0}{\omega} = 1 + \frac{i}{2\gamma R} \left[ \frac{4}{3} + \left( \frac{5}{3} - \gamma \right) Z_0 + \frac{\gamma - 1}{\gamma} f_0 \right]
\]

in the low-frequency limit. Expression (29) shows us that the dispersion of sound is negligible in the low-frequency region, while the sound absorption per wavelength is proportional to the sound oscillation frequency and can be written as a sum of viscous and thermal effects. Note that an additional contribution coming from internal relaxation appears in the absorption coefficient of polyatomic gases, a fact that allows us to determine the bulk viscosity by comparing the theoretical results with available experimental data. Moreover, it is important to mention that the classical Navier–Stokes–Fourier description leads to the same expressions for sound absorption and dispersion in the low-frequency limit. This result is in complete agreement with our expectations, since we have required the Chapman–Enskog solution of our kinetic model equation to be consistent with the usual macroscopic approach.

4. Comparison with experiments

In order to test the validity and the range of applicability of the generalized kinetic model equation proposed in this paper, we compare in figures 1 and 2 the sound wave absorption factor \( \alpha c_0/\omega \) and the reciprocal speed ratio \( c_0/v \) calculated from the solution of the corresponding dispersion relation (27) with the acoustic measurements of Greenspan in nitrogen and oxygen. These sound propagation measurements were made at a temperature of 300 K in a 11 MHz double-crystal interferometer for different values of the gas pressure. The sound wave absorption factor was obtained by a determination of the logarithmic decrement in the sound level of the signal as a function of the traveled sound path, whereas the reciprocal speed ratio was determined by measuring the phase difference between a direct signal from the driving oscillator and the signal received at the receiver as a function of the sound path [6, 20]. For the numerical calculations we used the following material parameters:

| Gas | \( \gamma \) | \( f_0 \) | \( Z_0 \) |
|-----|------------|-------|-----|
| N\(_2\) | 1.40 | 1.97 | 2.5 |
| O\(_2\) | 1.39 | 1.95 | 1.3 |

The values of the specific heat ratio \( \gamma \) and the Eucken factor \( f_0 \) were obtained by using the values of \( c_v \), \( c_p \), \( \mu_0 \) and \( \lambda_0 \) given in the CRC Handbook of Chemistry and Physics [21].
Figure 1. Attenuation factor $\alpha c_0/\omega$ and reciprocal speed ratio $c_0/v$ as a function of the rarefaction parameter $R = p_0/\mu_0\omega$ for nitrogen at 300 K. The predictions of our generalized kinetic model equation (---) are compared with the experimental data of Greenspan and the results of the usual macroscopic approach (--.--).

Figure 2. Attenuation factor $\alpha c_0/\omega$ and reciprocal speed ratio $c_0/v$ as a function of the rarefaction parameter $R = p_0/\mu_0\omega$ for oxygen at 300 K. The predictions of our generalized kinetic model equation (---) are compared with the experimental data of Greenspan and the results of the usual macroscopic approach (--.--).

while the values of the internal relaxation number $Z_0$ were obtained by using expression (29) to fit the sound absorption experiments of Greenspan in the low-frequency limit.

In figures 1 and 2 the attenuation factor $\alpha c_0/\omega$ and the reciprocal speed ratio $c_0/v$ are shown on a double logarithmic scale as a function of the rarefaction parameter $R = p_0/\mu_0\omega$.

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for nitrogen and oxygen, respectively. The solid line represents the theoretical sound propagation results derived from our generalized kinetic model equation, while the dashed line represents the theoretical results derived from the usual macroscopic (hydrodynamic) approach based on the laws of Navier–Stokes and Fourier with frequency independent transport coefficients. The open circles are the experimental data of Greenspan for sound wave absorption (lower curve) and dispersion (upper curve).

We verify from figures 1 and 2 that in the low-frequency region ($R \gg 1$) the theoretical sound propagation results derived from our generalized kinetic model equation are in complete agreement with the experimental data. Moreover, the predictions for sound wave absorption and dispersion are exactly the same as obtained by the macroscopic approach. Since we required the Chapman–Enskog solution of our model equation to be consistent with the usual macroscopic description, this result is in complete agreement with our expectations. In the transition region ($1 < R < 10$) we note that the kinetic theory proposed in this paper yields better results than the usual macroscopic approach. Whereas the latter predicts a value for the attenuation factor which is about 23% greater than the experimental value, the predictions derived from our generalized kinetic model equation are in good agreement with the absorption data up to a value of the rarefaction parameter of approximately 2. For smaller values of the rarefaction parameter, i.e., in the high-frequency region we observe that the usual macroscopic approach yields a qualitatively correct result for the absorption curve but fails to describe the dispersion data. In contrast, the theoretical results obtained from our generalized kinetic model equation for small $R$ are in good agreement with both, especially with the sound wave dispersion curve of nitrogen. Further, we can conclude from figures 1 and 2 that the agreement between theory and experiment in the high-frequency limit is better for nitrogen than for oxygen, i.e., for gases with higher values of $Z_0$ which can be explained in terms of the internal relaxation time $\tau = \mu_0 Z_0 / p$. A higher value of $Z_0$ means that the thermal relaxation process between translational and internal degrees of freedom runs more slowly and, therefore, has a greater influence on the propagating sound wave which is appropriately described by our generalized kinetic model equation.

The comparison presented in figures 1 and 2 indicates that there are still opportunities for further enhancements in the kinetic theory, such as including the complete frequency dependence of all transport coefficients or considering non-linearities in the model equation, but all in all, we want to remark that the kinetic theory is well suited to describe sound propagation in dilute polyatomic gases over a wide range of frequencies and provides a precise transition between low- and high-frequency limits. Whereas the macroscopic approach becomes unable to describe the acoustic measurements in the high-frequency region, the kinetic model equation derived in this work still provides a qualitatively correct description of the experimental data, even for values of the rarefaction parameter smaller than the unity.

5. Conclusion and outlook

In the present work, we are concerned with the time-dependent problem of sound propagation in dilute polyatomic gases with classical internal degrees of freedom. Since the macroscopic (hydrodynamic) approach fails to describe the experimental data in the high-frequency region, one needs to turn to a microscopic (kinetic) approach based on the
Boltzmann equation. Assuming that the Boltzmann collision operator can be replaced by a single relaxation time term in order to eliminate its mathematical complexity, we are able to derive a generalized kinetic model equation for dilute polyatomic gases which explicitly takes into account the frequency dependence of the thermal conductivity. By comparing the theoretical sound propagation results derived from our generalized kinetic model equation with the experimental data, we observe that the kinetic theory is well suited to describe sound propagation in dilute polyatomic gases over a wide range of frequencies. Whereas the macroscopic approach becomes unable to describe the acoustic measurements in the high-frequency region, the generalized kinetic model equation proposed in this work still provides a qualitatively correct description of the experimental data, even for values of the rarefaction parameter smaller than the unity. The presented comparison also indicates that there are still opportunities for further enhancements in the kinetic theory. One of the next steps for future work on this topic would be to include the complete frequency dependence of all transport coefficients into the kinetic model equation.

Finally, we want to close this section by remarking that for the application of our generalized kinetic model equation to a specific sound propagation problem no further information about the potential energy of interaction between the gas molecules is required because the acoustic properties are completely characterized by three parameters, namely the ratio of the specific heats $\gamma$, the Eucken factor $f_0$ and the internal relaxation number $Z_0$. Values of these parameters can easily be found in the literature or fitted to experimental data in the low-frequency limit.

**Appendix A**

In order to prove the $H$-theorem, let us rewrite our generalized kinetic model equation for dilute polyatomic gases as

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = C(f, f),$$

where

$$C(f, f) = \frac{f_r - f}{\tau}$$

and

$$f_r = f^{(0)} (1 + \phi_r) = f^{(0)} \left\{ 1 + \tau (1 - Z_0) \left[ \left( \frac{5}{3} - \gamma \right) \left( \beta C^2 - \frac{3}{2} \right) - (\gamma - 1) \left( \frac{E_s}{kT} - \frac{E}{kT} \right) \right] \frac{\partial v_r}{\partial x_r} + \tau \left[ \left( \beta C^2 - \frac{5}{2} \right) + \left( \frac{E_s}{kT} - \frac{E}{kT} \right) \right] \frac{C_i}{T} \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t') \partial T(x, t')}{\gamma} \partial x_i \right] \right\}.$$  

The multiplication of model equation (A.1) by an arbitrary function $\psi = \psi(x, c, t, s)$ and subsequent integration of the resulting equation over all values of the molecular velocity $c$ and internal degrees of freedom $s$ leads to the transfer equation

$$\frac{\partial}{\partial t} \int \psi f \, dc \, ds + \frac{\partial}{\partial x_i} \int \psi c_i f \, dc \, ds - \int \left[ \frac{\partial \psi}{\partial t} + c_i \frac{\partial \psi}{\partial x_i} \right] f \, dc \, ds = \int \psi C(f, f) \, dc \, ds.$$
Note that the right-hand side of the above transfer equation vanishes if \( \psi \) is a summational invariant. In the kinetic theory of gases, the specific entropy density \( \sigma \) is usually defined as

\[
\rho \sigma = -k \int f \ln(bf) \, dc \, ds,
\]

where \( b \) is a constant which makes the argument of the logarithm function dimensionless.

The balance equation for the entropy density \( \rho \sigma \) can be derived from transfer equation (A.4) by taking \( \psi = -k \ln(bf) \). Hence, we have

\[
\frac{\partial \rho \sigma}{\partial t} + \frac{\partial}{\partial x_i} (\rho \sigma v_i + \varphi_i) = \varsigma,
\]

where

\[
\varphi_i = -k \int f \ln(bf) C_i \, dc \, ds
\]

is the entropy flux and

\[
\varsigma = -k \int \ln(bf) C(f, f) \, dc \, ds = -\frac{k}{\tau} \int (f_r - f) \ln(bf) \, dc \, ds
\]

is the entropy production density. The model equation (A.1) satisfies an \( H \)-theorem if the entropy production density is a positive semi-definite quantity, i.e., \( \varsigma \geq 0 \). In order to prove this condition, we write entropy production density as

\[
\varsigma = -\frac{k}{\tau} \int (f_r - f) \ln(f/f_r) \, dc \, ds - \frac{k}{\tau} \int (f_r - f) \ln(bf_r) \, dc \, ds = \varsigma_1 + \varsigma_2.
\]

It is easy to verify that \( \varsigma_1 \) is positive semi-definite due to the inequality \((1 - x) \ln x \leq 0\) which is valid for all \( x = f/f_r > 0 \) with the equality sign just if and only if \( x = 1 \), i.e., when \( f = f_r \). The term \( \varsigma_2 \) may be rewritten as

\[
\varsigma_2 = -\frac{k}{\tau} \int (f_r - f) \ln(bf^{(0)}) \, dc \, ds - \frac{k}{\tau} \int (f_r - f) \phi_r \, dc \, ds.
\]

Since \( \ln(bf^{(0)}) \) is a summational invariant, the first term on the right-hand side of (A.10) vanishes. Concerning the second term on the right-hand side of (A.10) we have

\[
-\frac{k}{\tau} \int (f_r - f) \phi_r \, dc \, ds = \frac{k}{\tau} \int (f - f^{(0)}) \phi_r \, dc \, ds - \frac{k}{\tau} \int f^{(0)} \phi_r^2 \, dc \, ds.
\]

By using the conditions

\[
\int (f - f^{(0)}) \, dc \, ds = 0,
\]

\[
\int C_i (f - f^{(0)}) \, dc \, ds = 0,
\]

\[
\int \left[ \left( \beta C^2 - \frac{3}{2} \right) + \left( \frac{E_s}{kT} - \frac{E}{kT} \right) \right] (f - f^{(0)}) \, dc \, ds = 0,
\]

\[
k \int \left( \beta C^2 - \frac{3}{2} \right) (f - f^{(0)}) \, dc \, ds = -\frac{3}{2} \eta_0 \frac{\partial v_i}{\partial x_i},
\]

\[
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\]

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\[ k \int \left[ \left( \beta C^2 - \frac{5}{2} \right) + \left( \frac{E_s}{kT} - \frac{E}{kT} \right) \right] C_i(f - f^{(0)}) \, dc \, ds = - \int_0^t \frac{\lambda(t - t')}{T} \frac{\partial T(x, t')}{\partial x_i} \, dt', \] (A.16)

we get

\[ \frac{k}{\tau} \int (f - f^{(0)}) \phi_r \, dc \, ds = -(1 - Z_0) \frac{\eta_0}{T} \frac{\partial v_i}{\partial x_i} \frac{\partial v_j}{\partial x_j} \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \right] \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \] (A.17)

and

\[ \frac{k}{\tau} \int f^{(0)} \phi_r^2 \, dc \, ds = \left(1 - Z_0\right)^2 \frac{\eta_0}{Z_0} \frac{\partial v_i}{\partial x_i} \frac{\partial v_j}{\partial x_j} + \frac{\gamma \mu_0 c_v}{T^2} \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \right] \times \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \right]. \] (A.18)

Thus, by combining equations (A.10), (A.11), (A.17) and (A.18) we have

\[ \varsigma_2 = -(1 - Z_0) \left( \frac{5}{3} - \gamma \right) \mu_0 \frac{\partial v_i}{\partial x_i} \frac{\partial v_j}{\partial x_j} \left[ \frac{\partial T}{\partial x_i} - \int_0^t \frac{f(t - t')}{\gamma} \frac{\partial T(x, t')}{\partial x_i} \, dt' \right] \frac{\partial T}{\partial x_i}. \] (A.19)

For polyatomic gases \( \gamma < 5/3 \) and \( Z_0 > 1 \), so that the first term on the right-hand side of expression (A.19) is positive semi-definite. In our constitutive relation for the heat flux vector, the memory (or retardation) effect is associated with the coefficient of thermal conductivity so that the integral appearing in expression (A.19) can be approximated by performing the following Markovian approximation

\[ \int_0^t \lambda(t - t') \frac{\partial T(x, t')}{\partial x_i} \, dt' = \int_0^t \lambda(t') \frac{\partial T(x, t - t')}{\partial x_i} \, dt' = \frac{\partial T(x, t)}{\partial x_i} \int_0^\infty \lambda(t') \, dt'. \] (A.20)

By inserting (A.20) into (A.19) we get

\[ \varsigma_2 = -(1 - Z_0) \left( \frac{5}{3} - \gamma \right) \mu_0 \frac{\partial v_i}{\partial x_i} \frac{\partial v_j}{\partial x_j} + \frac{5}{4} c_v (\gamma - 1) \mu_0 \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i}, \] (A.21)

which is positive semi-definite. Thus we have proved that

\[ \varsigma = \varsigma_1 + \varsigma_2 \geq 0, \] (A.22)

i.e., our generalized model equation fulfils the requirement of an \( H \)-theorem.

**Appendix B**

The non-zero elements of the matrices \( M^{(0)} \) and \( M^{(1)} \) read

\[ M_{11}^{(0)} = W(z), \quad M_{12}^{(0)} = 2A(z), \quad M_{13}^{(0)} = B(z), \] (B.1)

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\[ M_{21}^{(0)} = \frac{M_{12}^{(0)}}{2}, \quad M_{22}^{(0)} = zM_{12}^{(0)}, \quad M_{23}^{(0)} = zM_{13}^{(0)}, \quad (B.2) \]

\[ M_{31}^{(0)} = (\gamma - 1)M_{13}^{(0)}, \quad M_{32}^{(0)} = 2(\gamma - 1)M_{23}^{(0)}, \quad M_{33}^{(0)} = (\gamma - 1)D(z) + \frac{3}{2} \left( \frac{5}{3} - \gamma \right) W(z), \quad (B.3) \]

\[ M_{12}^{(1)} = (1 - Z_0) \left( \frac{5}{3} - \gamma \right) B(z), \quad M_{13}^{(1)} = \left( 1 - \frac{f(\omega)}{\gamma} \right) C(z), \quad (B.4) \]

\[ M_{22}^{(1)} = zM_{12}^{(1)}, \quad M_{23}^{(1)} = zM_{13}^{(1)}, \quad (B.5) \]

\[ M_{32}^{(1)} = (1 - Z_0)(\gamma - 1) \left( \frac{5}{3} - \gamma \right) E(z), \quad M_{33}^{(1)} = \left( 1 - \frac{f(\omega)}{\gamma} \right) \left[ (\gamma - 1)F(z) + \frac{3}{2} \left( \frac{5}{3} - \gamma \right) A(z) \right], \quad (B.6) \]

with

\[ f(\omega) = - \frac{f_0}{1 - i\omega \tau_q} = f_0 \left( 1 - \frac{f_0}{\tau_q} \right)^{-1}, \quad \text{(B.7)} \]

being the frequency-dependent Eucken factor. Moreover, we have introduced the abbreviations

\[ A(z) = zW(z) + 1, \quad B(z) = \left( z^2 - \frac{1}{2} \right) W(z) + z, \quad \text{(B.8)} \]

\[ C(z) = z \left( z^2 - \frac{3}{2} \right) W(z) + z^2 - 1, \]

\[ D(z) = \left( z^4 - z^2 + \frac{5}{4} \right) W(z) + z^3 - \frac{z}{2}, \quad \text{(B.9)} \]

\[ E(z) = \left( z^4 - z^2 - \frac{1}{4} \right) W(z) + z^3 - \frac{z}{2}, \]

\[ F(z) = z \left( z^4 - 2z^2 + \frac{7}{4} \right) W(z) + z^4 - \frac{3}{2} z^2 + \frac{3}{2}, \quad \text{(B.10)} \]

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