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Rayleigh-Brillouin spectrum of compressed He, Ne, and Ar. I. Scaling

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The Rayleigh-Brillouin spectrum of He, Ne, and Ar is reported for 90° scattering at a number of densities spanning the kinetic and hydrodynamic regime. A purely experimental test of scaling is made and it is found that deviations from scaling at high density can be attributed to mean-field effects. At low densities there is evidence that deviations from scaling, which arise from the detailed dependence of the spectrum on the intermolecular potential, are detectable at the few percent level. Some insight into scaling is obtained by comparing the results at low densities with curves predicted from a $3E$ kinetic model and from hydrodynamic theory.

It is well known that the Rayleigh-Brillouin spectrum $S(k,\omega)$ is the Fourier transform of the Van Hove pair correlation function $G(\vec{r},t)$,[1] where $G(\vec{r},t)$ is the probability of finding an atom at position $\vec{r}$ at time t given that there was an atom at the origin at t equal to zero. The wave vector k for the space part of the transform is the difference between the scattered and incident wave vectors of the light and, to a high degree of approximation, is simply given by

$$k=|\vec{k}_s-\vec{k}_i|=(2\pi/\lambda)2\sin(\theta/2)\,,$$

where λ is the wavelength of the light in the medium and θ is the scattering angle. At high densities, $G(\vec{r},t)$ or the spectrum $S(k,\omega)$ may be calculated explicitly starting from the linearized equations for fluid mechanics,[2] while at low densities the spectrum may formally be derived from the Boltzmann equation.[3]

The two regions are typically characterized by the uniformity parameter y which is of the order of $1/kl$, where l is the mean free path; $y\approx 1$ is the kinetic region and $y\gg 1$ is the hydrodynamic regime. (The region $y\ll 1$ is the free-streaming region and yields the well-known Doppler profile, which is of no interest to us here.) Physically, $1/k$ is the spatial dimension of the density fluctuation probed by the scattering process so that the medium appears as a continuum if this is large compared to the mean free path; i.e., the equations of fluid mechanics may be used provided $1/kl$ is large compared to 1.

In the low-density or kinetic regime certain scaling laws have emerged which are now commonly used in almost all papers dealing with the Rayleigh-Brillouin spectra in gases. In some respects these laws follow rigorously from the Boltzmann equation, while in others they are approximate. In this article we wish to examine these scaling laws experimentally for the gases helium, neon, and argon over a wide range of density. One might expect the scaling laws to fail either because of their approximate nature or from the fact that the density was sufficiently large as to render the Boltzmann equation inappropriate.

The hypothesis of scaling as used in this paper is that the spectrum $S(k,\omega)$, which in principle is a function of k,ω, the intermolecular potential and the temperature of the fluid, is only a function of two variables, a reduced frequency x given by $x=\omega/\sqrt{2}kv_0$, and y, the uniformity parameter given by

$$y=\sqrt{2}mn_0v_0/3\eta k\,.$$

Here v_0 is a mean molecular speed $(k_BT/m)^{1/2}$, η is the shear viscosity, n_0 is the number density, and m is the mass of a molecule. Other definitions of y are given in the literature,[4–7] usually in terms of an eigenvalue of the collision operator for a particular force law.

It is appropriate to begin with a discussion of kinetic scaling. (We follow the nomenclature and approach of Sugawara *et al.*[8]) It may be shown that the spectrum $S(k,\omega)$ is given by

$$S(k,\omega)=2\,\mathrm{Re}\int_0^\infty f_0(\vec{v})f(k,\vec{v},\omega)d^3v\,,$$

where $f(k,v,\omega)$ satisfies the transformed, linearized Boltzmann equation

$$(i\omega-i\vec{k}\cdot\vec{v})f(k,v,\omega)=J[f(k,\vec{v},\omega)]+1\,. \qquad (1)$$

The linearized collision operator $J[f]$ is given by

$$J[f(k,\vec{v},\omega)]=n_0\int d\Omega\int d^3vf_0(\vec{v}_1,T)|\vec{v}-\vec{v}_1|I(\theta,|\vec{v}-\vec{v}_1|)[f(k,\vec{v}',\omega)+f(k,\vec{v}_1',\omega)-f(k,\vec{v},\omega)-f(k,\vec{v}_1,\omega)]\,. \qquad (2)$$

Here f_0, the absolute Maxwellian, is given by

$$f_0=(2k_BT/m)^{-3/2}e^{-mv^2/2k_BT}\,.$$

Since the Boltzmann equation is valid within the binary collision approximation and neglects the duration of a collision with respect to the time of flight between collisions, it follows that the $J[f]$ term which describes the rate of change of f due to collisions is proportional to the density and to some mean molecular speed, say v_0. The n_0 dependence is explicit in $J[f]$. In order to display the v_0 dependence which is implicit in the $|\overline{v}-\overline{v}_1|$ factor in $J[f]$, it is convenient to express all velocities in reduced form $\vec{v}^*=\vec{v}/v_0$. It is then trivial to show that Eqs. (1) and (2) can be written

$$i(\omega-v_0\vec{k}\cdot\vec{v}^*)f(k,\vec{v}^*,\omega)=n_0v_0\tilde{J}f(k,\vec{v}^*,\omega)+1\,, \tag{3}$$

and

$$\tilde{J}[f(k,\vec{v}^*,\omega)]=\int d\Omega\int d^3v_1^*f_0(\vec{v}_1^*)|\vec{v}^*-\vec{v}_1^*|I(\theta,|\vec{v}^*-\vec{v}_1^*|)[f(k,\vec{v}'^*,\omega)+f(k,\vec{v}_1'^*,\omega)-f(k,\vec{v}^*,\omega)-f(k,\vec{v}_1^*,\omega)], \tag{4}$$

from which it follows that the spectrum is a function only of ω/kv_0, of n_0/k, and, through the cross section appearing in $J[f]$, of the intermolecular potential. Thus, the kinetic scaling law states for atomic gases that experiments may be performed at different scattering angles, density, temperature, or with different lasers, but the same spectrum will result when plotted as a function of ω/kv_0 provided n_0/k is a constant. [To be precise, one has only removed the dominant part of the dependence of $J[f]$ on temperature or v_0. There is still a temperature dependence hidden in $f_0|\vec{v}^*-\vec{v}_1^*|\times I(\theta,|\vec{v}^*-\vec{v}_1^*|)$ which is presumed to be very small.]

The commonly accepted scaling law for Brillouin spectroscopy, which states that the spectrum is a function only of x and y, is an approximation as may readily be appreciated from the following argument. Consider the eigenvalue problem, $\tilde{J}[\psi_i]=\Lambda_i\psi_i$. Since $f(k,\vec{v}^*,\omega)$ may be expanded in terms of ψ_i, it then follows by the usual matrix techniques that the spectrum is a function of

$$\left(\frac{\omega}{kv_0},\frac{n_0\Lambda_1}{k},\frac{n_0\Lambda_2}{k},\ldots\right).$$

If one extracts a particular Λ, say Λ_1, then $S(k,\omega)$ can be written

$$S\left(\frac{\omega}{kv_0},\frac{n_0\Lambda_1}{k},\frac{\Lambda_2}{\Lambda_1},\frac{\Lambda_3}{\Lambda_1},\ldots\right).$$

The argument now runs that, although Λ_1 may vary from potential to potential, the ratios Λ_i/Λ_1 do not vary significantly so that as an approximation the spectrum is a function only of ω/kv_0 and $n_0\Lambda_1/k$. The usual practice is to take the Λ associated with shear viscosity as Λ_1 and to include a $\sqrt{2}$ factor in the reduced frequency so that x and y are as defined earlier. This is the form of scaling we wish to examine experimentally.

The experimental apparatus was similar to that used by Hubert and May,[9] so only a few details will be given here. The single-frequency Ar^+ laser had a combined jitter and drift of ±30 mHz over many hours and an output power of about 500–600 mW at 514.5 nm. The plane-parallel Fabry-Perot interferometer had a finesse of 80 and was digitally scanned. Typical count rates for the three gases are given in Table I.

For the worst possible case, He at y equal to 1.5, the total number of counts recorded at the laser frequency was 700 ± 28. The measured stray light was 57 ± 7 counts. Thus the corrected spectrum was reliably determined even in the extreme case. For the other gases, or at higher density, the stray light was essentially zero. The absence of stray light, which results from the 90° scattering geometry and the unique design of the light trap in the cell,[10] has an important consequence. The experimental spectra can now be normalized to unit area, and an absolute comparison can be made with other gases or with theoretical profiles. Without this, one loses information near zero frequency and, furthermore, must adjust the experimental or theoretical spectra to match at some point, such as the Brillouin peak, as Fookson *et al.* have done.[11] For further experimental details and data-reduction techniques the reader is referred to the work of Ghaem-Maghami.[12]

As one object of the experiment was to test experimentally the scaling of Rayleigh-Brillouin spectra without recourse to theoretical calculation, it is important that the instrumental contribution to the line profile does not enter the problem. For each gas the interferometer spacing was cho-

TABLE I. Typical signals (counts/sec).

Gas	Dark count	Stray light	Signal count	
			$y=19$	$y=1.5$
He	0.45	0.93	477	13
Ne	0.45	1.18	1270	24
Ar	0.45	1.0	5335	155

sen such that the instrumental profile, as measured in reduced frequency units x, was the same. Thus, experiments at the same y value should yield identical spectra, independent of the instrumental profile, provided of course that scaling is obeyed. The test to be made is then to record the spectra of He, Ne, and Ar, to normalize these to some fixed area when plotted as a function of $\omega/\sqrt{2}kv_0$, and to compare the three sets of results at the same value of y.

Figures 1, 2, and 3 are plots of the data before correction for dark count of the photomultiplier or for stray light. For the three gases, the densities correspond to the same values of y. The frequency scales while given in GHz have been chosen such that 1 cm on the page corresponds to the same number of x units for the three gases. The figures display the usual evolution of Rayleigh-Brillouin spectra from a single continuous profile in the kinetic or low-density region to the well-resolved triplet structure in the hydrodynamic or high-density domain. It is evident from the figures that the data are of high quality, and one can use them with confidence to examine scaling.

The striking similarity of the spectra already indicates, as a rough approximation, that scaling is valid. For a careful check of scaling it is desirable to carry out some manipulation of the raw data. The dark count and measured stray-light count were subtracted from the total counts. Then the positions of the Brillouin peaks were determined in GHz from the known interferometer spacing and from the measured separation of adjacent orders. (At least two complete Rayleigh-Brillouin spectra were recorded at each density.) For a given gas at a given density the four measurements of the Brillouin frequency ω_B agreed

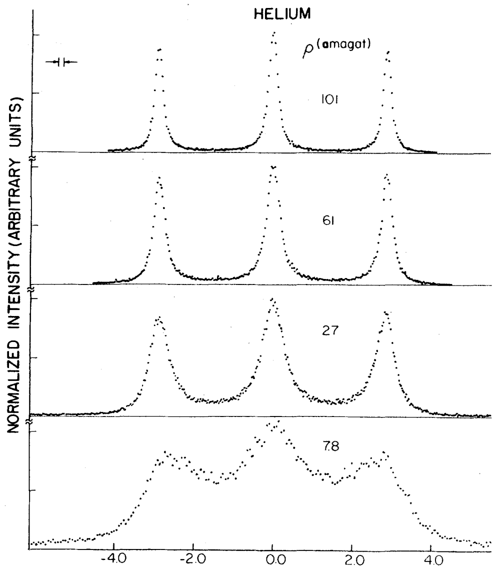

FIG. 1. A plot of the Rayleigh-Brillouin spectrum of He at several densities for 90° scattering. The instrumental width [full width at half maximum (FWHM)] is shown between arrows.

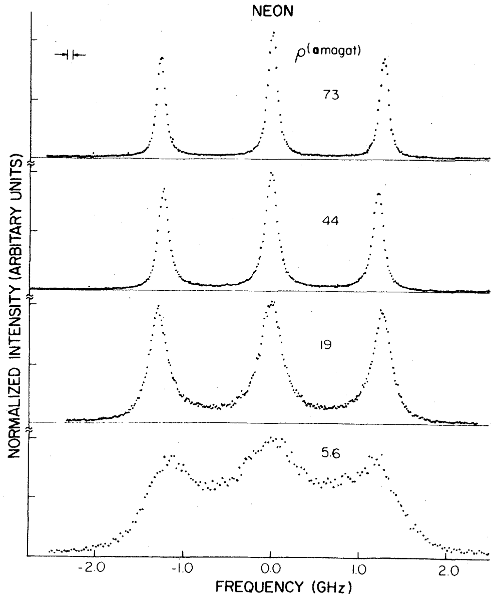

FIG. 2. A plot of the Rayleigh-Brillouin spectrum of Ne at several densities for 90° scattering. The instrumental width (FWHM) is shown between arrows.

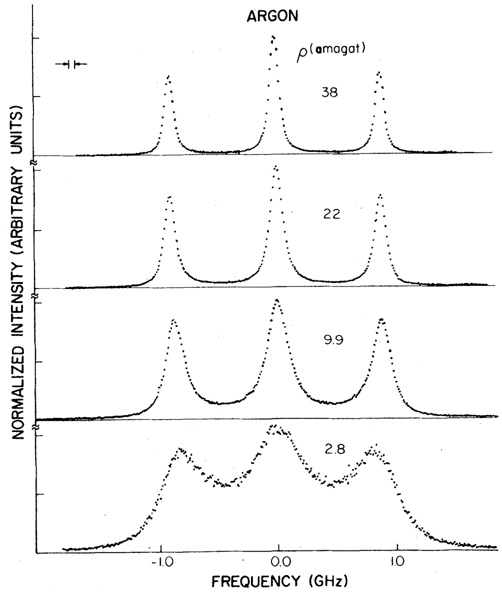

FIG. 3. A plot of the Rayleigh-Brillouin spectrum of Ar at several densities for 90° scattering. The instrumental width (FWHM) is shown between arrows.

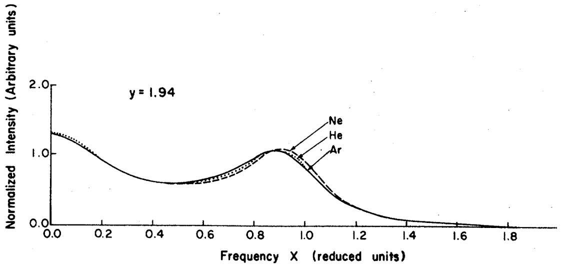

FIG. 4. An intercomparison of the experimental curves of He, Ne, and Ar at y equal to 1.94.

within $\pm\frac{1}{2}\%$. If such spectra were superimposed for data averaging then the Brillouin peaks would be artifically broadened by $\pm\frac{1}{2}\%$. To avoid this we made a minor adjustment to the frequency scale for each section of the spectrum such that the Brillouin positions all fell at the average value for that density. The spectra for two orders of the interferometer were then folded about the laser frequency and averaged. Next the counts were normalized to a common area measured from the laser frequency to one-half the spectral free range. All data points displayed in subsequent figures have been treated in this manner. Finally, to facilitate a check of scaling, a smooth curve was drawn through the points, and the three curves (one for each gas) were superimposed for each value of y.

Figures 4 to 7 show a comparison of the spectra for four values of the uniformity parameter. At y equal to 1.94, one is safely in the kinetic region. At y equal to 3.62, one is in the transition region between kinetic and hydrodynamic behavior. At y equal to 8.58 and 18.06 the spectrum has pure hydrodynamic characteristics. Clearly there are differences between the curves for He, Ne, and Ar, and one must conclude that departures from scaling are readily detectable.

There is little doubt that the departure from ideal scaling at large values of y arises from the fact that one is no longer in a region of density where the Boltzmann equation may be applied. The Boltzmann equation neglects the mean field or average interaction between the molecules. The mean field is responsible for the density dependence of the velocity of sound and for the deviation of the specific heats from their ideal-gas value. As is well known, in the hydrodynamic region the velocity of sound is directly proportional to the Brillouin frequency, while the intensities of the components are determined, via the Landau-Placzek relation, in terms of the specific heats. As the order of the pressures P required to reach the same y value is $P_{\mathrm{He}}>P_{\mathrm{Ne}}>P_{\mathrm{Ar}}$, one expects the Brillouin peaks to be ordered as to intensity and position as they are in the figures. A detailed quantitative analysis of the spectra in this region is possible and will be presented elsewhere. Suffice it to say that the spectra agree exactly with

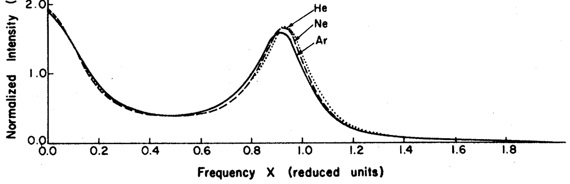

FIG. 5. An intercomparison of the experimental curves of He, Ne, and Ar at y equal to 3.62.

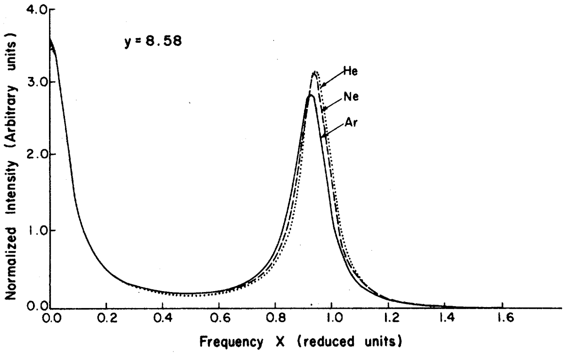

FIG. 6. An intercomparison of the experimental curves of He, Ne, and Ar at y equal to 8.58.

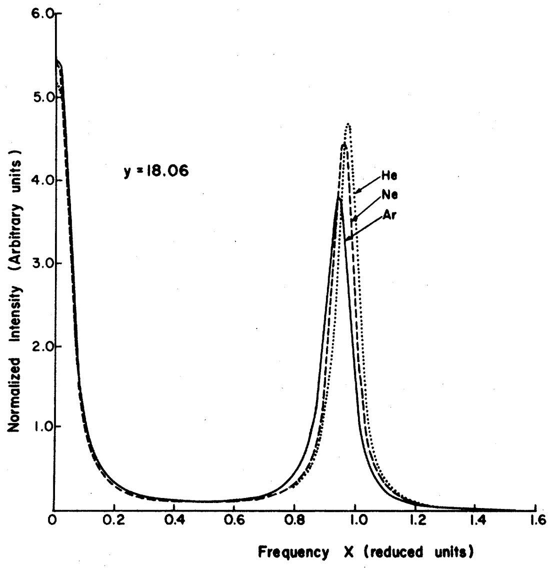

FIG. 7. An intercomparison of the experimental curves of He, Ne, and Ar at y equal to 18.06.

those predicted by hydrodynamic theory, and the differences in the spectra arise from the density dependence of the various input parameters, i.e., arise from the mean-field effects.

The situation is less clear at low values of y. Results were obtained at y equal to 1.52, 1.94, 3.62, and 5.28. We do not reproduce all the results here; the interested reader may refer to Ref. 12 for more details. There does not appear to be any systematic variation among the spectra except that small mean-field effects are detectable at y equal to 5.28. The general level of disagreement is of the order shown in Fig. 4. As this is the order of the statistical spread in the points shown in the raw-data curve of Fig. 1, one might dismiss the differences as due to experimental error. However, this is not completely justifiable. Typical counts per channel were 900, while the spectrum from x equal to zero to x equal to 1 was recorded in 100 channels. The fluctuation per channel is then ±30 counts, or 3%, which is the level of differences in Fig. 4. However, as a rough estimate let us assume that the smoothing averages five channels, each of which has four data points. Thus, the error bar associated with the smoothed curves should be $\sqrt{20}$ smaller than that for a single data point, or less than 1%. We thus conclude that scaling in the kinetic region is obeyed at the 3% level, i.e., is an excellent approximation, but that differences of the order of say 2% or less may exist for the gases He, Ne, and Ar. It is perhaps coincidental that Sugawara *et al.*[5] noticed differences of the same size between the theoretical curves for Maxwell and hard-sphere molecules, and that the differences occurred in the neighborhood of the Brillouin component, as they do in Fig. 4. We have therefore confirmed experimentally that Brillouin spectra in the kinetic region are relatively insensitive to details of the intermolecular potential. Although small differences may exist at the few percent level, meaningful measurements of these differences will only be possible with an improvement in the signal to noise of about 10. This will require an increase of 100 in the product of the laser power and integration time, which in practice will be very difficult to achieve.

Fookson *et al.*[11] have also reported on the Rayleigh-Brillouin spectra of He, Ne, and Ar at low y values. They compared their results with those calculated for Maxwell molecules. They do not comment on the large discrepancy between the calculated and observed spectra at low frequency for He and Ne. Presumably, the disagreement arises from an uncertainty in the stray-light correction. In the region between the central and Brillouin peak and around the Brillouin peak, there is general agreement between theory and experiment. For He, however, they find slightly better agreement if y was determined from the thermal conductivity rather than viscosity. For a consistent use of y this indicates that they also have detected small differences between the spectra for the three gases; i.e., they have detected small departures from scaling.

Clark[13] has examined the Rayleigh-Brillouin spectrum of Xe for values of y from 0.1 to 6 and compared the results both with kinetic and hydrodynamic calculations. In the kinetic regime Fig. 6 of Ref. 13 appears to show that the spectra are very slightly better described by a hard sphere rather than by a Maxwell molecule calculation. While not an explicit test of scaling, Clark's results are consistent with those presented here.

Some physical insight into the near success of scaling at low densities can be obtained by comparing the experimental results with certain theoretical curves. Starting with Boltzmann's equation the only exact calculations of Rayleigh-Brillouin spectra which have been carried out are for Maxwell molecules and for hard spheres.[8] As the existence of only two solutions is solely due to the mathematical complexity of the problem, it is not surprising that several authors[6,14,15] have resorted to model solutions. We choose to compare our results with what we call the S6R model. This, in terms of the jargon of the field, is a $3E$ model and can be obtained from the S6 molecular relaxation model[15] by suppressing the effects of internal degrees of freedom. (We are indebted to G. Tenti for supplying us with the program for the computation.) This theory is particularly satisfying as it has no adjustable parameters, requires only the viscosity and thermal conductivity (or equivalently y) and the Eucken ratio to specify the molecular interaction, has the correct free-streaming limit at low densities, and yields at high densities the correct hydrodynamic spectrum. By "correct hydrodynamic" we mean the ideal-gas hydrodynamic limit, or one in which mean-field effects are neglected. The second set of theoretical curves are those predicted by Mountain[2] using pure hydrodynamics. For both cases, the theoretical curves were convoluted with the instrumental profile, with allowance made both for overlapping orders of the interferometer and for the spread in wave vectors resulting from the finite cone of observation. They were then normalized to the same area as the experimental profiles. The input data were obtained from Refs. 16 to 23.

Figure 8 shows the experimental points for Ar compared with curves computed for S6R and by Mountian[2] at the two lowest values of y. The model solution describes the experimental results within the spread in points at all frequencies, ex-

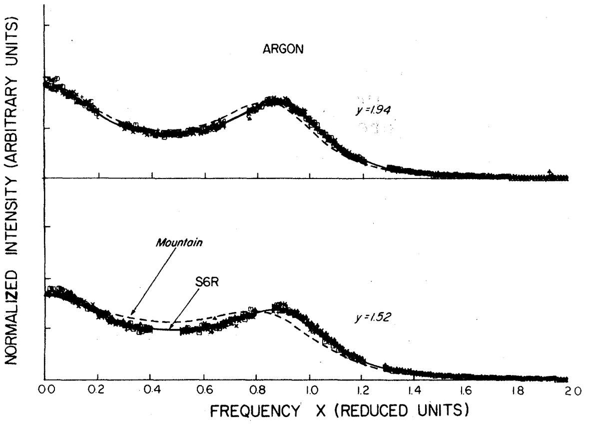

FIG. 8. A comparison of the experimental points for Ar at y equal to 1.94 and 1.52 with the curves predicted by hydrodynamics (Ref. 2) and by kinetic modeling (S6R).

cept for a small region near zero frequency at y equal to 1.52. This is remarkable agreement considering the simplicity of the model. The hydrodynamic curves, while not as successful, do approximate the experimental spectra. At lower values of y, one expects the model solution to give an adequate description, since as y approaches zero it becomes exact, whereas it is well known that the hydrodynamic curves diverge rapidly. As the major input parameters to the S6R calculation are the hydrodynamic quantities, viscosity, and thermal conductivity, one can conclude that the hydrodynamic modes dominate the collision term $J[f]$, i.e., they dominate the spectrum at all densities, the Knudsen region obviously being excluded from this statement. This in turn gives us a clearer insight into why the scaling law is so closely obeyed. The S6R spectrum, while a function of x, y, and the Eucken ratio E, is in fact insensitive to the variation in E at least over the range encountered in nature. That E varies but little simply reflects that it is a ratio of transport coefficients, both of which are a measure of the mean free path. The introduction of E into the theoretical spectrum is thus equivalent to a reintroduction of y, and therefore redundant. Thus the spectrum is a function of only two parameters.

The high-density behavior is related to these comments. If one neglects the density dependence of the velocity of sound, thermal conductivity, etc., and takes the Eucken ratio as a constant, then it is easy to show that the hydrodynamic equations can be expressed as a function of x and y alone. As the density dependence of the various parameters is not large, we understand why the spectra in the hydrodynamic region are similar at the same values of y. With mean-field effects included, one could make the spectra more nearly identical by modifying the frequency scaling from $[(\frac{1}{2})^{1/2}]\omega/kv_0$ to $[(\gamma/2)^{1/2}]\omega/kC_0$. This would place the Brillouin positions at the same value of x at all densities. However, it is not possible to modify the definition of y to simulate the kinetic scaling law. Intrinsically, the spectrum *is* a function of four parameters, as the reader may easily verify by examining Eq. (13) of Ref. 2.

In summary, we have carried out an experimental test of scaling for the rare gases He, Ne, and Ar. At high densities, departures from scaling can be attributed to mean-field or non-ideal-gas effects. In the kinetic region, although scaling is obeyed at the 3% level, the experiments indicate that differences of the order of 1 to 2% may exist.

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