Sound Propagation in Dilute Polyatomic Gases

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Sound propagation in dilute pure gases, both monatomic and polyatomic, has been considered from the point of view of the Waldmann-Snider equation. It is shown that the commonly employed assumption that sound propagation in gases is equivalent to the propagation of plane waves is valid only in the region where collisions restore equilibrium faster than it is perturbed by the sound waves. A systematic truncation procedure for an expansion of the perturbation function in irreducible Cartesian tensors is introduced and then illustrated in solutions for three specific kinds of molecules, helium, nitrogen and rough spheres. The agreement between theory and experiment is rather good for sound absorption in the region where the ratio of the collision and sound frequencies is greater than 1.5. The agreement in the case of dispersion is good over the whole measured pressure range. One useful result obtained is to show the polyatomic gas calculations in second approximation have as good agreement with experiment as the calculations for noble gases in third approximation. This can be related to the possession by the polyatomic gas of a bulk viscosity which dominates in sound propagation.

1. Introduction

A quantitative description of bulk molecular phenomena in gases has long been the aim of kinetic theory. One of the problems which has been of central interest in this field has been the development of an accurate description of the propagation of sound waves in gases. Most descriptions of sound propagation start from an implicitly assumed equivalence between the experimental fact that sound waves are transmitted through the gas and the theoretical description of plane wave propagation. A critical examination of this assumption (see Section 2) shows that the equivalence is valid only when the collision frequency in the gas is greater than the sound frequency, so that the higher the sound frequency, the higher the density at which the propagation of sound can no longer be described in terms of plane wave propagation.

Basically, there are two approaches to the solution of the problem of plane wave propagation in gases: these may, in essence, be termed the macroscopic and microscopic approaches. In the former approach, the hydrodynamic equations for the gas are derived from the Boltzmann equation or, for gases with degenerate internal degrees of freedom, the Waldmann-Snider equation [1,2]. Then the (common) space and time dependence of a plane wave is imposed upon the macroscopic variables, i.e., these variables are assumed to behave as $\exp(i\omega t - \varkappa z)$, with $\varkappa$ a (complex) propagation constant, for a sound wave travelling in the z-direction. Following this, the equations for the macroscopic variables are linear-ized with respect to the acoustic disturbances, the linearization procedure giving rise to a compatibility condition on $\varkappa$ which can then be solved to determine $\varkappa$ as a function of the angular frequency ω. The macroscopic approach suffers, however, from one rather serious drawback and that is the use of a Chapman-Enskog procedure [3,4] in solving the Boltzmann equation: this has as a consequence that only normal solutions (in the sense of Hilbert [5]) are permitted. The very nature of the problem would suggest that these solutions are too restrictive. In fact, it has been found that higher approximations in the Chapman-Enskog scheme give slightly worse results than the lowest approximation [6]. This indicates a possible nonconvergence of the method. Moreover, it has been shown [7] that the agreement between the results obtained by employing the Fourier-Navier-Stokes hydrodynamic equations and experiment is largely fortuitous. For these reasons, the macroscopic approach will not be considered further in this article. In contradistinction to the macroscopic approach, the microscopic approach directly imposes the space and time dependence of a plane wave solution upon the perturbation from equilibrium which appears in the linearized Boltzmann equation. After this step has been taken, there are a number of solution procedures possible. Of these only one will be utilized and this will be described in detail in Section 3.

As has already been remarked in passing, the correct kinetic equation for gases possessing internal degrees of freedom is the linearized Waldmann-Snider equation. For certain specific cases, such as

that of a noble gas where the intermolecular potential is strictly spherical or of a gas possessing internal degrees of freedom none of which are degenerate, the Waldmann-Snider equation reduces to the more commonly-known kinetic equations of BOLTZMANN and WANG CHANG and UHLENBECK[8], respectively. However, for a description of rotational relaxation, the linearized Waldmann-Snider equation should be employed since, in general, rotational energy levels are degenerate.

In recent years the quantitative description of sound absorption and dispersion in dilute gases has been of considerable interest. Much of this interest has centred around the possibility of utilizing a study of the deviation of sound absorption and dispersion from the Navier-Stokes description as an experimental test of the validity of the (linearized) Boltzmann equation. In order to do this, quantitative theoretical expressions are necessary for the absorption and dispersion of sound. Quantitative calculations, however, require either a detailed knowledge of the eigenvalue spectrum of the collision operator (together with the eigenfunctions) or a procedure of arriving at reasonably accurate approximations thereto. One procedure, recently introduced by FOCH[9], makes use of the knowledge of the spectrum of the collision operator for Maxwell molecules in order to give a perturbation theory treatment for the addition of the (inhomogeneous) flow term to the Boltzmann equation for a spatially homogeneous system. This gives rise to a power series expansion in the ratio of the sound frequency to the collision frequency. The results of such a development and a comparison of theory and experiment for monatomic molecules has been given by FOCH and FORD[10] in an article in the De Boer-Uhlenbeck series.

While the procedure developed by Foch works fairly well (at very low frequencies) for monatomic gases where Maxwell molecules can be employed in zeroeth order, it is at the present time not possible to do the same for polyatomic gases where the (in general non-self-adjoint) Waldmann-Snider collision operator must be considered. Hence some other method of calculating sound absorption and dispersion from the Waldmann-Snider equation must be evolved.

Most of the recent work on sound propagation has made use of model equations. Although apparent good agreement with experiment has been obtained

over an extensive pressure range (or, equivalently, frequency range) by such a procedure (see, e.g., the work of HANSON, MORSE and SIROVICH[11]), "the method of model equations remains an uncontrolled approximation method"[10]. The present work does not attempt to explain sound absorption and dispersion over the whole measured frequency range but rather concentrates on calculating, in as accurate a manner as possible, these phenomena in the low frequency range where, in fact, meaningful comparison with experiment is possible. One of the particular aims of this work is to examine the influence of internal states on sound absorption and dispersion.

The calculational procedure employed here is essentially that introduced earlier by WANG CHANG and UHLENBECK[12] in their classic work on sound propagation in monatomic gases. This truncated expansion procedure, with the slight modifications required when describing polyatomic gases, is shown to give as good agreement with experiment for diatomic gases as it gives for monatomic gases, thus putting all gases on the same footing. This is illustrated explicitly in Section 4. The gases chosen as representative of their classes are helium for the monatomics and nitrogen for the diatomics: in addition to this, the rough sphere model has also been utilized as an example of a polyatomic gas. Although the method used in this paper requires not only experimental data on sound propagation but also those on the SENFTLEBEN-BEENAKKER effects[13], the field of gases is not essentially narrowed by the latter requirement. In fact, it appears that nitrogen is almost the only diatomic gas for which extensive measurements are available for sound absorption and dispersion[14].

2. General Theory

The absorption and dispersion of sound waves in a pure gas is governed by the Waldmann-Snider equation. Since the perturbation from equilibrium caused by the sound wave is (supposedly) small, the linearized version of this equation may be used. It has the form

$$- \partial \varphi / \partial t - V \hat{\boldsymbol{k}} \cdot \boldsymbol{W} (\partial \varphi / \partial z) = \mathscr{R}_0 \varphi . \quad (2.1)$$

As usual, the perturbation of the distribution function-density matrix f from its (absolute) equilibrium value f_0 is denoted by $f_0 \varphi$ so that $f = f_0 (1 + \varphi)$,

with f_0 given by

$$f_0 = (2 \pi m k T)^{-3/2} Q^{-1} \exp[-W^2 - (\mathscr{H}_{\text{int}}/kT)].$$
(2.2)

In Eq. (2.2), W is the reduced peculiar velocity, $\mathscr{H}_{\text{int}}$ the Hamiltonian for internal states and Q the internal state partition function,

$$Q = \text{Tr} \exp[-\mathscr{H}_{\text{int}}/kT].$$

Further, V in Eq. (2.1) is the quantity $(2kT/m)^{1/2}$, while $\hat{k}$ is the unit vector in the (positive) z-direction, the direction in which the acoustic disturbance travels. The operator $\mathscr{R}_0$ is the (accretive) linearized Waldmann-Snider collision superoperator, the explicit form of which will not be needed here. The actual form of $\mathscr{R}_0$ is not required because the various matrix elements arising in the calculation of sound absorption and dispersion can be evaluated from other (independent) experimental data, in particular, from Senftleben-Beenakker data.

In order for a solution of Eq. (2.1) to represent a sound wave, it is necessary to specify the boundary conditions. A derivation of the requisite boundary conditions for a typical (idealized) experiment will now be given. Let the acoustic source, e.g., a crystal transducer or a condenser microphone, be represented by an infinite, flat, sinusoidally oscillating wall in the xy-plane ($z = 0$). The velocity of this wall (in the z-direction) is then given by

$$w = w_0 \sin \omega t,$$
(2.3)

where the amplitude w_0 is infinitesimally small. If it is assumed that there is perfect accommodation at this wall, then the distribution function of the gas at $z = 0$ will have the form

$$f(z = 0, t) \qquad\qquad (2.4)$$
$$= f_0 \exp\{(\hat{k} \cdot W)^2 - (\hat{k} \cdot W - \tfrac{1}{2} A_0 \sin \omega t)^2\},$$

where $A_0 = -2 w_0/V$. The assumption is made that the boundary layers (with thickness of the order of a few mean-free-path lengths) are thin compared with the distance between the sound source and the sound receiver. The boundary condition at $z = 0$, making use of the smallness of the disturbance, is given by

$$\varphi(0, t) = A_0 k \cdot W \sin \omega t.$$
(2.5)

In order to simplify the calculations, the complex analogue of this equation,

$$\varphi(0, t) = \varphi_0 \exp(i \omega t) = A_0 k \cdot W \exp(i \omega t), \quad (2.6)$$

will be employed in the following. This is a valid

procedure since the problem is a linear one. For $k \cdot W \neq 0$ (molecules with $k \cdot W = 0$ do not participate in the processes causing sound absorption and dispersion), the formal solution of Eq. (2.1) satisfying the boundary condition (2.6) is

$$\varphi(z, t) = \exp\{i \omega(t - z/V k \cdot W) - (z/V k \cdot W) \mathscr{R}_0 \cdot \varphi_0.$$
(2.7)

At this point it is useful to examine in detail the measuring process in a typical sound experiment. The most reliable techniques presently available use either a double crystal or double microphone interferometer, so that the receiver is sensitive to exactly the same type of disturbance as has been created by the transmitter. Thus, the signal monitored with the receiver will be proportional to the quantity[14a]

$$Q(z) = (k \cdot W \eta(k \cdot W), \varphi(z)),$$
(2.8)

where $\eta(x)$ is the Heaviside function [$\eta(x) = 1$ for $x > 0$, $\eta(x) = 0$ for $x < 0$] and where the inner product of two operators A and B is defined by

$$(A, B) \equiv \text{Tr} \int d\boldsymbol{p} f_0 A^\dagger B,$$
(2.9)

with the trace being over all quantum mechanical states and the dagger representing a quantum mechanical adjoint. Further, $\varphi(z)$ appearing in Eq. (2.8) is the space dependent part of the disturbance, $\varphi(z) = \varphi(z, t) \exp(-i \omega t)$. Absorption and dispersion are obtained experimentally from the amplitude and phase records versus distance, respectively, so that the absorption co-efficient $\alpha(z)$ and the sound velocity $u(z)$ are inferred from

$$\alpha(z) = -d \ln |Q|/dz \qquad (2.10)$$

and

$$\frac{\omega}{u(z)} = -\frac{d}{dz} \arctan(\text{Im} \, Q/\text{Re} \, Q), \quad (2.11)$$

respectively. Note that both of these quantities are, in general, functions of z, the distance between transmitter and receiver.

When the gas is extremely dilute, the collision operator may be dropped from the solution (2.7) so that $Q(z)$ is given by

$$Q(z) = A_0 \pi^{-1/2} \int_0^\infty (k \cdot W)^2$$
$$\times \exp\{-i \omega z/(V k \cdot W) - (k \cdot W)^2\} d(k \cdot W). \quad (2.12)$$

A similar form has been obtained by KAHN and MINTZER[15] following a different line of argument. Their result for the limiting low density absorption

and dispersion, which is strongly dependent on z, is identical with the result derived from Equation (2.12). They have shown that this result is in good agreement with experiment. If it is assumed that the boundary conditions are the same both for monatomic and for polyatomic molecules, then it is clear that in this case, as $Q(z)$ is independent of the collision operator, it is insensitive both to the intermolecular potential and to the presence or absence of internal states in the molecules. Hence, as the principal purpose of this work is to study the effect of internal states on sound absorption and dispersion, such a case is not of further interest.

Of interest here, then, is the case for which the collision frequency is larger than the frequency of the sound wave being propagated. When this condition is satisfied, a molecule will undergo several collisions in the time between two successive disturbances caused by the source so that it will have "forgotten" that the source is present when it is disturbed anew. This means that the distribution will return to its equilibrium value in a time small compared with the characteristic time associated with the sound wave. In practice, this allows the ratio of collision frequency to sound frequency to approach 1 (the lowest limiting value is often found to be of the order of 1.5).

For the case described above, consider the operator

$$\varkappa(\omega) = (V \, \boldsymbol{k} \cdot \boldsymbol{W})^{-1} (\mathscr{R}_0 + i \, \omega) . \quad (2.13)$$

If this operator has a complete set of eigenfunctions $\psi_\varkappa$ with eigenvalues $i\varkappa^*(\omega)$ for any value of ω, i.e.,

$$(V \, \boldsymbol{k} \cdot \boldsymbol{W})^{-1} (\mathscr{R}_0 + i \, \omega) \, \psi_\varkappa = i \varkappa^*(\omega) \, \psi_\varkappa , \quad (2.14)$$

then the initial disturbance φ_0 can be expanded in terms of the $\psi_\varkappa$ as

$$\varphi_0 = \Sigma_\varkappa \varrho_\varkappa \psi_\varkappa .$$

Inserting this expansion into the formal solution (2.7) gives for the space dependent part of $\varphi(z, t)$ the result

$$\varphi(z) = \Sigma_\varkappa \varrho_\varkappa \exp[-iz \operatorname{Re} \varkappa - z \operatorname{Im} \varkappa] \, \psi_\varkappa . \quad (2.15)$$

In the limit of large z, the only contribution to the sum (2.15) will be the one with the minimal value of $\operatorname{Im}\varkappa$: let the propagation constant corresponding to this minimal value be $\varkappa_0$ [16]. The asymptotic behaviour of $\varphi(z)$ as $z \to \infty$ is then

$$\varphi(z) \underset{z \to \infty}{\sim} \varrho_{\varkappa_0} \psi_{\varkappa_0} \exp[-iz \operatorname{Re} \varkappa_0 - i \operatorname{Im} \varkappa_0] , \quad (2.16)$$

so that

$$Q(z) \underset{z \to \infty}{\sim} \varrho_{\varkappa_0}(\boldsymbol{k} \cdot \boldsymbol{W} \, \eta \, (\boldsymbol{k} \cdot \boldsymbol{W}), \psi_{\varkappa_0})$$
$$\times \exp[-iz \operatorname{Re} \varkappa_0 - z \operatorname{Im} \varkappa_0] . \quad (2.17)$$

In the limit $z \to \infty$, the absorption and dispersion are given by [see Eqs. (2.10) and (2.11)]

$$\alpha = \operatorname{Im} \varkappa_0 \quad \text{and} \quad \omega/u = \operatorname{Re} \varkappa_0 \quad \text{or} \quad u = \omega/\operatorname{Re} \varkappa_0 , (2.18)$$

respectively.

Equation (2.14) is equivalent to (since $\boldsymbol{k} \cdot \boldsymbol{W} \neq 0$)

$$(-i \, \omega + i \varkappa^* \, V \, \boldsymbol{k} \cdot \boldsymbol{W}) \, \psi = \mathscr{R}_0 \psi . \quad (2.19)$$

This equation may be obtained from Eq. (2.1) by setting $\varphi = \psi \exp(i \, \omega t - \varkappa^* z)$. It is thus seen that in the case that collisions restore equilibrium faster than the acoustic disturbance destroys it, the obsorption and dispersion of sound waves are identical with the absorption and dispersion of the plane wave solution of the Waldmann-Snider equation with minimal absorption in the limit of an infinitely long interferometer. A plane wave solution is not obtained at low number densities since the solution (2.12) is certainly not represented by a plane wave for any finite z, and small values of z are required by experimentalists at low pressures in order to overcome the increase in sound attenuation.

3. Methods of Solution

Three methods for obtaining solutions of Eq. (2.19) have been developed, two of which make use of the fact that Eq. (2.19) is equivalent to the (infinite) set of coupled equations obtained by expanding ψ in a complete set of basis functions orthogonal with respect to the inner product (2.9) and then taking the inner product of the resulting equation with each of the basis functions in turn. If this set of equations is to have a nontrivial solution, the infinite determinant of the coefficients of these equations must vanish. This requirement gives a condition on $\varkappa^*$: the value of $\varkappa^*$ satisfying this condition and with minimal imaginery part is then the sought-after propagation constant.

An infinite set of equations is clearly intractable and so an approximation procedure has to be devised. The method originally proposed by WANG CHANG and UHLENBECK[12] simply truncated the basis set after N terms. Mathematically, this may be expressed in the following way. Let P_N be the projection operator on the subspace spanned by the

first N basis functions. Then the truncation method in essence replaces Eq. (2.19) by

$$P_N(-i\omega + i\varkappa^* V \hat{\boldsymbol{k}} \cdot \boldsymbol{W}) P_N \psi = P_N \mathscr{R}_0 P_N \psi . \quad (3.1)$$

Since this method has been used with considerable success in other problems involving the solution of the Waldmann-Snider equation[13], good results might be expected in this way. Indeed, for pressures for which the collision frequency is larger than the sound frequency, this is so (see Section 4). Such a result is not unexpected for small values of N since $\hat{\boldsymbol{k}} \cdot \boldsymbol{W}$ couples a second set of expansion tensors strongly to the set which would be employed for higher frequencies (or lower pressures). But, as Eq. (2.19) is strictly valid only in the cases where Eq. (3.1) is expected to yield good results, this truncation procedure appears to be suitable. It is known from the extensive numerical investigations of PEKERIS et al.[17,18] that taking N as large as a few hundreds does not appreciably increase the range of frequencies and pressures over which the solution of Eq. (3.1) agrees with experiment. Since the *method* should work much better at lower pressures for high N, it is evident that an *assumption* that Eq. (2.19) is valid for all pressures and frequencies would be at fault, as has been seen in Section 2.

Since it is the Waldmann-Snider collision operator which is employed and since the eigenfunctions of this operator are unknown, the same type of basis used successfully in solving a number of problems involving the Waldmann-Snider equation, i.e., an expansion of ψ in irreducible Cartesian tensors[19], associated Laguerre polynomials in the reduced translational energy and Wang Chang-Uhlenbeck-De Boer polynomials[8] in the Hamiltonian for the internal states of the molecules will be utilized in this work.

The second method involving expansion of ψ in a chosen basis set involves the replacement of Eq. (2.19) by a model equation[20] of the form

$$(-i\omega + i\varkappa^* V \boldsymbol{k} \cdot \boldsymbol{W} + C) \psi$$
$$= P_N \mathscr{R}_0 P_N \psi + C P_N \psi , \quad (3.2)$$

where C is an adjustable constant. A formal solution for ψ is given by

$$\psi = \frac{P_N \mathscr{R}_0 P_N \psi + C P_N \psi}{-i\omega + i\varkappa^* V \boldsymbol{k} \cdot \boldsymbol{W} + C} . \quad (3.3)$$

A closed set of equations is now generated by expanding ψ in the first N basis functions and taking

moments of the resultant equation with each of these basis functions in turn. With a suitably chosen value of C, it is possible to obtain solutions which fit the experiment data not only at higher pressures but also at lower pressures. There are, however, a number of objections that can be raised with respect to this method of solution. Firstly, there is an adjustable parameter in the equations; secondly, these "good" solutions can only be obtained by analytically continuing the solutions for low frequencies (or high pressures) beyond a "cutoff frequency" that is always found and which results from the replacement of the unbounded Boltzmann collision operator by a bounded one[21].

The third method of solution of Eq. (2.19) was initiated by FOCH[9]. He regards Eq. (2.19) as a perturbed eigenvalue equation, $\varkappa^*$ being the small perturbation parameter. Expansions of ψ and ω in terms of $\varkappa^*$ results in a hierarchy of equations for the coefficients of successive powers of $\varkappa^*$. In this way, ω is obtained as a power series in $\varkappa^*$; inversion of this series then gives $\varkappa^*$ as a function of ω. This procedure has the disadvantage that the radii of convergence of the different series involved are not easily ascertained except in the case of hard sphere molecules[22]. The inherently simpler truncation method should give at least equivalent results if the basis is successively enlarged as follows: the $(n + 1)^{st}$ approximation has as a basis the functions originally employed in the nth approximation together with those functions which are coupled to the functions of the smaller basis by the term $\hat{\boldsymbol{k}} \cdot \boldsymbol{W}$ in Eq. (2.19). The truncation method employed here, with the above-described extension scheme, is a simple method for the solution of Eq. (2.19): in particular, for polyatomic molecules, it will be shown that in second approximation where all of the relevant collision integrals entering into sound absorption and dispersion can be evaluated from Senftleben-Beenakker measurements plus measurements of the field-free transport coefficients, the description of sound obsorption and dispersion given by the present procedure is as good as that for the noble gases in third approximation. Further, it seems worth noting that the present results are in good agreement with experiment over a range of pressures which extends about a factor ten lower than that achieved by means of the Foch and Ford procedure. In fact, at all pressures and frequencies where Eq. (2.19) may be expected to be valid, the theoretically

calculated results are well within the experimental uncertainty of the measured results. The next section presents certain numerical results and their comparison with experiment.

4. Numerical Results

a) *Helium*

The absorption and dispersion for helium have been calculated for the first, second and third approximations. The expansion of ψ takes the form:

$$\psi = a^{00} + a^{01}\left(\tfrac{3}{2} - W^2\right) + a^{10}\,\boldsymbol{W}\cdot\hat{\boldsymbol{k}}$$
$$+ a^{11}\left(\tfrac{5}{2} - W^2\right)\boldsymbol{W}\cdot\hat{\boldsymbol{k}} + a^{20}[\boldsymbol{W}]^{(2)} : [\boldsymbol{k}]^{(2)}$$
$$+ a^{02}\left(\tfrac{15}{8} - \tfrac{5}{2}W^2 + \tfrac{1}{2}W^4\right) + a^{21}\left(\tfrac{7}{2} - W^2\right)$$
$$\cdot\,[\boldsymbol{W}]^{(2)} : [\hat{\boldsymbol{k}}]^{(2)} + a^{30}[\boldsymbol{W}]^{(3)} \odot^3 [\hat{\boldsymbol{k}}]^{(3)}. \quad (4.1)$$

The first three terms in this expansion (the summational invariants) are used in the first approximation with the result of zero absorption and a speed of sound equal to the adiabatic one. The second approximation takes the first five terms of Eq. (4.1) into account, while the third approximation takes all eight terms into account. Compatibility conditions on $\varkappa^*$ are obtained by setting the designated 3×3, 5×5 subdeterminants and the whole 8×8 determinant given in (4.2) equal to zero, respectively

$$\left|\begin{array}{cccccccc}
i\omega & 0 & -\tfrac{1}{2}i\varkappa^*V & 0 & 0 & 0 & 0 & 0 \\
0 & \tfrac{3}{2}i\omega & \tfrac{1}{2}i\varkappa^*V & -\tfrac{5}{4}i\varkappa^*V & 0 & 0 & 0 & 0 \\
-\tfrac{1}{2}i\varkappa^*V & \tfrac{1}{2}i\varkappa^*V & \tfrac{1}{2}i\omega & 0 & -\tfrac{1}{3}i\varkappa^*V & 0 & 0 & 0 \\
0 & -\tfrac{5}{4}i\varkappa^*V & 0 & \tfrac{5}{4}i\omega + \tfrac{5}{3}n^{-1}[{}^{20}_{20}] & \tfrac{1}{3}i\varkappa^*V & \tfrac{5}{4}i\varkappa^*V & -\tfrac{7}{6}i\varkappa^*V & 0 \\
0 & 0 & -\tfrac{1}{3}i\varkappa^*V & \tfrac{1}{3}i\varkappa^*V & \tfrac{1}{3}i\omega + \tfrac{2}{3}n^{-1}[{}^{20}_{20}] & 0 & \tfrac{2}{3}n^{-1}[{}^{20}_{21}] & -\tfrac{3}{10}i\varkappa^*V \\
0 & 0 & 0 & \tfrac{5}{4}i\varkappa^*V & 0 & \tfrac{15}{8}i\omega + n^{-1}[{}^{02}_{02}] & 0 & 0 \\
0 & 0 & 0 & -\tfrac{7}{6}i\varkappa^*V & \tfrac{2}{3}n^{-1}[{}^{20}_{21}] & 0 & \tfrac{7}{6}i\omega + \tfrac{2}{3}n^{-1}[{}^{21}_{21}] & \tfrac{3}{10}i\varkappa^*V \\
0 & 0 & 0 & -\tfrac{3}{10}i\varkappa^*V & 0 & \tfrac{3}{10}i\varkappa^*V & \tfrac{3}{10}i\omega + \tfrac{9}{10}n^{-1}[{}^{20}_{20}]
\end{array}\right| \quad (4.2)$$

The determinant (4.2) has been obtained by inserting Eq. (4.1) into Eq. (2.19) and forming moments with the expansion tensors [22].

The collision brackets $[{}^{pq}_{pq'}]$ are defined in the usual way: If $\mathbf{A}$ and $\mathbf{B}$ are the expansion tensors (*not* including $\boldsymbol{k}$-dependence!) corresponding to pq and pq', respectively, then

$$[{}^{pq}_{pq'}] = (2p + 1)^{-1}(\mathbf{A}\odot^p, \mathscr{R}_0\mathbf{B}). \quad (4.3)$$

Note that the tensorial ranks of $\mathbf{A}$ and $\mathbf{B}$ have to be equal; this is because of rotational invariance of $\mathscr{R}_0$ and the absence of internal states. In writing down Eq. (4.2), use has been made of two exact (for molecules without internal degrees of freedom) relations,

$$[{}^{11}_{11}] = \tfrac{5}{3}[{}^{20}_{20}] \quad (4.4)$$

and

$$[{}^{30}_{30}] = \tfrac{9}{4}[{}^{20}_{20}]. \quad (4.5)$$

These relations may be proven by going over to center-of-mass and relative coordinates and performing the integration over the center-of-mass velocity. All other collision brackets were obtained from the ratios

$$[{}^{20}_{21}][{}^{20}_{20}]^{-1} = \tfrac{7}{4} - \tfrac{1}{2}\left(\Omega^{(2,3)}/\Omega^{(2,2)}\right), \quad (4.6)$$

$$[{}^{21}_{21}][{}^{20}_{20}]^{-1} = 301/48 - \tfrac{7}{4}\left(\Omega^{(2,3)}/\Omega^{(2,2)}\right)$$
$$+ \tfrac{1}{4}\left(\Omega^{(2,4)}/\Omega^{(2,2)}\right), \quad (4.7)$$

and

$$[{}^{02}_{02}][{}^{20}_{20}]^{-1} = 5/2. \quad (4.8)$$

These expressions may be obtained in the same way as Eqs. (4.4) and (4.5). Using the tables given by HIRSCHFELDER, CURTISS and BIRD [23] for He, assuming a Lennard-Jones $6-12$ interaction potential, gives for these ratios the values

$$[{}^{20}_{21}][{}^{20}_{20}]^{-1} = -0.177, \quad [{}^{21}_{21}][{}^{20}_{20}]^{-1} = 4.215,$$
$$[{}^{02}_{02}][{}^{20}_{20}]^{-1} = 2.50. \quad (4.9)$$

The numerical evaluation of $\varkappa^*$ was done on an IBM 360/75 computer, using a FORTRAN IV programme [24]. In Fig. 1, the quantities $\alpha u_0/\omega$ and u_0/u, with u the sound speed, u_0 the adiabatic sound speed and α the absorption coefficient, are plotted versus the dimensionless parameter $r = 2[{}^{20}_{20}]/n\omega$. The second and third approximations are shown.
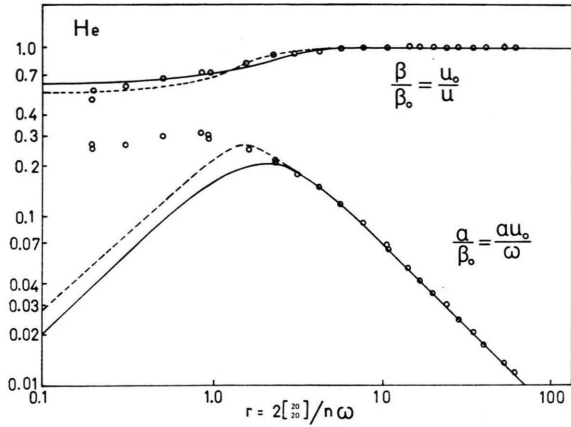
Fig. 1. Absorption and dispersion coefficients of helium. The solid line represents the second approximation calculation, the dashed line represents the third approximation calculation and the open circles represent experimental results taken from Ref. 6.

Due to the choice of variables, the solid curves are universal for any noble gas, since the actual value of the collision bracket $[^{20}_{20}]$ is not needed. The dispersion relation in the second approximation is[15]

$$\varkappa^4\left(\frac{15}{64}-\frac{25}{192}\,i\,r\right)+\varkappa^2\left(\frac{13}{16}+\frac{5}{6}\,i\,r+\frac{25}{144}\,r^2\right)$$
$$+\left(\frac{5}{16}-\frac{25}{48}\,i\,r-\frac{5}{24}\,r^2\right)=0\,,\quad(4.10)$$

where $\varkappa = V\varkappa^*/\omega$. This relation was used to check the computer programme, devised so as to recognize a polynomial in a function defined in determinantal form. The experimental data displayed in Fig. 1 have been taken from the measurements by GREEN-SPAN[6] at 11 MHz, using a double crystal interferometer. As expected, the differences between the second and third approximations are relatively small.

The discussion in Section 2 showed that absorption and dispersion of sound waves are identical with the absorption and dispersion of the plane wave solution of the Waldmann-Snider equation (in the limit of an infinitely long interferometer) when collisons restore equilibrium faster than the

acoustic disturbance destroys it. This means that the ratio $\omega_{\text{coll}}/\omega$ must be greater than 1: the parameter r (called the rarefaction parameter) is essentially that ratio. For practical purposes it can be expected on the basis of the arguments employed in Section 2 that a physically meaningful description of sound absorption and dispersion is given by the present solution procedure of the Waldmann-Snider equation for values of r greater than or approximately equal to 2. This is indeed found to be the case. From Fig. 1, it is seen that the second approximation is in good agreement with the experimental data for $r \gtrsim 2.5$ while the third approximation is in good agreement with experiment for $r \gtrsim 1.5$. In contrast, the range of agreement found using the perturbation procedure of FOCH[9] is $r \gtrsim 10$. It should be remarked that the dispersion appears to be in surprisingly good agreement with experiment over the whole range of r-values measured, especially in the third approximation.

b) *Nitrogen*

As an example of a polyatomic gas, a calculation for N_2 was performed. The situation is slightly complicated in this case by the fact that in a polyatomic gas energy may be exchanged between the translational and rotational degrees of freedom. In second approximation, the only one considered for polyatomic gases in this work, ψ is expanded as

$$\psi = a^{0000} + a^{0010}(\tfrac{3}{2}-W^2) + a^{0001}(BJ^2 - \langle BJ^2\rangle_0)$$
$$+ a^{1000}\,\boldsymbol{W}\cdot\hat{\boldsymbol{k}} + a^{1010}(\tfrac{5}{2}-W^2)\,\boldsymbol{W}\cdot\hat{\boldsymbol{k}}$$
$$+ a^{1001}(BJ^2-\langle BJ^2\rangle_0)\,\boldsymbol{W}\cdot\hat{\boldsymbol{k}}$$
$$+ a^{2000}[\boldsymbol{W}]^{(2)}:[\hat{\boldsymbol{k}}]^{(2)}\,.\quad(4.11)$$

Here $\boldsymbol{J}$ is the (nuclear) rotational angular momentum operator, B is the rotational constant $\hbar^2/2\,I\,k\,T$, with I the moment of inertia of the molecule; the angular brackets $\langle\cdots\rangle_0$ designate an average taken with the weight function $n^{-1}f_0$. The condition on $\varkappa^*$ is inferred from the determinental Eq. (4.12), obtained in the same way as Eq. (4.2).

(4.12)

$$\begin{vmatrix} i\,\omega & 0 & 0 & -\tfrac{1}{2}\,i\varkappa^*V & 0 & 0 & 0 \\ 0 & \tfrac{3}{2}\,i\,\omega+n^{-1}[^{0010}_{0010}] & n^{-1}[^{0010}_{0010}] & \tfrac{1}{2}\,i\varkappa^*V & -\tfrac{5}{4}\,i\varkappa^*V & 0 & 0 \\ 0 & n^{-1}[^{0010}_{0010}] & (c_{\text{int}}/k)\,i\,\omega+n^{-1}[^{0010}_{0010}] & 0 & 0 & -\tfrac{1}{2}\,(c_{\text{int}}/k)\,i\,\varkappa^*V & 0 \\ -\tfrac{1}{2}\,i\varkappa^*V & \tfrac{1}{2}\,i\varkappa^*V & 0 & \tfrac{1}{2}\,i\,\omega & 0 & 0 & -\tfrac{1}{3}\,i\varkappa^*V \\ 0 & \tfrac{5}{4}\,i\varkappa^*V & 0 & 0 & \tfrac{5}{4}\,i\,\omega+n^{-1}[^{1010}_{1010}] & n^{-1}[^{1010}_{1001}] & \tfrac{1}{3}\,i\varkappa^*V \\ 0 & 0 & -\tfrac{1}{2}\,(c_{\text{int}}/k)\,\varkappa^*V & 0 & n^{-1}[^{1010}_{1001}] & \tfrac{1}{2}\,(c_{\text{int}}/k)\,i\,\omega+n^{-1}[^{1001}_{1001}] & 0 \\ 0 & 0 & 0 & -\tfrac{1}{3}\,i\varkappa^*V & \tfrac{1}{3}\,i\varkappa^*V & 0 & \tfrac{1}{3}\,i\,\omega+\tfrac{2}{3}\,n^{-1}[^{2000}_{2000}] \end{vmatrix} = 0$$

For N_2, c_{int}/k has the value 1. The collision brackets occurring in the determinant (4.12) can be evaluated with the aid of recently derived approximate relations[25] for homonuclear diatomic molecules (for which the dominant nonspherical part of the intermolecular potential may be assumed to be of the (single) P_2-type) in conjunction with the experimental shear viscosity η_0 and the Senftleben-Beenakker effects (magnetic field dependence of the transport coefficients). This is achieved in the following manner. The collision bracket $\begin{bmatrix} 2000 \\ 2000 \end{bmatrix}$ is obtained directly from η_0, $\begin{bmatrix} 0010 \\ 0010 \end{bmatrix}$ and $\begin{bmatrix} 1010 \\ 1001 \end{bmatrix}$ are given in terms of the saturation value and position at half-height on the H/p axis (H is the magnetic field strength and p is the pressure) of the Senftleben-Beenakker shear viscosity effect. For the evaluation of the bracket $\begin{bmatrix} 1010 \\ 1010 \end{bmatrix}$, η_0 and the shear viscosity saturation value are required while for evaluation of $\begin{bmatrix} 1001 \\ 1001 \end{bmatrix}$ the saturation value and half-value position for the shear viscosity effect are needed as well as the position on the H/p axis of the thermal conductivity effect. The explicit evaluation of these collision brackets can be carried out with the aid of the numerical values of the corresponding cross sections given in Ref. [26] together with their relation to the collision brackets given in [27].

For N_2, the relevant ratios so found are:

$$\begin{bmatrix} 0010 \\ 0010 \end{bmatrix} \begin{bmatrix} 2000 \\ 2000 \end{bmatrix}^{-1} = 0.70,$$

$$\begin{bmatrix} 1010 \\ 1010 \end{bmatrix} \begin{bmatrix} 2000 \\ 2000 \end{bmatrix}^{-1} = 2.15,$$

$$\begin{bmatrix} 1010 \\ 1001 \end{bmatrix} \begin{bmatrix} 2000 \\ 2000 \end{bmatrix}^{-1} = 0.29, \qquad (4.13)$$

$$\begin{bmatrix} 1001 \\ 1001 \end{bmatrix} \begin{bmatrix} 2000 \\ 2000 \end{bmatrix}^{-1} = 0.85.$$

The numerical results obtained from the solution of Eq. (4.12) with the values (4.13) are shown in Fig. 2, where they are compared with the experimental data of GREENSPAN[28]. Agreement is excellent for $r \gtrsim 1.5$ for the absorption and again over the whole measured range for the dispersion.

c) Rough Sphere Gas

A calculation was also made for a gas of rough spherical molecules with a value for the dimensionless moment of inertia $\varkappa = 4I/m\sigma^2$ of 0.05, a value appropriate for CH_4, e.g., considered as a rough sphere. For rough spheres, c_{int}/k has the value 1.5 in Eq. (4.12). The ratios of the relevant collision brackets for this case, are, in $\varkappa$-dependent form,

Fig. 3. Comparison of the dispersion coefficients for a noble gas (solid line), nitrogen (dashed line) and for a rough sphere gas with $\varkappa = 0.05$ (stippled line).
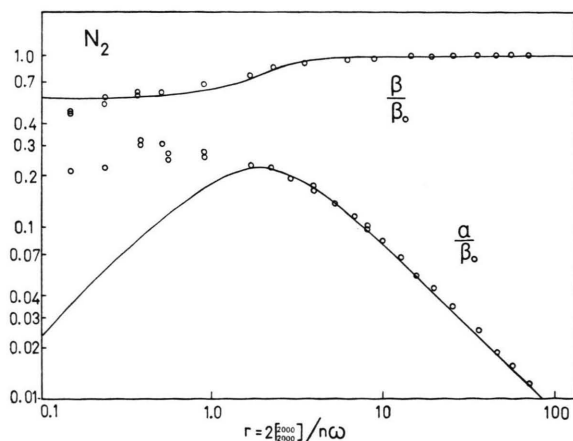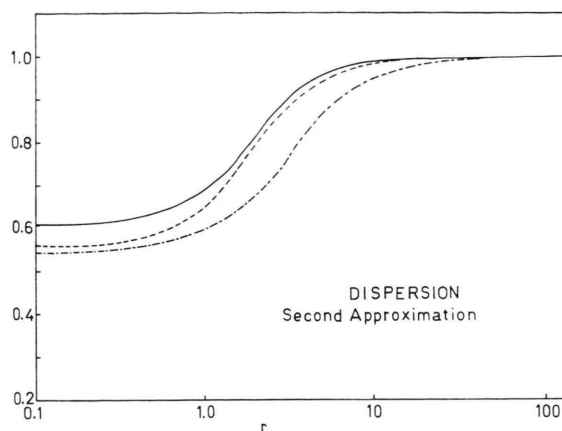

Fig. 2. Absorption and dispersion coefficients of nitrogen in the second approximation (solid lines); the open circles represent experimental results taken from Ref. 28.
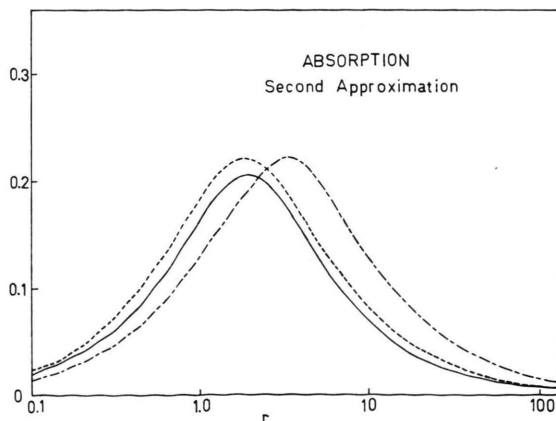

Fig. 4. Comparison of the absorption coefficients for a noble gas (solid line), nitrogen (dashed line) and for a rough sphere gas with $\varkappa = 0.05$ (stippled line).

given by [29,30]

$$[\begin{smallmatrix}0010\\0010\end{smallmatrix}] [\begin{smallmatrix}2000\\2000\end{smallmatrix}]^{-1} = 30 \, (13\varkappa + 6)^{-1} ,$$

$$[\begin{smallmatrix}1010\\1010\end{smallmatrix}] [\begin{smallmatrix}2000\\2000\end{smallmatrix}]^{-1} = \tfrac{5}{4} \, (17\varkappa + 4) \, (13\varkappa + 6)^{-1} , \qquad (4.14)$$

$$[\begin{smallmatrix}1010\\1001\end{smallmatrix}] [\begin{smallmatrix}2000\\2000\end{smallmatrix}]^{-1} = (25/2) \, (13\varkappa + 6)^{-1} ,$$

$$[\begin{smallmatrix}1001\\1001\end{smallmatrix}] [\begin{smallmatrix}2000\\2000\end{smallmatrix}]^{-1} = (15/2) \, (2\varkappa^2 + 2\varkappa + 1) \cdot (13\varkappa + 6)^{-1}$$

In Figs. 3 and 4, the dispersion and absorption, respectively, of the three cases considered in this work, i.e., noble gas, diatomic gas (N_2) and rough sphere gas with $\varkappa = 0.05$, are compared. These figures show explicitly the influence of the presence and number of rotational degrees of freedom in sound absorption and dispersion.

5. Discussion

The phenomenon of sound propagation in pure gases, including polyatomic gases, has been treated from the point of view of the Waldmann-Snider kinetic equation which allows for inelastic collisions. Using a moment method in which the successive approximations are generated through the operation of the flow term on the preceeding approximation (the starting point is, of course, the summational invariants for the gas) sound absorption and dispersion have been calculated using no adjustable parameters and compared with the experimental results for the noble gases and for nitrogen. The method of solution has been shown to be valid in the low frequency or high pressure regime and, in this regime, the agreement with experiment is good. That the moment method should break down for high frequencies or low pressures is not unexpected since in the low density regime more and more expansion terms must be included in the truncated expansion scheme. Basically, this occurs because as the importance of the collision operator decreases, the flow term $\hat{\boldsymbol{k}} \cdot \boldsymbol{W}$ becomes increasingly important with the consequence that many more expansion terms are coupled in. In the limit of a collisionless gas, an infinite number of expansion terms would be required to give a correct description of "sound propagation". This same breakdown of the moment method occurs in the description of other bulk phenomena, perhaps the best known being that of depolarized Rayleigh light scattering [31] where a description of the Doppler-broadened line by this method would also require an infinite number of moments.

An interesting feature of the general solution of the linearized Waldmann-Snider equation is the result that as the number density decreases (the parameter r is proportional to n/ω) for fixed angular sound frequency ω, the solution φ ceases to depend upon molecular collisions or the presence of internal states: this has the implication that for the parameter r sufficiently small, the sound absorption and dispersion should be the same for both noble and polyatomic gases. In fact, this is illustrated in Fig. 5
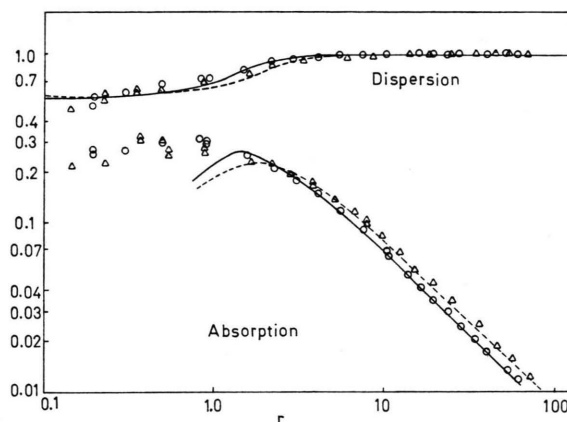

Fig. 5. A comparison of sound absorption and dispersion for a noble gas calculated in third approximation (solid line) with that for nitrogen, calculated in second approximation (dashed line) while the open circles and triangles represent experimental results: $\bigcirc$: experimental points from Ref. 6. $\triangle$: experimental points from Ref. 28.

where these quantities have been plotted for noble gases in the 3rd approximation and for N_2 in the 2nd approximation together with the measured values of GREENSPAN [6,28]. As can be seen, the experimental points are, within experimental accuracy, coincident for $r \lesssim 1.5$. The effect of collisions and internal states is reflected in the decrease of the absorption from a constant value for $r \gtrsim 1.5$. Further, note that the presence of internal states in N_2 has resulted in the theoretical curve obtained in 2nd approximation giving as good a description of the experiment as the noble gas third approximation. This is likely due to the introduction of the bulk viscosity in the case of N_2: when there is a bulk viscosity present, it dominates sound absorption and is itself included in the second approximation procedure.

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