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LETTER TO THE EDITOR

The speed of sound in moderately dense gases†

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Abstract. We present and discuss a theoretical prediction concerning the density correction term to the speed of sound in a monatomic gas. We predict that this correction term disappears at frequencies in excess of the frequency of three-particle collisions between gas atoms; i.e., the speed of sound reverts to the ideal gas value at these higher frequencies. Since the rate of ternary collisions is slow and can be varied by varying the density of the gas, experimental verification of this theoretical prediction appears eminently possible, at frequencies in the normal acoustic range. Estimates are given of the magnitude of the expected effect.

At low enough frequencies, the speed of sound in a gas can be computed purely thermodynamically, from the adiabatic compressibility. The argument for this is quite general and is accepted universally. If the gas is only moderately dense, so that its equation of state is well approximated by the first two terms of the virial series:

$$pV = NkT[1 + (N/V)B(T) + \ldots]$$ (1)

then the result for the speed of sound c is:

$$c = c_0[1 + (N/V)q(T) + \ldots].$$ (2)

Here c_0 is the ideal gas value of the speed of sound:

$$c_0 = (5kT/3m)^{1/2}$$ (3)

and the coefficient $q(T)$ can be computed from the second virial coefficient $B(T)$ and its first two derivatives with respect to the temperature:

$$q(T) = B(T) + \tfrac{2}{3}TB'(T) + \tfrac{2}{15}T^2B''(T).$$ (4)

These standard results certainly hold at low enough frequencies. But just what is 'low enough'? As an example, consider hydrogen gas, where atoms may associate into binary molecules H_2. The *thermodynamic* equation of state relates the pressure p to the absolute temperature T and to the number density N/V of *protons*. In thermodynamics, it is assumed that the system is in full equilibrium at any one temperature and pressure; this includes chemical equilibrium between hydrogen atoms and hydrogen molecules. Yet, no one would calculate the speed of sound in actual hydrogen from *this* equation of state. It is well known that the rate of chemical reactions is too slow for this. The

'adiabatic compressibility' which enters the general formula for the speed of sound is actually computed by considering the gas as a mixture of two gases, one a gas of hydrogen atoms, the other a gas of hydrogen molecules, each with given, time-independent numbers of particles. The sound wave oscillates too rapidly to permit attainment of full equilibrium; the 'equilibrium' on which the calculation is based is only a partial, hindered equilibrium, not full thermodynamic equilibrium.

This argument establishes: (i) the coefficient $q(T)$ in equation (2) may be a function of the frequency of the sound, not only a function of the temperature; as a function of the frequency it may show significant frequency dependence at extremely low frequencies; (ii) there may exist regions of frequency, other than the extreme low-frequency region, in which 'simple' results can be expected for the speed of sound, but the simple result may differ from the extreme low-frequency, full thermodynamic value.

In this letter, we make a theoretical prediction concerning the speed of sound in *monatomic gases of moderate density*. This prediction is based on new transport equations developed recently (Barber *et al* 1975). These equations allow for time-dependent pair correlations in the distribution function of the gas, and for the effect of binary collisions. They do not, in the form given in Barber *et al* (1975), allow for the effects of ternary and higher-order collisions.

The equations of Barber *et al* (1975) are consistent with the equilibrium distribution function of the gas (in the same approximation as equation (1)); but unlike the Boltzmann equation, the new equations do not provide an automatic approach to the equilibrium state from an arbitrary state. To get that, one would have to include the effects of at least ternary collisions. With binary collisions only, it turns out that the pair correlation function defined by:

$$\sigma(1, 2) = f_2(1, 2) - f_1(1)f_1(2) \tag{5}$$

satisfies an approximate conservation law:

$$\int\int \sigma(1, 2) \, d\tau_1 d\tau_2 = \text{constant in time} \tag{6}$$

where the integration is over the full phase space of the two particles. This conservation law is inconsistent with an approach to full equilibrium, because the integral (6) has a definite, temperature-dependent value in the equilibrium state (that value is closely related to the second virial coefficient $B(T)$ in equation (1)), and thus the value of the integral (6) must change as the temperature is changed. Since the temperature within a sound wave is not constant (conditions are adiabatic, not isothermal) we see that the approximate conservation law (6) cannot be reconciled with the argument which leads to the thermodynamic sound velocity (2), (3), and (4).

Of course, (6) is only an approximation. It is obtained from equations which ignore ternary and higher-order collisions, and thus (6) holds only up to time intervals of the order of a mean free time between ternary collisions. The inverse of this mean free time is a frequency, which we shall denote by the symbol F. This can be estimated to be of order:

$$F \sim (N/V)^2 b^5 c_0 \tag{7}$$

where N/V is the number of gas atoms, c_0 is given by (3) and represents an estimate of the mean speed of gas atoms, and b is a length of the order of the range of interaction between gas atoms, presumably between 10^{-8} cm and 4×10^{-8} cm. For krypton at

normal temperature and pressure, this yields $1 \cdot 4 \times 10^3 < F < 1 \cdot 4 \times 10^6$ Hz for the critical frequency F. Furthermore, F varies with the square of the density of the gas, and is therefore easily variable by the experimenter. For a pressure of $0 \cdot 1$ atm, we get $14 < F < 14000$ Hz, completely within the normal acoustic range.

The thermodynamic value for the speed of sound applies at sound frequencies f well below F. For $f \gg F$, on the other hand, the approximate conservation law (6) is effective, and the value of the speed of sound is different from the thermodynamic result.

The equations of Barber *et al* (1975) can be solved by using the same approximations which lead from the Boltzmann equation (applicable to a very dilute gas) to the dilute–gas result (3) for the speed of sound. One assumes that the wavelength of the sound is much longer than a mean free path between successive binary collisions, and one expands the deviation of the one-particle reduced distribution function f_1 from the equilibrium (Maxwell) distribution in a series of Burnett functions (Foch and Ford 1970). Only the lowest few terms are retained—for the speed (but not the attenuation) of sound it suffices to retain just three Burnett functions (see Foch and Ford 1970, pp 158–9).

Although the calculation with the new equations is rather more complex than with the Boltzmann equation, the final result is simple: *at sound frequencies f well in excess of F the speed of sound reverts to its zero density value, equation* (3); *the density correction factor q in equation* (2) *becomes zero*.

Striking as this effect is, it is not likely to have been observed accidentally. F lies in the normal acoustic range only if the pressure is rather low, probably between $0 \cdot 1$ and 1 atm. At these low pressures, the entire density correction to the speed of sound is small, of the order of 10^{-5} to 10^{-4}. This is possible to see if one looks for it specifically, but it is unlikely to have been seen accidentally.

Consider an acoustic cavity filled with a monatomic gas. The resonant frequency f is a geometrical constant times the speed of sound. Thus one way to look for the new effect is to measure f as a function of the density N/V of the gas filling the cavity. Within the range of validity of equation (2), f is a linear function of N/V, extrapolating to some definite value f_0 for a very dilute gas. However, the linear relation fails when F, as estimated by (7), drops below f. At densities below that point, f should approach f_0 much faster than merely linearly, and should then remain independent of density, equal to f_0. If the resonant frequency of the cavity is in the acoustic range, the crossover point is expected to be between $0 \cdot 1$ and 1 atm, and an accuracy better than 1 part in 10^4 must be maintained to see the effect (this includes temperature control to that accuracy, and an adequate Q-value for the cavity). It may be easier to go to somewhat higher frequencies; at 10^6 Hz, the crossover point should be between 1 and 10 atm, and an accuracy of better than $0 \cdot 1\%$ should suffice.

References

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