LIGHT SCATTERING FROM GAS MIXTURES

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The special features of the light scattering spectrum of disparate-mass gas mixtures are analyzed via the dispersion equation for the hydrodynamic modes.

Recently Aref'ev [1] has discussed the practical importance of Brillouin-Mandelstam (BM) scattering for determining the diffusion coefficient in gas mixtures. More recently, Rayleigh and Brillouin-Mandelstam scattering experiments in disparate-mass gas mixtures with differebt concentrations were performed by Gornall et al. [2]. The observed spectrum shows (i) a BM shift smaller than that calculated from the adiabatic sound velocity, (ii) a broadening of the BM lines upon increasing the mass fraction of the light component. These features were interpreted in ref. [2] as the result of the strong coupling between the hydrodynamic modes, caused by the high diffusion rate.

In this letter the special features of the light scattering spectrum of disparate-mass gas mixtures are analyzed via the dispersion equation for the hydrodynamic modes. From this analysis it appears that: (i) mode coupling indeed causes a lowering of the sound velocity, but the departure from the adiabatic value is not towards the isothermal one as argued by Gornall et al. [2]; (ii) the broadening of the BM lines cannot be accounted for on the basis of coupling effects, but can be explained by simple thermodynamic arguments.

Since we are primarily interested in the role of diffusion, we neglect the other transport phenomena (thermal conductivity, viscosity, Soret and Dufour effects). Then the hydrodynamic equations for a binary mixture can be written as [3]

$$\partial_t^2 \delta\rho = \Delta \delta p \,, \tag{1}$$

$$\partial_t \delta c = D\,[\Delta \delta c + (k_p/p)\,\Delta \delta p] \,, \tag{2}$$

$$\partial_t\,[\delta s - (\delta s/\delta c)_{p,T}\,\delta c] = 0. \tag{3}$$

Under the assumptions mentioned above $(\delta s)_c = \delta s - (\partial s/\partial c)_{p,T}\delta c$ corresponds to an (undamped) normal mode and thus the sound wave propagates at constant $(\delta s)_c$. With $(\delta s)_c$, δp and δc as independent variables $\delta\rho$ can be written as

$$\delta\rho = (\partial\rho/\partial s)_{p,c}(\delta s)_c + (\partial\rho/\partial p)_{s,c}\delta p + (\partial\rho/\partial c)_{p,T}\delta c \,,$$

which expression is substituted into eq. (1). Using (3) one then obtains from eqs. (1) and (2) two coupled equations in δp and δc, which are Fourier-Laplace transformed to yield the dispersion equation

$$z^3 + Dk^2(v_0/v_x)^2 z^2 + (kv_0)^2 z + Dk^2(kv_0)^2 = 0 \,, \tag{4}$$

where $v_0^{-2} = (\partial\rho/\partial p)_{s,c}$ and

$$v_x^{-2} = v_0^{-2} + \rho^{-2}(\partial\rho/\partial c)_{p,T}^2/(\partial\mu/\partial c)_{p,T} \,.$$

In the limiting case of small scattering vectors ($Dk^2 \ll kv$) the roots of the dispersion equation (4) are given by

$$-Dk^2;\; kv_0\left[\pm i - \frac{1}{2}\,\frac{Dk}{v_0}\,\frac{v_0^2 - v_x^2}{v_x^2}\right]. \tag{5}$$

In the opposite limiting case of large scattering vectors ($Dk^2 \gg kv$) one finds

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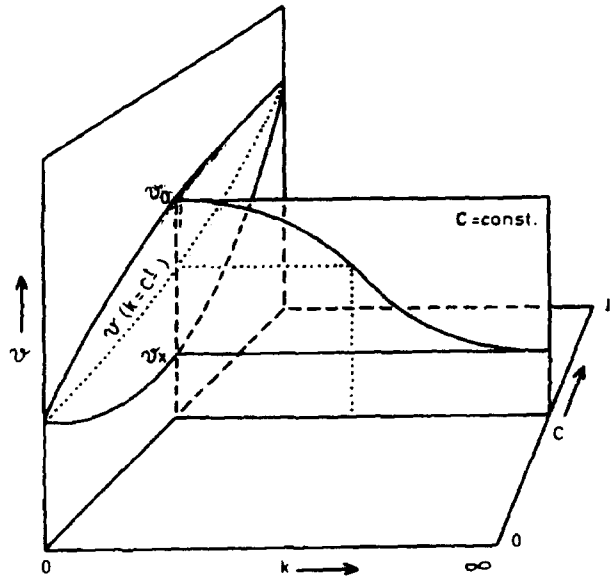

Fig. 1. Velocity of temporally absorbed soundwaves in a gas mixture as a function of scattering vector and concentration. Here C refers to the mass fraction of the light component. (The diagram is based upon calculations for He-Xe mixtures, assuming ideal gas behavior and concentration independent diffusion coefficient.)

$$-Dk^2(v_0/v_x)^2; \; kv_x\left[\pm i - \frac{1}{2}\frac{v_x}{Dk}\,\frac{v_0^2 - v_x^2}{v_0^2}\right]. \qquad (6)$$

From these results it is clear that the coupling between the concentration mode and the sound modes causes the sound velocity to change from its adiabatic value v_0 to the lower value v_x. It can be shown that v_x is the velocity of sound propagating at constant $(\delta s)_c$ and $\delta c + (k_p/p)\delta p$, and thus is not to be interpreted as the isothermal velocity. As an illustration the qualitative behavior of the sound velocity as obtained from the dispersion equation (4) ($v = |\mathrm{Im}\, z|k^{-1}$) is represented in fig. 1 as a function of scattering vector and concentration.

From (5) and (6) it is also clear that the coupling between the sound modes and the concentration mode causes a broadening of the central line and a narrowing of the BM lines. Therefore the broadening of the BM lines observed in [2] can not be explained on the basis of mode coupling. According to us fig. 1 suggests the correct interpretation: increase of the concentration of the light component (up to a certain value, which apparently was not exceeded in [2]) causes an increase of the thermodynamic quantity $(v_0^2 - v_x^2)$ and thus a broadening of the BM lines.

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