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## Sound Dispersion in Simple Fluids

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### Abstract

Sound dispersion in simple fluids is analyzed applying a generalized hydrodynamic method for time correlation functions. The effects of shear relaxation on the sound dispersion are examined for liquid argon and a dilute hard-sphere gas. In the case of liquid argon, the dispersion predicted by the theory over quite a wide range of wavenumbers exhibits the combined effects of shear relaxation and structural correlations. The results for a dilute gas indicate that the inclusion of shear relaxation gives a qualitative improvement of Navier-Stokes theory.

### 요 약

시간상관 함수를 일반화된 동력학적 수력학에 의해 기술하는 방법을 이용하여 단순 유체내에서의 소리의 산포를 분석 검토하였다. 소리의 산포에 대한 전단응력의 음의 산포에 영향을 액체알곤과 희석 경구형개스에 대해 검토하였다. 액체알곤의 경우에는 광범위한 파수영역에 걸쳐 이론적으로 예언된 산포는 전단응력 이완상관과 구조상관의 복합된 영향을 나타내었다. 희석개스에 대한 결과는 전단응력 이완을 포함시킨 이론이 나비에-스톡스 이론보다 정성적으로 우수함을 보였다.

### 1. Introduction

The purpose of this work is to discuss the dispersion of sound velocity<sup>1)</sup> in liquid argon and in a dilute gas of hard-spheres. Our attention will be focused on the effects of introducing the Maxwell(or shear) relaxation mechanism into the ordinary linearized hydrodynamic description. This approach is basically

an application of the Martin formalism<sup>2)</sup> of linear response theory. The present problem constitutes a related application of basically the same approach used in Ref. 3-5. Also we will study the validity of this approach for dilute fluids. In this context results of the linearized Burnett equations<sup>6)</sup> and modeled kinetic equation<sup>7)</sup> will be considered.

In Section 2 we introduce dispersion equations<sup>8)</sup> and define the various "sound" veloci-

ties which we can consider. In Section 3 we present the results of relaxation theory for the dispersion behavior in liquid argon and show that it can cover wavenumber values ranging from those appropriate to ultrasonics to those of neutron scattering. We then examine the applicability of the same theory to a dilute gas of hard-spheres in Section 4. We observe a qualitative improvement of Navier-Stokes theory by comparison with Burnett and kinetic calculations. We will discuss the more interesting features in our calculations in Section 5.

## 2. Dispersion Equations and Sound Velocities

There are several ways to discuss the dispersion and the velocity of sound in a fluid. Among these we will consider the following; the temporal decay of a spatially periodic disturbance (free sound waves), the spatial decay of a disturbance driven at a definite frequency (forced sound waves), the frequency shift of light scattered by a fluid (Brillouin scattering), and the frequency shift of longitudinal current excitations from molecular dynamics and neutron scattering. The last technique is an extension of light scattering to the large  $\kappa$  and  $\omega$  region.

The convenient quantity to describe density fluctuations in a fluid is the dynamic form factor  $S(\kappa, \omega)$ , which is directly measurable by light scattering and neutron scattering experiments. We have demonstrated<sup>3)</sup> that this quantity can be expressed in terms of the damping function. We have presented detailed analyses of correlation functions using the damping function derived from the linearized hydrodynamic description which includes the Maxwell relaxation. This approach will be

referred to as LHM in this work. In the limit  $\omega\tau \ll 1$  this damping function reduces to that obtained from the usual equations of linearized hydrodynamics which will be denoted as LH,  $\tau$  being the Maxwellian (or shear) relaxation time. (See Eq. (9).) We already know that the Maxwell relaxation time is very important in the transition region<sup>3)</sup>. We want to examine the effects of viscous relaxation in describing the dispersion of sound.

We now define the dispersion equation<sup>8)</sup> and several velocities to be discussed. In the case of free and forced sound wave we look for solutions to the dispersion equation

$$G(\kappa, s) = 0 \quad (1)$$

where  $G(\kappa, s)$  is obtained with explicit wave-number dependence from  $S(\kappa, \omega)$  which is cast into the form

$$S(\kappa, \omega) = S(\kappa) \sigma(\kappa, \omega) \quad (2)$$

$$\sigma(\kappa, \omega) = \frac{1}{\pi} \text{Re} F(s) / G(s) \quad (3)$$

where  $S(\kappa)$  is the static structure factor, and  $F(s)$  and  $G(s)$  are polynomials of  $s$ ,  $s$  being  $i\omega$ . In the forced sound wave case  $\omega$  is real and  $\kappa$  complex, so we define the sound velocity as

$$v_\omega = \omega / \text{Re} \kappa. \quad (4)$$

In the free sound wave case,  $\kappa$  is real and  $\omega$  complex, and the sound velocity may be defined as

$$v_\kappa = \text{Re } \omega / \kappa. \quad (5)$$

In Brillouin scattering we define the sound velocity

$$v_p = \omega_p (\text{value of } \omega \text{ at the Brillouin peak}) / \kappa \quad (6)$$

We will see that  $v_p$  is different from  $v_\kappa$  whenever there exists the overlapping of isobaric entropy fluctuations represented by the central heat diffusion peak with the Brillouin peak corresponding to sound propagation. Strictly speaking, without the overlapping  $v_p$  and  $v_\kappa$  are still different<sup>9)</sup>. The

reason is that  $v_\kappa$  is determined by Eq. (1), but  $v_p$  depends not only on the poles of  $S(\kappa, \omega)$ , the roots of Eq. (1) but also the strength of the Brillouin component. As  $\kappa$  increases, the width of the Brillouin component also increases and eventually the Brillouin peak disappears. If we still want to discuss sound dispersion in this situation, we have to define another sound velocity as

$$v_{lm} = (\omega_l)_{\max} / \kappa \quad (7)$$

where  $(\omega_l)_{\max}$  is the frequency at which the power spectrum of the longitudinal current correlation function, which is proportional to  $\omega^2 S(\kappa, \omega)$ , shows a peak. This frequency has been observed in molecular dynamics and inelastic neutron scattering experiments from liquids and has been interpreted as an elementary excitation frequency of longitudinal modes in liquids. The shift of this frequency as a function of wave-number may be interpreted as showing the dispersion of longitudinal modes. In the same spirit we may discuss the dispersion of sound velocity defined by Eq. (7). This velocity is the only meaningful one for the transition region and can be extended to the hydrodynamic region of  $\kappa$  and  $\omega$ . We then expect that  $(\omega_l)_{\max}$  is very close to  $\omega_p$  but is shifted toward slightly higher frequency.

We can easily show that the dispersion equations for LH and LHM are

$$\text{LH: } s^2 + v_o^2 \kappa^2 / \tau + \frac{s(1-1/\tau)v_o \kappa^2}{s + a\kappa^2} + sb_o \kappa^2 = 0 \quad (8)$$

$$\text{LHM: } s^2 + v_o^2 / \tau + \frac{s(1-1/\tau)v_o^2 \kappa^2}{s + a\kappa^2} + \frac{sb_o \kappa^2}{1 + s\tau} = 0 \quad (9)$$

where  $v_o$  is the ordinary adiabatic sound velocity,  $\tau$  the ratio of specific heats,  $a = \lambda / mnC_v$ ,  $\lambda$  being the heat conductivity,  $m$  the atomic mass,  $n$  the number density, and  $C_v$  the specific heat at constant volume,  $b_o = 4\eta_s / 3mn$ ,  $\eta_s$  being the shear viscosity, and  $\tau$  the shear relaxation time. Here we may

generalize Eqs. (8) and (9) by making all the quantities dependent on  $\kappa$  according to the prescriptions used in Ref. 3. This has to be done for liquids<sup>3)</sup>, but is not necessary for dilute gases. We will discuss separately the sound dispersion in liquid argon and a dilute gas in the next sections. In both cases it is important to realize that the maximum dispersion predicted by LHM occurs when  $\omega\tau$  or  $v\kappa\tau$  is of order unity. Of course  $v$  can be any of those defined in this section. As another remark, we note that the dispersion equation will include additional relaxation terms in the case of polyatomic fluids.

### 3. Dispersion in Liquid Argon

We will not consider the LH results for liquid argon, since we already know that LH fails in the large  $\kappa$  and  $\omega$  region. We do not consider the forced sound wave case, since ultrasonic measurements do not indicate any dispersion of sound in liquid argon.

In the free sound wave case, we have to solve Eq. (9) with  $\kappa$  real and  $\omega = -is$  complex. We cannot solve this equation analytically, because it is a sixth order equation in  $\omega$ . We have found that the approximate velocity  $v_a$  given by

$$v_a^2(\kappa) = \frac{v_o^2(\kappa)}{\tau} + \frac{[v_a(\kappa)\kappa\tau(\kappa)]^2[v_o^2(\kappa) - v_o^2(\kappa)]}{1 + [v_a(\kappa)\kappa\tau(\kappa)]^2} + \frac{(1-1/\tau)v_o^2(\kappa)[v_a(\kappa)\kappa\tau(\kappa)]^2}{[v_a(\kappa)\kappa\tau(\kappa)]^2 + (a\kappa^2)^2} \quad (10)$$

is very close to the  $v_p$  obtained numerically from the Brillouin peak in  $S(\kappa, \omega)$ . Notice that this equation is obtained from the real part of Eq. (9) by setting  $v_a(\kappa) = Re\omega/\kappa$ . In actual calculations we have ignored  $a\kappa^2$  compared with  $v_a(\kappa)\kappa\tau(\kappa)$ , which is not quite correct when  $\kappa \sim 1\text{\AA}^{-1}$ . Here all the quantities are  $\kappa$ -dependent. The quantities in Eq. (10) are given below<sup>3)</sup>.

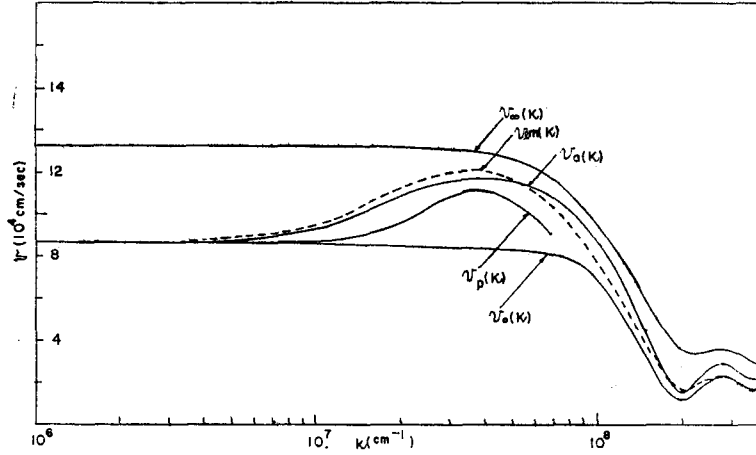


Fig. 1. Dispersion of various velocities in liquid argon at 76°K and 1.407g/cm³ as a function of wavenumber.

$$v_o^2(\kappa) = \tau / \beta m S(\kappa) \quad (11)$$

$$v_-^2(\kappa) = [4G_-(\kappa)/3 + K_-(\kappa)] / mn \quad (12)$$

$$\tau^{-2}(\kappa) = (8/3)[v_-^2(\kappa) - v_o^2(\kappa) - 1/\beta m]\kappa^2 + \frac{\tau^{-2}(0) - (8/3)[v_-^2(0) - v_o^2(0) - 2/\beta m]\kappa^2}{1 + (\kappa/\kappa_o)^2} \quad (13)$$

$$\tau^{-1}(\kappa=0) = [v_-^2(0) - v_o^2(0)]mn / (4\eta_s/3 + \eta_b), \quad \kappa_o = 1.5 \text{ \AA}^{-1} \quad (14)$$

where  $G_-(\kappa)$  and  $K_-(\kappa)$  are high frequency shear and bulk moduli,  $\beta$  is the inverse temperature in energy units, and  $\eta_b$  is the bulk viscosity. We recall that Eq. (13) is the interpolation formula of Akcasu and Daniels<sup>10)</sup> for the relaxation time. We can calculate  $v_o(\kappa)$  for  $\kappa > .5 \times 10^8 \text{ cm}^{-1}$  with the  $S(\kappa)$  taken from Rahman's work<sup>11)</sup>. For the values of  $\kappa < .5 \times 10^8 \text{ cm}^{-1}$  we use a smooth interpolation between  $S(\kappa)$  at  $\kappa = .5 \times 10^8 \text{ cm}^{-1}$  and  $S(0)$  obtained from the measured  $v_o(0)$ <sup>12)</sup>. For  $\kappa > .5 \times 10^8 \text{ cm}^{-1}$   $v_-(\kappa)$  is already available from Rahman<sup>11)</sup> and our calculation<sup>3)</sup> using the pair distribution function from Verlet<sup>13)</sup> and the Lennard-Jones potential. For smaller values of  $\kappa$  we use the small  $\kappa$  expansion of the molecular expression for  $v_-^2(\kappa)$  and take  $v_-^2(0)$  and the first order term. There is no

computational problem in evaluation  $v_-^2(0)$ . By checking the values of  $v_-^2(\kappa)$  for  $\kappa$  of the order of  $10^7 \text{ cm}^{-1}$  as calculated from the exact expression and those from the expansion method, we have found the expansion method to be reliable for small values of  $\kappa$ . At very

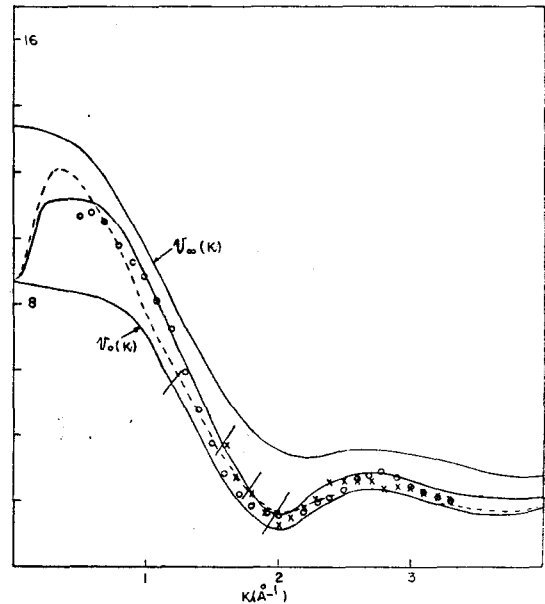


Fig. 2. Dispersion of  $v_{\infty}$  and  $v_o$  in liquid argon in the transition region.

small  $\kappa$  values we encountered computational difficulty using the exact molecular expression. Detailed expressions for the expansion method are given in Appendix A.

In Fig. 1 we show the variation of various velocities with number from  $10^6$  to  $4 \times 10^8 \text{ cm}^{-1}$ . We have found no dispersion in any of the velocities up to  $10^6 \text{ cm}^{-1}$ . We see two regions of  $\kappa$  which show interesting characteristics. The first region is between  $10^6$  and  $.4 \times 10^8 \text{ cm}^{-1}$ , where the dispersion due to the shear relaxation can be as much as  $\sim 36\%$ . The second region is from  $.4 \times 10^8$  to  $4 \times 10^8 \text{ cm}^{-1}$  where even more significant variations of the velocities are apparent. In comparison to the monotonic positive dispersion in the first region we now see a sharp negative dispersion. We interpret this as arising from the combined effects of the shear relaxation and the structural or spatial correlations among argon atoms. The latter effect is represented by the  $\kappa$ -dependence in Eqs. (11) to (13). These results indicate that structural effects dominate in the region.

In Fig. 2 we show a magnified picture of Fig. 1 for the  $10^8 \text{ cm}^{-1}$  region. We include the experimental results for  $v_{lm}(\kappa)$  obtained from computer molecular dynamics experiments<sup>11)</sup> (solid circles) and neutron scattering (crosses for the data of Skold and Larsson<sup>14)</sup> and bars for those of Chen *et al.*<sup>15)</sup>). In the case of molecular dynamics  $v_{lm}(\kappa)$  is obtained by drawing a smooth curve through Rahman's data. The agreement between  $v_{lm}(\kappa)$  from LHM and those from experiments is similar to that observed in Ref. 3. We also note that the approximate velocity is not very different from the other velocities. As is shown in Eq. (10), it is easy to see that  $v_o(\kappa)$  becomes  $v_s(\kappa)$  when  $\kappa$  is very small and approaches to  $v_{\infty}(\kappa)$  as  $\kappa$  increases. However,  $v_s(\kappa)$  cannot

be  $v_{\infty}(\kappa)$  because of the  $a\kappa^2$  term in Eq. (10).

A number of other features are observable from these figures. None of the velocities approaches  $v_{\infty}(\kappa)$  in the regions considered. It is not surprising to see that  $v_b(\kappa)$  cannot be defined for  $\kappa > 5 \times 10^7 \text{ cm}^{-1}$ .  $v_o(\kappa)$  is very close to  $v_{lm}(\kappa)$  and all the velocities lie between  $v_o(\kappa)$  and  $v_{\infty}(\kappa)$  over the entire range of  $\kappa$ . If we consider  $v(\kappa)/v_o(\kappa) - 1$  as giving the sign of the dispersion, every velocity shows positive dispersion. Notice that here we have included the  $\kappa$ -dependence in  $v_o(\kappa)$  through  $S(\kappa)$  which shows a significant variation over the entire range of  $\kappa$ . In the ultrasonic region this velocity is considered as a constant which corresponds to  $v_o(\kappa=0)$  in our definition. As a final note, it is unfortunate that there is no experimental measurement in the first  $\kappa$  region. At the present time neither light scattering whose maximum accessible  $\kappa$  value is about  $2 \text{ \AA}^{-1}$  nor neutron scattering whose minimum accessible  $\kappa$  value is about  $5 \text{ \AA}^{-1}$  can be used to test the prediction shown in the first  $\kappa$  region. However, we have found that the maximum dispersion occurs when  $\omega\tau$  or  $v(\kappa)\kappa\tau$  is about unity. In liquid argon this occurs at  $\kappa \sim .4 \times 10^8 \text{ cm}^{-1}$ . This means that shear relaxation is responsible for the dispersion. Due to the small value of the relaxation time ( $10^{-13}$  sec.) the range of  $\kappa$  exhibiting the dispersion lies beyond that accessible by light scattering. On the other hand, in liquids like glycerine with large  $\tau$  it is possible to observe the dispersion by light scattering technique.

#### 4. Dispersion in a Dilute Gas

Recalling that the condition of  $v\kappa\tau=1$  is critical for observing the dispersion and that in a gas  $v$  does not differ much from  $v$  in liquid

state, we expect that the range of  $\kappa$  can fall in the light scattering region by making  $\tau$  large enough. This can be realized in a gas, since  $\tau$  is inversely proportional to the density of the gas. This idea has led us to consider the dispersion of sound in a dilute gas<sup>16)</sup>. We also want to know what shear relaxation in LHM can do to the results of LH which are known to be incapable of predicting of sound dispersion in the kinetic regime<sup>17,18)</sup>.

Table 1. Dispersion Coefficients for "LH", "LB", and "LHM"

	$C_\kappa$	$C_\omega$	$C_\alpha$
LH	$+\frac{141}{72}$	$-\frac{55}{72}$	$-\frac{1559}{432}$
LB	$+\frac{215}{72}$	$+\frac{19}{72} - \frac{6217}{10368} \left( \frac{\eta' \kappa}{v_o} \right)^2$	$-\frac{4203}{432}$
LHM	$+\frac{141}{72}$	$+\frac{389}{72} - \frac{960717}{576} \left( \frac{\eta' \kappa}{v_o} \right)^2$	$-\frac{3559}{432}$

We choose a gas composed of hard-sphere molecules, since all the quantities appearing in the expression of  $S(\kappa, \omega)$  are simple,

$$r=5/3 \quad (15)$$

$$v_o^2=5/3\beta m \quad (16)$$

$$\eta_s=G_\infty\tau=n\tau/\beta \quad (17)$$

$$a=5\eta_s/2mn \quad (18)$$

$$v_\infty^2=3/\beta m \quad (19)$$

$$\eta_s=(K_\infty-K_o)\tau=0 \quad (20)$$

Notice that Eq. (18) gives the Eucken constant as 5/2. We show in Appendix A that Eqs. (16), (17), (18) and (19) are the dilute gas limits of the  $\kappa$ -dependent quantities for hard-sphere molecules. It is known that the Eucken constant is nearly equal to 5/2 for a wide class of intermolecular potentials and the experimental values for noble gases are very close to 5/2. It is also well known that this constant for Maxwell molecules is 5/2. Therefore the results of LH<sup>17)</sup> to be discussed are

the same for hard-sphere and Maxwell molecules. The results of the linearized Burnett equations (LB) are worked out for Maxwell molecules<sup>6,18)</sup>. We will compare the results of these theories with those of the modeled kinetic equations of Sugawara and Yip for hardsphere molecules<sup>7)</sup>.

First we examine the dispersion for small  $\kappa$  and  $\omega$ . The LH results for  $v_o, v_\kappa$  and  $\alpha$  are known<sup>17)</sup>,  $\alpha$  being the absorption coefficient, and are given in Table 1. There we define the "dispersion coefficients",

$$C_\kappa=(v_\kappa/v_o-1)(v_o^2/\eta'\omega)^2 \quad (21)$$

$$C_\omega=(v_\omega/v_o-1)(v_o^2/\eta'\omega)^2 \quad (22)$$

$$C_\alpha=(v_o^3\alpha/\eta'\omega^2-7/6)(v_o^2/\eta'\omega)^2 \quad (23)$$

where  $\eta'=\eta_s/mn$ . The LB results for Maxwell molecules are also listed in Table 1.

For LHM we recall Eq. (9) in the form

$$\begin{aligned} \omega^4 - i(\tau^{-1} + 3v_o^2\kappa^2\tau/2)\omega^3 - 33v_o^2\kappa^2\omega^2/10 \\ + i(v_o^2\kappa^2\tau^{-1} + 21v_o^2\kappa^4\tau/10)\omega + 9v_o^2\kappa^4/10 = 0 \end{aligned} \quad (24)$$

By putting

$$\omega = v_o\kappa(1 + a\kappa + b\kappa^2 + \dots)$$

or putting

$$\kappa = \frac{\omega}{v_o} (1 + a\omega + b\omega^2 + \dots)$$

and determining the coefficients by equating equal powers of  $\kappa$  or  $\omega$ , we find the results of LHM,

$$\begin{aligned} \omega = v_o\kappa \left[ 1 - i7\eta'/6v_o + \frac{389}{72} \left( \frac{\eta'\kappa}{v_o^2} \right)^2 + i \frac{7943}{216} \right. \\ \left. \cdot \left( \frac{\eta'\kappa}{v_o} \right)^3 - \frac{960717}{576} \cdot \left( \frac{\eta'\kappa}{v_o} \right)^4 + \dots \right] \end{aligned} \quad (25)$$

$$\begin{aligned} \kappa = \frac{\omega}{v_o} \left[ 1 - 7\eta'\omega/6v_o^2 - \frac{141}{72} \left( \frac{\eta'\omega}{v_o^2} \right)^2 \right. \\ \left. + i \frac{3559}{432} \left( \frac{\eta'\omega}{v_o^2} \right)^2 + \dots \right]. \end{aligned} \quad (26)$$

We then obtain from Eq. (25)

$$\begin{aligned} (v_\omega)_{LHM} = v_o \left[ 1 + \frac{389}{72} \left( \frac{\eta'\kappa}{v_o} \right)^2 \right. \\ \left. - \frac{960717}{576} \left( \frac{\eta'\kappa}{v_o} \right)^4 \right] \end{aligned} \quad (27)$$

and from Eq. (26)

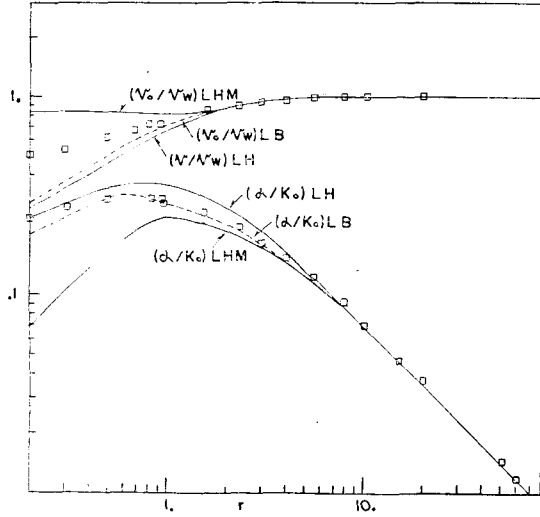


Fig. 3. Dispersion and absorption of forced sound waves in a dilute hard-sphere gas.

$$(v_\kappa)_{LHM} = v_0 \left[ 1 + \frac{141}{72} \left( \frac{\eta' \omega}{v_0^2} \right)^2 \right] \quad (28)$$

$$(\alpha)_{LHM} = \frac{\eta' \omega^3}{v_0^3} \left[ \frac{7}{6} - \frac{3559}{432} \left( \frac{\eta' \omega}{v_0^2} \right)^2 \right] \quad (29)$$

These are included in Table 1. We see that the first-order sound dispersion for free and sound waves in LHM is different but positive

in both cases. However, the coefficients  $C_\omega$  and  $C_\kappa$  are different from those in LB which are known to be correct<sup>6)</sup>. We thus have shown that LHM gives the correct sign but not the magnitude of dispersion.

We next examine the exact results of LH and LHM which are obtained numerically from each dispersion equation and  $S(\kappa, \omega)$ . It is convenient in the forced sound wave case to define<sup>19)</sup>

$$r = p/\omega\eta_s \quad (30)$$

where  $p$  is the pressure and

$$R = \kappa/\kappa_0 \quad (31)$$

Here  $\kappa$  is complex and  $\kappa_0$  real, defined by

$$\kappa_0 = \omega/v_0 \quad (32)$$

From the equation of state for a dilute gas,  $p = n/\beta$  and Eq. (17) we show that

$$r = 1/\omega\tau \quad (33)$$

In terms of these parameters the dispersion in the forced sound wave case becomes

$$\text{LH: } R^4(9i/10r - 6/5r^2) - R^2(1 + 23i/10r) + 1 = 0 \quad (34)$$

$$\text{LHM: } R^4(7/r - 3i) + R^2(10r - 15/r + 33i)/3 - 10(r + i)/3 = 0 \quad (35)$$

We then solve these equations for  $R$ . The

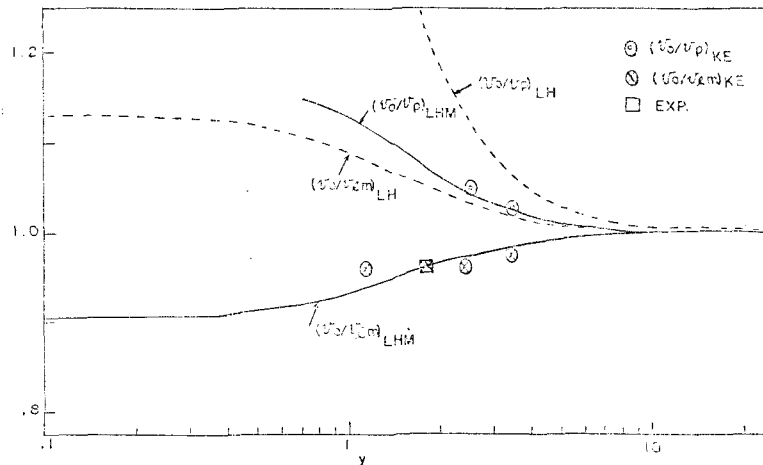


Fig. 4. Dispersion of  $v_p$  and  $v_{lm}$  in a dilute hard-sphere gas as a function of  $y$ .

real part of the solution is the ratio of velocities,  $v_o/v_\omega$ , and the imaginary part of  $R$  is  $\alpha/\kappa_o$ .

In Fig. 3 we compare three hydrodynamic calculations (LH, LHM and LB) of  $v_o/v_\omega$  and  $\alpha/\kappa_o$  with the Greenspan's experiment<sup>19)</sup> in helium gas. We see in the comparison of  $v_o/v_\omega$

that LHM gives an overestimate. Though their first order terms are the same as shown in Table 1, the exact results for LH and LHM are different. In LHM  $v_o/v_\omega$  approaches the asymptotic value of  $\sqrt{5/7}$  as  $r$  goes to zero, which can be easily shown from Eq. (35). On the other hand,  $v_o/v_\omega$  approaches zero in LH

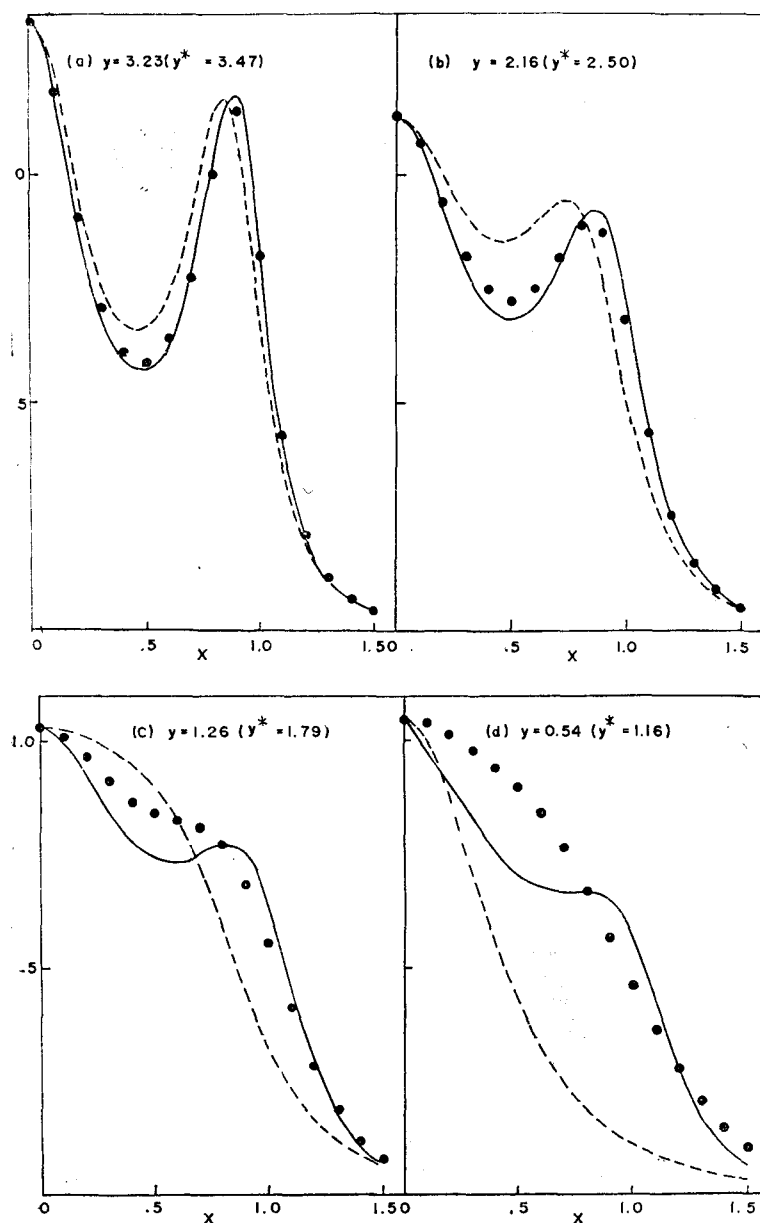


Fig. 5. Spectra of density fluctuations,  $S(k, \omega)$ , in a dilute hard-sphere gas.



and LB. The comparison of  $\alpha/\kappa_0$  shows that LHM underestimates  $\alpha/\kappa_0$  for  $r \leq 3$ , LH overestimates it for  $r < 4$ , and LB begins to underestimate it at  $r \sim 3$ . We may explain the overcorrection of LHM in comparison with LH noticing that in LHM the shear viscosity term in  $\alpha$  is, roughly speaking, proportional to  $\eta_s/(1+\omega^2\tau^2)$ . Since this factor is simply  $\eta_s$  in LH, LHM underestimates the viscosity effect by the factor of  $(1+\omega^2\tau^2)^{-1}$ . The fact that LHM does not give a good agreement with the experiment for  $r < 1$  suggests that the Lorentzian frequency dependence in the damping function is not adequate for that region: Since very small  $r$  corresponds to rarefied gas state, the frequency dependence obtained from an ideal gas is expected to give better result. We note that LHM does not take into account properly the streaming of the molecules which plays more important role than the collision among them. This will also has some bearing on the underestimate of  $v_o/v_\omega$  by LHM.

We cannot solve Eqs. (8) and (9) analytically for the free sound wave case. However, it is possible to calculate  $v_s$  and  $v_{im}$  numerically, as was done for liquid argon in Section 3. It is convenient to express  $S(\kappa, \omega)$  in terms of  $x$  and  $y$  defined by

$$x = \omega/v_o\kappa \quad (36)$$

$$y = 1/v_o\kappa\tau \quad (37)$$

The result for LHM is

$$S(x, y) = (\pi\tau v_o\kappa)^{-1} F(x, y)/G(x, y) \quad (38)$$

where

$$F(x, y) = [x^2(4y/5 + 3/5y) + 9/5y + 3y/5] \\ (x^2 + y^2) (x^2 + 9/4y^2) \quad (39)$$

$$G(x, y) = [x^6 + x^4(y^2 + 9/4y^2 - 9/5) \\ + x^2(-y^2 - 9/4 - 63/20y^2) - 27/20]^2 \\ + x^2[x^2(4y/5 + 3/5y) + 9/5y + 3y/5]^2 \quad (40)$$

In Fig. 4 we compare  $v_o/v_s$  and  $v_o/v_{im}$  in LH and LHM with a few points from the

kinetic results of Sugawara and Yip<sup>7)</sup> as function of  $y$ . In view of the excellent agreement of the kinetic results (KE) with the experiment of Greytak and Benedek<sup>20)</sup>, the point at  $y^* = 1.79$  [see (41)] can be regarded as an experimental result. For LHM we have included the  $\kappa$ -dependence in the relaxation time which leads to an effective  $y^*$  defined by

$$y^* = y[\tau(0)/\tau(\kappa)] \quad (41)$$

where  $\tau(\kappa)$  is given by Eq. (14). We see that LH gives  $v_s$  and  $v_{im}$  of negative dispersion and LHM and KE are in agreement, both giving  $v_s$  and  $v_{im}$  of opposite sign. This opposite sign can be explained from simple geometrical consideration of the peaks of  $S(\kappa, \omega)$  and  $\omega^2 \times S(\kappa, \omega)$  with a fixed value of  $v_o$ . In Fig. 5 we present the comparison of  $S(\kappa, \omega)$  or  $S(x, y)$  from LH and LHM with that from KE<sup>7)</sup> at four values of  $y^*$ . We see clear improvement of LHM over LH at all values of  $y^*$ . Even at  $y^* = 3.473$  at which LH is supposed to be good, LHM gives better result than LH. At  $y^* = 1.79$  and 1.27 we see the failure of LHM at which we have to use more complicated frequency dependence of the damping function, as pointed out earlier.

## 5. Discussion

In this work we have examined the dispersion of sound in simple fluids like liquid argon and in a dilute gas of hard-sphere molecules. Specifically, we have compared the results of the linearized hydrodynamics plus relaxation theory with those of the ordinary hydrodynamics (Navier-Stokes), Burnett, and kinetic theories. We have shown that in most cases LHM gives better results than LH. This might be expected from the success of LHM in analyzing various correlation functions as demonstrated in Ref.

3-5. We see the simplicity and utility of the Martin formalism of linear response theory in discussing the dispersion of sound in terms of the damping function. The simple frequency dependence of the damping function assumed in LHM is not sufficient to deal with a very dilute gas. One reason is that it still does not treat properly the streaming of the molecules.

In liquid argon calculations we have demonstrated that our LHM with the  $\kappa$ -dependence used in Ref. 3-5 provides us with a theory which is capable of treating the sound dispersion consistently through a wide range of  $\kappa$ . This extends from the region of interest in the ultrasonic measurements to that in the neutron scattering and molecular dynamics experiments. We defined a velocity  $v_{lm}$  which is useful in the large  $\kappa$  and  $\omega$  region, as long as the frequency wavenumber relation in that region is well defined. We also demonstrated that the values of  $\kappa$  where  $v\kappa\tau=1$  lie in the region between light scattering and neutron scattering measurements. Recalling that the  $\kappa$ -dependent relaxation time gives better results in analyzing the correlation functions of liquids, we hope that careful measurement of the sound dispersion may provide one with a method to determine this  $\kappa$ -dependence. LHM predicted the maximum dispersion of  $\sim 36\%$  using the relaxation time of the Akcasu and Daniels prescription in the  $\kappa$  region where the shear relaxation effect is dominant. In the region of  $\kappa \gtrsim 5 \times 10^8 \text{ cm}^{-1}$  we have seen the structural correlation effect overwhelms the shear relaxation effect and the theoretical velocities are in good agreement with those estimated from the molecular dynamics and inelastic neutron scattering data. In all these calculations the  $\kappa$ -dependence in the elastic moduli,  $v_s(\kappa)$ , and  $\tau(\kappa)$  play an important role in liquid. On the other hand, the  $\kappa$ -

dependence has little effect in a dilute gas.

Without such  $\kappa$ -dependence we have shown that the dispersion of sound in a dilute gas of hard-spheres can be examined by the same approach as in liquid argon. We have seen the superiority of LHM over LH in giving the correct sign of the dispersion and in comparison with the kinetic theory of Sugawara and Yip. In the forced sound wave case LHM underestimates the observed  $v_\omega$  and the absorption coefficient in the rarefied gas region. The comparison with the kinetic theory at the kinetic region of  $\kappa$  indicates that the damping function with a Lorentzian frequency dependence is not appropriate in treating the streaming of the gas molecules. It is possible that LHM will provide us with a tractable and reasonably accurate theory for dealing with dense gases. For a dense gas of hard-sphere molecules the  $\kappa$ -dependence in  $v_s(\kappa)$ ,  $v_\infty(\kappa)$ , and  $G_\infty(\kappa)$  may be estimated by the results given in Appendix A. It will be of interest to apply  $\kappa$ -dependent quantities to sound dispersion measurements in a dense gas.

## Appendix A

### Sum-Rules in a Dilute Gas of Hard-spheres

Using hard-sphere potential, Percus Yevick equation for  $\phi(r)$  vs.  $g_2(r)$ <sup>(21)</sup>, and the assumption  $g_2(r) = e^{-\phi(r)/\beta 22}$ , we can derive the following sum-rules and the structure factor in a dilute gas of hard-spheres:

$$\begin{aligned}
 (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &= \frac{3n}{\beta} \\
 &- \frac{24n\eta^*}{\beta y^2} \left[ B \left\{ \frac{1}{3} - \frac{2}{y^2} \left( 1 - \frac{\sin y}{y} \right) \right\} \right. \\
 &\quad \left. + C \left\{ 1 - \frac{18}{y^3} \left( \sin y - \frac{4}{3y} \right) \right\} \right] \quad (A 1) \\
 (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &= \frac{n}{\beta}
 \end{aligned}$$

$$\begin{aligned}
& -\frac{4n\eta^*}{\beta y^2} \left[ B \left\{ \frac{1}{3} + \frac{1}{y^2} \left( -\frac{\sin y}{y} + \cos y \right) \right\} \right. \\
& \quad \left. + C \left\{ 1 + \frac{3}{y^2} \left( -\frac{\sin y}{y} + \cos y \right) \right\} \right] \quad (\text{A } 2) \\
S(\kappa) = & \left[ 1 - \frac{24\eta^*}{y^2} \left\{ A \left( -\cos y + \frac{\sin y}{y} \right) \right. \right. \\
& + B \left( -\cos y \left( 1 - \frac{2}{y^2} \right) + \frac{2}{y} \left( \sin y - \frac{1}{y} \right) \right) \\
& + C \left( \cos y \left( -1 + \frac{12}{y^2} - \frac{24}{y^4} \right) \right. \\
& \left. \left. + \frac{4 \sin y}{y} \left( 1 - \frac{6}{y^2} \right) + \frac{24}{y^4} \right\} \right]^{-1} \quad (\text{A } 3)
\end{aligned}$$

where  $y = \sigma\kappa$ ,  $\eta^* = \pi n \sigma^3/6$ ,

$$A = -\frac{(1+2\eta^*)^2}{(1-\eta^*)^4}, \quad B = \frac{6\eta^*(1+\eta^*/2)^2}{(1-\eta^*)^4}$$

and  $C = \frac{-\eta^*(1+2\eta^*)^2}{2(1-\eta^*)^4}$ ,  $\sigma$  being the diameter of a hard-sphere. We may expand these expressions for small  $\kappa$  using

$$\begin{aligned}
\sin x &= x - x^3/3! + x^5/5! - x^7/7! + \dots \\
\cos x &= 1 - x^2/2! + x^4/4! - x^6/6! + \dots
\end{aligned}$$

The results are

$$\begin{aligned}
(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &\simeq \lim_{\kappa \rightarrow 0} (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle \\
&+ (3n\eta^*/35\beta) y^2 (B/9 + 13C/8) \quad (\text{A } 4)
\end{aligned}$$

$$\begin{aligned}
(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &\simeq \lim_{\kappa \rightarrow 0} (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle \\
&+ (3n\eta^*/35\beta) y^2 (B/3 + C) \quad (\text{A } 5)
\end{aligned}$$

where the  $\kappa \rightarrow 0$  limits<sup>23)</sup> can be calculated exactly and are given by

$$\begin{aligned}
\lim_{\kappa \rightarrow 0} (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &= (n/\beta) [3 - 8\eta^*/5(B/4 + 2C)] \quad (\text{A } 6)
\end{aligned}$$

$$\begin{aligned}
\lim_{\kappa \rightarrow 0} (mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &= (n/\beta) [1 - 4\eta^*/5(B + 3C)] \quad (\text{A } 7)
\end{aligned}$$

Similarly we can show that

$$\begin{aligned}
\lim_{\kappa \rightarrow 0} S(\kappa) &= [1 - 24\eta^* (A/3 + B/4 - 19C/30)]^{-1} \quad (\text{A } 8)
\end{aligned}$$

We can also show that the small  $\kappa$  expansions of  $(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle$  and  $(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle^{24-26}$  lead to

$$(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle \simeq \lim_{\kappa \rightarrow 0} \frac{mn}{\kappa^2} \langle \omega_i^2(\kappa) \rangle$$

$$-\frac{\pi n^2 \kappa^2}{21} \int_0^\infty dr r^6 g_2(r) \left( \frac{1}{2} \frac{d^2 \phi}{dr^2} + \frac{1}{5r} \frac{d\phi}{dr} \right) \quad (\text{A } 9)$$

$$\begin{aligned}
(mn/\kappa^2) \langle \omega_i^2(\kappa) \rangle &\simeq \lim_{\kappa \rightarrow 0} \frac{mn}{\kappa^2} \langle \omega_i^2(\kappa) \rangle \\
&- \frac{\pi n^2 \kappa^2}{42} \int_0^\infty dr r^6 g_2(r) \left( \frac{1}{5} \frac{d^2 \phi}{dr^2} + \frac{4}{5r} \frac{d\phi}{dr} \right) \quad (\text{A } 10)
\end{aligned}$$

where

$$\begin{aligned}
\lim_{\kappa \rightarrow 0} \frac{mn}{\kappa^2} \langle \omega_i^2(\kappa) \rangle &= \frac{3n}{\beta} \\
&+ (2\pi n^2/5) \int_0^\infty dr r^4 g_2(r) \left( \frac{d^2 \phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} \right) \quad (\text{A } 11)
\end{aligned}$$

$$\begin{aligned}
\lim_{\kappa \rightarrow 0} \frac{mn}{\kappa^2} \langle \omega_i^2(\kappa) \rangle &= \eta/\beta \\
&+ (2\pi n^2/15) \int_0^\infty dr g_2(r) \frac{d}{dr} \left( r^4 \frac{d\phi}{dr} \right) \quad (\text{A } 12)
\end{aligned}$$

Notice that we have used Eqs. (A9) and (A 10) to compute  $\langle \omega_i^2(\kappa) \rangle$  and  $\langle \omega_i^2(\kappa) \rangle$  for  $\kappa < 1 \text{ \AA}^{-1}$ .

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