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Experimental bulk viscosities of argon, krypton, and xenon near their triple point

P. Malbrunot, A. Boyer, and E. Charles
Laboratoire de Physique Appliquée, Centre d'Etudes d'Electronique des Solides,[*]
Université des Sciences et Techniques du Languedoc,
34060 Montpellier-Cedex, France
H. Abachi
Laboratoire d'Interactions Moléculaires,[†] *Université des Sciences et Techniques du Languedoc,*
34060 Montpellier-Cedex, France

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Precise measurements of acoustic attenuation were carried out near the triple point of argon, krypton, and xenon. The results obtained eliminate the discrepancies in the data for the bulk viscosity η_v for simple fluids. The value of η_v does not vanish near solidification and the ratio η_v/η_s, where η_s is the shear viscosity, remains low: 0.3—0.5. This result is fundamentally different from the Enskog theoretical value of 1.2 but agrees with those given both by the molecular-dynamic calculations for hard spheres and for Lennard-Jones fluids.

I. INTRODUCTION AND BRIEF SURVEY OF THE BULK VISCOSITY PROBLEM FOR SIMPLE FLUIDS

Bulk viscosity is a thermodynamic property whose existence can be linked to the progress in acoustic experimentation. In fact, it measures the difference between the real absorption of acoustic waves and those, called classical, given by the Stokes and Kirchoff theories. The two latter, which only involve the shear viscosity and the thermal conductivity, lead to the value

$$\alpha_{\text{cl}}=\frac{2\pi^2 f^2}{\rho c^3}\left[\frac{(\gamma-1)k}{c_p}+\frac{4}{3}\eta_s\right], \tag{1}$$

where f is the acoustic frequency, ρ is the density, c is the acoustic velocity, $\gamma=c_p/c_v$ is the ratio of the specific heats, k is the heat conductivity, and η_s is the shear viscosity. On the other hand, experimental absorption observed can only be written as

$$\alpha_{\text{obs}}=\frac{2\pi^2 f^2}{\rho c^3}\left[\frac{(\gamma-1)k}{c_p}+\frac{4}{3}\eta_s+\eta_v\right], \tag{2}$$

where η_v is the bulk viscosity

$$\eta_v=\frac{\alpha\rho c^3}{2\pi^2 f^2}-\left[\frac{(\gamma-1)k}{c_p}+\frac{4}{3}\eta_s\right]. \tag{3}$$

As for most liquids, the term linked to the thermal conductivity is very small with respect to the shear viscosity

$$\frac{\eta_v}{\eta_s}=\frac{4}{3}\left[\frac{\alpha_{\text{obs}}-\alpha_{\text{cl}}}{\alpha_{\text{cl}}}\right], \tag{4}$$

which is a measure of the difference relative to the classical attenuation. Two important facts can be noted: (i) whatever the liquid, this ratio remains on the order of a few units, and (ii) it varies only relatively slightly with temperature and density.

After its experimental discovery[1-3] this attenuation was the subject of many theoretical developments.[4-7] In the particular case of polyatomic fluids, it was associated with a molecular relaxation process, and more precisely, a thermal process to which must be added a structural relaxation for the associated liquids. Hence it is difficult to evaluate the exact role of the intrinsic bulk viscosity which is linked to a process of dilatation compression as can be done for the shear viscosity itself linked to a shearing process. This is why the study of monoatomic fluids, which should lead to a conclusive answer, is particularly interesting. For a long time, however, monoatomic fluids which do not present this type of relaxation were not supposed to have an excess, as this was considered quite logically as only possible in the case for dilute gases. In this study we have been able to demonstrate the existence of such an attenuation and hence of an intrinsic bulk viscosity.

Enskog's theory[8] for hard-sphere fluids can be used as a possible model to predict bulk viscosity for monoatomic fluids. There is no theory for more realistic model fluids, but computer simulations do exist.[9-12] These essentially confirm the existence of a bulk viscosity but indicate behavior very different from that predicted by Enskog's theory, especially near the triple point. On the other hand, experimental results for argon are contradictory and almost nonexistent for krypton and xenon. In fact, at 85 K near the triple point of argon, Galt,[13] using classical acoustic attenuation, and Rand and Stoïcheff,[14] using Brillouin-scattering experiments, found a low bulk viscosity. The attenuation they measured corresponded practically to the classical value, and led almost to a value of zero for the ratio η_v/η_s. At the same temperature, Naugle and Squire,[15] using identical acoustic measurements, found a large value leading to a ratio $\eta_v/\eta_s=0.75$, while Mikhailenko[16] later reported 0.56. Again at 85 K, Baharudin *et al.*,[17] with Brillouin scattering, gave $\eta_v/\eta_s=0.42$, while measurements carried out at higher temperatures and pressures[18–22] also corroborate a rather large value for η_v. As for krypton, the only measurements undertaken near the triple point are those of Baharudin's using Brillouin spectroscopy,[17] which yield $\eta_v/\eta_s=0.43$. A few degrees higher, at 120 K, Mikhailenko *et al.*[16] gave $\eta_v/\eta_s=0.46$. For xenon, Baharudin *et al.*[23] are again the only ones to have obtained results near the triple point, leading to $\eta_v \simeq 0$. These authors did not, in fact, give this value when they determined η_v. They mistakenly neglected the attenuation due to thermal conductivity. On the other hand, at a temperature 10 K higher than the triple point, Mikhailenko *et al.*[16] find $\eta_v/\eta_s=0.54$. In view of these results our aim was to provide additional experimental data at the triple point for argon, krypton, and xenon.

II. ANALYSIS OF THE ERRORS OF THE EXPERIMENTAL VALUES OF THE BULK VISCOSITY

Acoustic propagation (including the Brillouin spectrum study which corresponds to propagations of pressure fluctations at constant entropy) constitutes the only experimental technique available for the determination of bulk viscosity. Expression (3), which determines this bulk viscosity, is a difference between two terms and calls for a detailed error analysis. Writing (3) in the form

$$\eta_v = A - B \; , \tag{5}$$

where A corresponds to the acoustic measurements and B to thermodynamic data, and after differentiation, we obtain

$$\frac{\Delta\eta_v}{\eta_v} \le \frac{\Delta A}{A-B} + \frac{\Delta B}{A-B} \; , \tag{6}$$

where $A-B \neq 0$. Since the terms B and $\Delta B/B$ are independent of the acoustic measurements, it is possible to assume $\eta_v = xB$. With $\beta=\Delta B/B$,

$$\frac{\Delta\eta_v}{\eta_v} \le \frac{x+1}{x}\frac{\Delta A}{A} + \frac{\beta}{x} \; . \tag{7}$$

This equation enables us to estimate the relative importance of various sources of error in the existing data and to establish conditions under which new measurements should be undertaken.

Table I shows that there are too few thermodynamic results in the literature to make it possible to determine a mean value of the error $\Delta B/B$ with any significance. The value of $\Delta B/B = 4\%$ was therefore calculated using the largest difference between the various results obtained from the different sources. As this value is generally larger than the errors actually claimed by the respective authors, one can consider that 4% constitutes a maximum value for the error in B. Given this value of $\Delta B/B = 4\%$, in Fig. 1 we represent the final error $\Delta\eta_v/\eta_v$ as a function of x for various estimated values of the precision of the acoustic measurements $\Delta A/A$, which are generally of 5–10%; β/x is also plotted in order to stress the relative importance of the uncertainty of the thermodynamic data. These curves show, especially for low values of η_v, the important effect on $\Delta\eta_v/\eta_v$ of the subtraction represented in (3). Likewise, they reveal the relative prevalence of errors in the acoustic measurements with respect to those of the thermodynamic data, although it is often believed that the latter are the main cause of inaccuracy in the determination of η_v. Analyzed in this way, the liquid-argon bulk viscosity data that we previously mentioned may reveal errors of more than 100% in the case of Galt,[13] Rand and Stoïcheff,[14] and Baharudin *et al.*[17] who only

TABLE I. Uncertainties regarding the thermodynamic data from the cited references.

	$\frac{\Delta c_p}{c_p}$ (%)	$\frac{\Delta(\gamma-1)}{(\gamma-1)}$ (%)	$\frac{\Delta k}{k}$ (%)	$\frac{\Delta\eta_s}{\eta_s}$ (%)	$\beta=\frac{\Delta B}{B}$ (%)
References	30,31,16	32,33,26,16	34,35	36,37	
Argon	3.5	6	2.5	1	4
Krypton[a]					
Xenon[a]					

[a] For each property only one datum is available so, the determination of the several uncertainties is impossible.

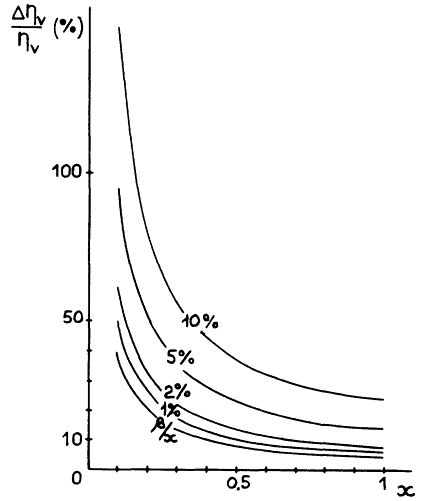

FIG. 1. Final accuracy of bulk viscosity determination for different conditions of η_v value and of accuracy of acoustic attenuation measurement. The uncertainty of the thermodynamic data is 4%.

claim 13%, 12%, and 11%, respectively, and an error of about 35% for Naugle and Squire who gave 7% for $\Delta A/A$. The first three results, which are almost in agreement in spite of their lack of accuracy, show that bulk viscosity can have a value of zero. Naugle and Squire are the only ones to have quoted a nonzero value for this viscosity. What is more, the error bandwidth of the latter authors and those of the others do not even overlap (Fig. 2), thereby revealing a large uncertainty as to the value and even the existence of η_v. For krypton and xenon only one series of results exists for each thermodynamic quantity needed for the determination of B. Hence we have calculated $\Delta B/B$ from the error given for each series, its value of 2.5% being approximately identical for krypton and xenon. In spite of this more favorable $\Delta B/B$, Baharudin's results for the bulk viscosity of krypton[17] could be in error by 70%. The same authors obtained for the bulk viscosity of xenon[23] a result which could be in error by 400%. Once again the extrapolation of results of Mikhailenko *et al.*, obtained at higher temperature, to the triple-point temperature is hazardous since their accuracy is no better than 40% for the older data[22] and 30% for the more recent data.[16]

In order to clarify the situation, we have carried out a new series of measurements with improved precision so as to obtain 2.5% for $\Delta A/A$ instead of the values of 7–13% in the existing data.[13–15,17] An acoustic method was chosen which we hoped would yield a better accuracy than the one used to determine Brillouin linewidths. This is the well-known pulse-echo technique used for a variable acoustic path. To obtain the best possible precision we have made certain improvements in both the usual electronic setup and absorption cell. MATEC equipment especially adapted to ultrasonic pulse-echo experiments was used, and, in particular, this included the MATEC attenuation measurer which permits direct and reproducible measurements without any tricky adjustments of the signal amplitudes on an oscilloscope screen. The variable-path-length system used has been designed as a result of a preliminary detailed analysis of the errors that the several defects of the echo signal involve. The sharp shape of the echo signal was ensured as follows: (i) by a well-adapted transducer holder with elaborate electrical contacts, (ii) by optically flat surfaces both for the reflector and for transducer surfaces, and (iii) by a high degree of precision in the parallelism of the transducer surfaces. Good stability of the echo signal was obtained by the use of relatively short acoustic paths which obviates the need for large gain in the receiver amplifier which leads to a poor signal-to-noise ratio. Another improvement in the echo signal stability was obtained by a rigorous elimination of the temperature gradient between transducer and reflector. Finally, we performed our attenuation measurements very near the triple point in the best possible temperature conditions using a precision cryostat. This was established very accurately with a standardized platinum resistance thermometer directly immersed in the liquid rare-gas sample.

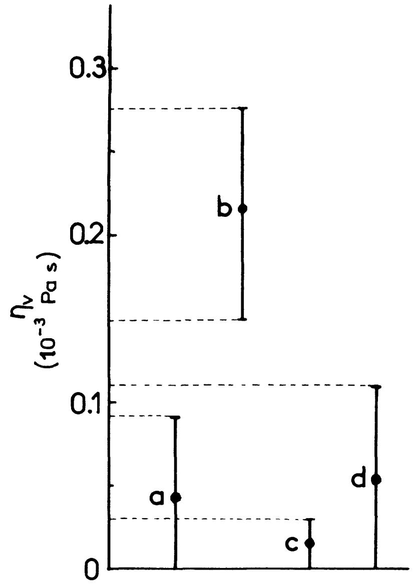

FIG. 2. Experimental situation of the bulk viscosity of argon near its triple point. (a) Galt (Ref. 13), (b) Naugle and Squire (Ref. 15), (c) Rand and Stoïcheff (Ref. 14), and (d) Baharudin *et al.* (Ref. 17).

III. MEASUREMENTS OF THE ULTRASONIC ATTENUATION

A. Experimental details

Figure 3 represents the measurement cell used. The quartz is set on an annular slide to avoid any parasitic effects due to a plane support, the back wave being largely absorbed by a cone device. The movement of the reflector is without play owing to a longitudinal guide (ball-type device); this is controlled by a screw outside the cryostat and conveyed by a long thin guide tube. The displacements are read on a precise micrometer. The parallelism between the quartz and the reflector is adjusted with the help of a simple device with three differential screws which makes possible an adjustment to better than 3″ of arc.[24] A platinum resistance thermometer dips in the liquid along the sample column owing to a special housing in the cell (see Fig. 3). Lastly, a group of differential thermocouples placed at the top and bottom of the useful part of the liquid sample enables one to check the thermal gradient and its elimination by controlling two heating resistances outside the cell.

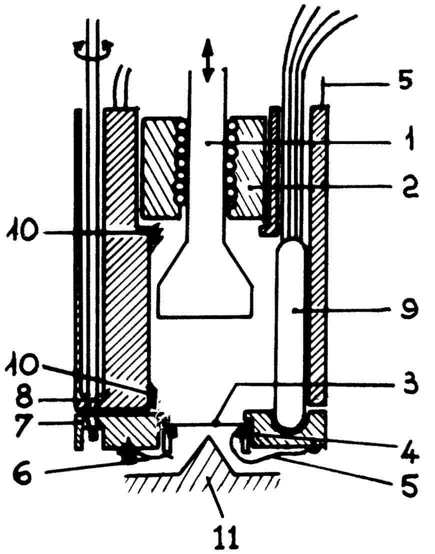

FIG. 3. Our measurement cell. 1, longitudinally movable reflector with an optically flat face (within 0.2 μm); 2, longitudinal guide (ball-type device); 3, transducer: X cut piezoelectric quartz with optically ground faces (flat within 0.2 μm, parallel within 3″ of arc); 4, high-frequency electrode, it consists of two rings: one in metal is in contact with the transducer and it is surrounded by the second in teflon which ensures the electrical insulation; 5, small coaxial cable; 6, one of the three light spring leaves; 7, movable transducer holder (for parallelism adjustments); 8, one of the three differential screws; 9, platinum resistance thermometer; 10, differential thermocouples; and 11, cone absorption device.

The electronic apparatus was composed of a MATEC group comprising a receptor generator 6000 and an attenuation measurer 2470 A.

The measuring cell is housed in a low-temperature cryostat, similar to the one already described,[25] with a stability on the order of several thousandths of one degree kelvin between 78 and 300 K.

B. Measurements

Attenuation readings were carried out under conditions of what the manufacturers of the electronic apparatus call "single echo" by comparing the echo's height to a fixed reference value. From the differences in height of the first echo for each reflector position we obtained the attenuation values for each corresponding acoustic path. These values were corrected for diffraction effects (see Sec. III C 2) and fitted by a straight line. The slope is the attenuation per centimeter. At the same time, the divergence from linearity was calculated for each point. In each case it was inferior to the reading accuracy on α (see Table II). It is therefore possible to assert (i) that losses due to diffraction were well corrected (see Sec. III C 2) and (ii) that there is no major flaw in the parallelism for the successive positions of the reflector.

The quartz was tuned to the right resonance with an uneven harmonic which guarantees the best possible conditions for the signal-to-noise ratio by giving the maximum height for the first echo. This tuning frequency was measured by a classic method, the hf voltage of the cell being picked up through a high-impedance probe. This was added to the voltage of the steady wave whose frequency was adjusted by noting a zero beat. A frequency meter then determined the corresponding frequency. The nondispersive behavior of simple liquids, which is easily predictable in the field of acoustic frequencies, has been so often experimentally confirmed that it was not deemed necessary to repeat the measurements at different frequencies. A frequency of 42 MHz was used which corresponds to good conditions given our equipment: (i) small diffraction corrections and (ii) attenuation values high enough for an acceptable relative accuracy of the measurements.

The speed of sound was not measured considering the highly accurate data available. The values given by Lim and Aziz[26,27] were chosen in view of the care and accuracy with which their experiments were carried out and also with respect to both the level of acoustic and of temperature measurements.

TABLE II. Present results of attenuation measurements and of bulk viscosity calculations performed with data of the references cited in Table I. (a) argon, (b) krypton, and (c) xenon. x [formula (7)] has approximately a constant value on the order of 0.3 for argon and of 0.2 for krypton and xenon.

T K	α (dB/cm)	$\Delta\alpha/\alpha$ (%)	α/f^2 (10^{-15} m^{-1}s^2)	η_s (mPa s)	ρ (kg m^{-3})	c (m s^{-1})	k (W K^{-1}m^{-1})	c_p (J kg^{-1}K^{-1})	γ	η_v (mPa s)	η_v/η_s
					(a)						
83.86	2.22	0.35	14.60	0.300	1414	860.7	0.1258	1093.2	2.01	0.150_6	0.5
84	2.22	0.35	14.60	0.295	1413.5	859.8	0.1256	1093.9	2.01_3	0.155	0.52_5
85	2.23	0.25	14.65	0.285	1407	853	0.1246	1096.4	2.02_6	0.151_5	0.53_2
86	2.24_8	0.4	14.77	0.276	1401	846.2	0.1236	1099.4	2.04	0.150	0.54_4
88	2.27_5	0.3	14.95	0.259	1388	832.5	0.1215	1106.7	2.07_1	0.143_6	0.55_4
90	2.30_5	0.25	15.15	0.243	1376	818.6	0.1194	1115.2	2.10_6	0.137	0.56_3
93	2.39	0.25	15.70	0.226	1357	794.4	0.1163	1130.2	2.16_2	0.120_2	0.53_1
95	2.47	0.3	16.23	0.216	1344	783	0.1143	1139.0	2.19_8	0.122_2	0.56_6
97	2.59_5	0.26	17.05	0.207	1331	768.6	0.1122	1149.0	2.23_7	0.125_2	0.60
		Average 0.30									
					(b)						
115.83	3.16_5	0.22	21.6_3	0.457	2442	700.6	0.0928	535.8	1.99_5	0.138_5	0.30_3
116	3.16_5	0.25	21.63	0.455	2440	700	0.0927	535.8	1.99_5	0.138_3	0.30_4
117	3.16_9	0.7	21.66	0.440	2433	696	0.0920	535.9	2.00_5	0.141	0.32
118	3.18_4	0.25	21.76	0.424	2426	692	0.0913	536.1	2.01_5	0.148	0.35
120	3.21_4	0.3	21.9_7	0.403	2411	684	0.090	537	2.03_6	0.148	0.36_7
125	3.36_5	0.25	23.00	0.362	2373	663.7	0.087	540.5	2.09_7	0.149	0.41_2
130	3.80	0.3	26.00	0.323	2333	642.9	0.084	544.1	2.16_1	0.207	0.64
		Average 0.25									
					(c)						
161.44	4.11_4	0.2	26.9_7	0.572	2962	654.9	0.075	343.03	2.00_8	0.153_7	0.27
162	4.12	0.2	27.00	0.555	2959	653.4	0.0747	343.10	2.00_9	0.169_4	0.30_5
163	4.13_2	0.2	27.10	0.540	2952	650.7	0.0743	343.26	2.01_4	0.177	0.32_8
165	4.18	0.18	27.40	0.528	2939	645.2	0.0734	343.5	2.02_2	0.173_3	0.33
170	4.32	0.18	28.30	0.492	2906	631.5	0.0712	345.77	2.05_4	0.176_2	0.36
175	4.55_4	0.19	30.0	0.453	2872	617.6	0.0689	349.2	2.09_3	0.208_2	0.46
180	4.99_5	0.22	33.2	0.418_5	2838	603.5	0.0666	353.4	2.13_8	0.276_7	0.66
		Average 0.2									

C. Errors and corrections in attenuation determination

1. Losses due to the nonparallelism between the reflector and the transducer

These losses fall into two classes: (i) geometric losses due to the beam returning to the transducer in a direction which is not exactly perpendicular to its faces. In the present case, the nonparallelism being within 3″ of arc and only the first echo being used, these losses do not exceed under the most unfavorable conditions 10^{-4} (maximum acoustic path; i.e., 40 mm), and (ii) losses due to phase differences between the different parts of the cross section of the received beam on the active area of the transducer. This corresponds to a slightly different path induced by imperfection in the angular alignment between transducer and reflector. Such losses can be important if the phase differences attain quadrature or opposition. This happens when $a\theta$ is not small with respect to λ, a being the transducer radius, θ the angle between the reflector and the transducer (nonparallelism), and λ the wavelength. We avoided such losses by keeping $a\theta \leq 0.1$ μm for $\lambda = 20$ μm and provided that the parallelism was checked and adjusted slightly, if necessary, after each displacement of the reflector, as did Cowan and Ball.[21] The total incidence of these losses on the measured attenuation is calculated by integrating the effects of the phase differences at all radial distances from the center of the transducer.[28] In our case, where $\theta = 3''$, these losses would be 2×10^{-4} dB/cm, it is entirely negligible for attenuation values between 2.2 and 5 dB/cm.

2. Diffraction losses

Considering the restricted dimensions of our apparatus and the frequency of the measurements, the work was carried out in the Fresnel zone and therefore does not call for complicated diffraction corrections. These were established using the approximation proposed by Bass,[29]

$$R = \frac{|P_{\mathrm{av}}|^2}{|P_{0\mathrm{av}}|^2} = 1 - 2(\pi\zeta)^{-1/2}\left[1 - \frac{\zeta^2}{2k^2a^2}\right] + 2(\pi\zeta)^{-1}\left[1 - \frac{\zeta^2}{2k^2a^2}\right]^2 .$$

This makes it possible to calculate the ratio of the two pressure amplitudes, P acting on the transducer, and P_0 which would be observed in the absence of diffraction for the same acoustic path z; k is the magnitude of the wave vector, a is the radius of the transducer, and ζ is a variable which is a function of the acoustic path and of the experimental conditions. ζ is defined as

$$\zeta = \frac{k}{2}[(z^2 + 4a^2)^{1/2} - z] ,$$

which is only valid for $\zeta > 1$, i.e., for $z/a < ka/4\pi$. Since there is a direct proportionality between V, the voltage at the transducer terminals, and the acoustic pressure P, we have

$$R = \frac{V^2}{V_0^2} ,$$

where the index 0 indicates the absence of diffraction.

In the present case, one may assume that intrinsic losses due to attenuation and diffraction losses can be added. Thus to attain the attenuation alone, the voltage corresponding to each echo should be increased by an amount corresponding to that lost by diffraction. Since the measured attenuation is given by $\alpha_m = 10\log_{10}(V_r^2/V^2)$, where V_r is the reference voltage mentioned earlier (Sec. III B concerning the "single echo" conditions of the MATEC attenuation measurer), the real attenuation will be

$$\alpha_m = 10\log_{10}\frac{V_r^2}{V^2 + V^2(1-R)} = 10\log_{10}(V_r^2/V^2)\left[\frac{1}{1+(1-R)}\right] \simeq 10\log_{10}\frac{V_r^2}{V^2}R .$$

As for each of our measurements, $1 - R \ll 1$,

$$\alpha = \alpha_m + 10\log_{10}R .$$

Finally, α was deduced from two attenuation readings α_1 and α_2 corresponding to two the distances z_1 and z_2,

$$\alpha = \alpha_2 - \alpha_1 = \alpha_{m_2} - \alpha_{m_1} + 10\log_{10}(R_2/R_1) .$$

This diffraction correction is not constant for a given acoustic path length $z_2 - z_1$ and, it increases as one gets closer to the transducer, i.e., when z decreases (see Fig. 4). Each attenuation reading was thus corrected. The error being on the order of 1% here, they must be taken into account. It must be added that in the present case the approximate character of the Bass equation has no noticeable influence on the final values of α (less than 0.1%).

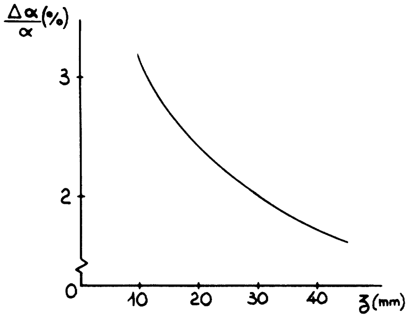

FIG. 4. Variation of the correction of diffraction losses with acoustic path z.

3. Disturbances due to the formation of bubbles

The fact that measurements were carried out near the triple point, i.e., near the lowest possible saturation pressures, dictated that precautions should be taken with respect to bubble formation. The pulse-echo method is preferable since it practically eliminates any heating effects on the liquid, so in the present case, the total ultrasonic energy supplied to the liquid cell is, at most, 10^{-3} J.

As for the acoustic pressure whose maximum is on the order of the vapor pressure, it is hard to evaluate under what conditions microvapor bubbles (dissolved gases being eliminated by the filling conditions which result from a distillation under a secondary vacuum) are created and are unable to disappear or appear at 40 MHz and oscillating around an average diameter resulting in the medium being inhomogeneous. With the equipment used it was impossible to analyze any such phenomenon, but we did verify that under the most extreme measurement conditions, i.e., when the acoustic pressure and the pressure in the cell equal the vapor pressure, no disturbance of the echo or modification of the attenuation value could be found.

4. Reflection losses

These correspond to the part of the wave that is transmitted in the reflector mass. They were eliminated by the differential determination procedure of attenuation from the difference of heights of the first echo when the acoustic path length varies (see Sec. III B).

5. Precision

Readings of α_1 and α_2 were carried out at 0.1 dB. The corresponding mean error on α, calculated using our program for $\alpha = f(z)$, is approximately 2%. As for the frequency, the reproducibility of our determination by canceling on beats (Sec. III B) is 0.1%; i.e., 0.2% for f^2 leading finally to a maximum error of 2.2% for α/f^2. The densities of the saturation curve are given within 0.1% and the speeds within 0.1%, which gives

$$\frac{\Delta A}{A} \leq 2.2 + 0.1 + 0.3 \simeq 2.5\% \ .$$

IV. RESULTS

These are listed in Table II. As for the measurements, i.e., α/f^2, they are in agreement with those given by Cowan and Ball[21] but differ slightly from those of Mikhailenko[16] (see Fig. 5). The fact that our values are systematically lower than those previously obtained by Soviet and Canadian authors can be largely attributed to diffraction corrections that these authors did not explicitly mention. With regard to the argon bulk viscosity, the uncertainty of 4% over B (see Sec. II above) is of course a maximum value, but at present no criterion enables us to choose any particular value from the available data. We have kept this value of 4% in our error analysis. Thus the maximum error calculated using expression (7) and the mean values of x given in Table II is 20%. For krypton and xenon, the uncertainty of 2.5% for B, expression (7), and x values of Table II lead to a maximum uncertainty of 25% in our η_v data. Although this precision is still far from satisfactory, it is sufficient to assert the existence of a bulk viscosity for simple liquids at the triple point and a lowering of the ratio to values definitely less than 1. As for the difference in values between argon and other liquids, it is hazardous to attempt an interpretation in view of the lack of precision of the results. Nevertheless, one is tempted to attribute this difference to the fact that krypton and xenon, being more dense near solidification, would have a more "rigid" behavior towards the dilation compression of ultrasonic waves, whereas their classical absorption (thermal and shear) would increase as for argon.

V. COMPARISON OF OUR RESULTS WITH THE THEORETICAL RESULTS AND WITH THOSE OF MOLECULAR DYNAMICS

The first step in this confrontation is, of course, a comparison of the different values of the ratio η_v/η_s given by experiment, theory, and simulation. This comparison enables one to appreciate the degree of coherence of the theory, or that of the simulation, for both properties linked to the mechanical deformations of the medium while freeing it of any adjustments of the molecular parameters: sphere diameter for rigid spheres, diameter of the potential

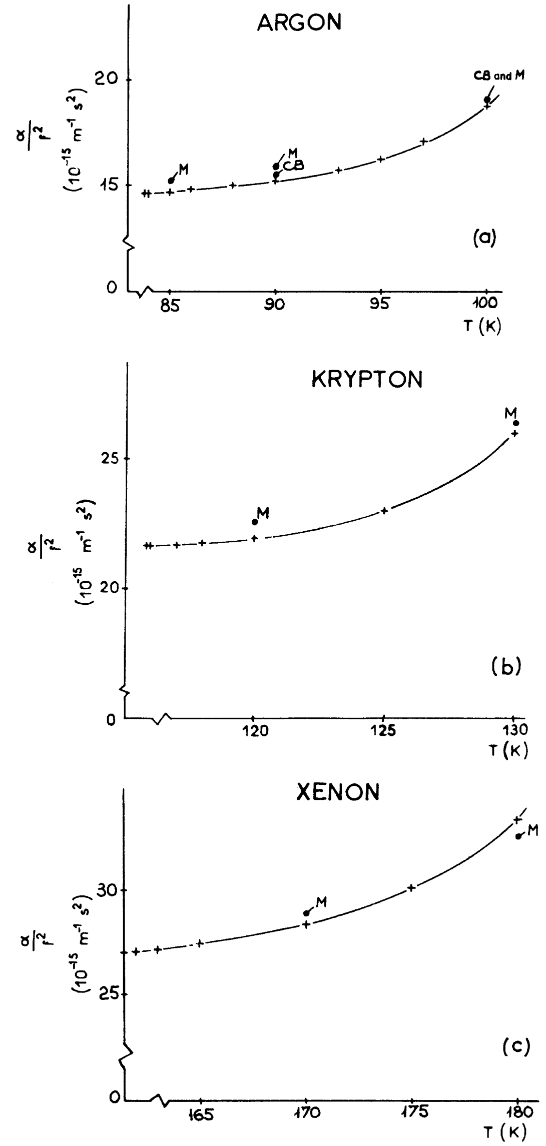

FIG. 5. Acoustic attenuation on saturation curve near the triple point for argon, krypton, and xenon. CB, Cowan and Ball (Ref. 21), and M, Mikhailenko *et al.* (Ref. 16).

cancellation, depth of the well for Lennard-Jones, etc. Further, it is evident that an examination of η_v and then η_s is necessary since the uncertainties related to the choice of the molecular parameters are a part of the difficulties of this confrontation.

Up until now, the only theory of transport phenomena in dense fluids elaborated is the one due to Enskog and its several improvements, all other results being due to computer simulations. In the following comparison, we classify all data according to the interaction model from which they were obtained.

A. Hard-sphere fluid

This is the basis of Enskog's theory. Under present conditions, i.e., high densities near solidification (with no reference to the triple point which does not exist for a hard-sphere fluid), the ratio stemming from Enskog's theory[8] is 1.2, a value in total disagreement with our results. In fact, the relative importance of bulk viscosity results from the fact that this potential has no distance effect; therefore, only the kinetic effects contribute to the fluid's elastic response. This response is low and yields too long a relaxation time for pressure variations.

The detail of η_s and η_v values expressed in real units is presented in Table III. The hard-sphere diameter used was the one advocated by Abachi.[38] It corresponds to a packing fraction equal to 0.491 at solidification. One notes that in spite of this precaution to fit the model as closely as possible to the actual fluid, there is still no agreement even regarding the shear viscosity. This shortcoming in Enskog's theory at high densities is not only due to the form of the potential for hard spheres, but also to the basic hypotheses themselves which neglect multiple collisions and consider particle velocities as independent of their position. This is contrary to the collective character of the kinetic momenta transfer which the shear viscosity represents. Furthermore, Vermesse's[39] comparison for argon's dense gas corroborates this point of view as the difference is of the same order in a field where kinetic effects are larger. Finally, the best proof of these assertions is given by the molecular-dynamics calculation performed by Alder, Gass, and Wainwright on the model of hard spheres.[9] Their values also figure in Table III as these authors themselves gave their results in relation to the Enskog theory. Their calculations, which are carried out on assemblies of 108 and 500 particles, account for evolution in time of the autocorrelation function corresponding to each transport property. Thus they found that at high densities the autocorrelation function of the stress tensor is prolonged for a long collision time showing a memory effect due to collective phenomena. In particular, they showed that it was the potential contribution (which only intervenes for hard spheres at the time of collision) which plays a role in this effect. For the shear viscosity, this results in a noticeable increase, and the value is even higher than the actual one; bulk viscosity itself is decreased and is therefore closer to actual values. As a consequence, Alder's, Gass's, and Wainwright's ratio η_v/η_s is also nearer to the experimental results. The agreement is probably a little fortuitous given the low accuracy with which η_v is obtained either experimentally or using the molecular-dynamics techniques. If

TABLE III. Comparison of viscosities obtained from experiment, from Enskog's theory, from "kinetic reference theory" and from molecular dynamics for hard-sphere and soft-sphere fluids.

	Experiment's temperature: 0.1 K above triple point			Enskog's theory			"Kinetic reference theory"			Molecular dynamics Hard-sphere fluid			Molecular dynamics Soft-sphere fluid		
	η_s (mPa s)	η_v (mPa s)	$\frac{\eta_v}{\eta_s}$	η_s (mPa s)	η_v (mPa s)	$\frac{\eta_v}{\eta_s}$	$\eta_s{}^a$ (mPa s)	$\eta_v{}^a$ (mPa s)	$\frac{\eta_v}{\eta_s}{}^a$	η_s (mPa s)	η_v (mPa s)	$\frac{\eta_v}{\eta_s}$	η_s (mPa s)	η_v (mPa s)	$\frac{\eta_v}{\eta_s}$
Argon	0.300	0.150	0.50	0.230	0.280	1.2	0.224 0.342 0.377	0.20 0.247 0.257	0.89 0.72 0.68	0.496	0.168	0.34	0.325		
Krypton	0.455	0.139	0.30_5	0.345	0.415	1.2				0.745	0.249	0.33	0.494		
Xenon	0.555	0.170	0.30_6	0.430	0.517	1.2				0.928	0.310	0.33	0.617		

[a] The three values correspond to three different sphere diameter determinations (see Ref. 40).

this ratio has, therefore, a realistic value, the disagreement in the actual value of shear viscosity is largely a scale problem due to the choice of diameter for hard spheres (η_s is proportional to σ^3). One can then conclude that Enskog's theory and especially the molecular-dynamics results of Alder, Gass, and Wainwright are close enough to the actual behavior of fluids to serve as the basis for perturbation theories which fit the sphere's diameter more adequately as a function of density and temperature.

The recent "kinetic mean-field theories" of Karkheck and Stell[40] can be both considered as perturbation theories and as improvements of the Enskog theory. Their application to real fluids is achieved through the method of the adjustment of the sphere diameter using one of the well-known perturbation theories. For argon, near the triple point, the generalized theory (called kinetic reference theory by the authors) leads to a ratio η_v/η_s between 0.7 and 0.9 according to the method of determination of the sphere diameter. This constitutes a notable improvement on the ratio given by Enskog in spite of the discrepancies of η_s and η_v with respect to experimental data (see Table III).

B. Soft-sphere fluid

Hoover and co-workers obtained η_s and η_v by simulating Couette flow and cyclic dilatation compressions using so-called nonequilibrium molecular dynamics. They obtained both shear[41] and bulk[11] viscosities for a soft-sphere fluid having a potential

$$\Phi(r)=\epsilon\left[\frac{\sigma}{r}\right]^{12}.$$

This was chosen during the perfecting of their technique because it constituted an interesting stage before a Lennard-Jones fluid. Evaluated with respect to simple fluids, their results led to a shear viscosity, near solidification, of the order of the experimental values. For the values of σ and ϵ/k chosen, the difference is 10% (Table III). This choice of parameters for this potential is purely arbitrary as the model is still far from that of a real fluid. This model only takes into consideration the fluid-solid transition. It does not distinguish between the gas and liquid phases, and its thermodynamic properties are proportional to $\rho^4(\epsilon/k)$ (i.e., one isotherm determines all "state" properties). We chose the ϵ/k of the Lennard-Jones potential (120 K for argon, 171 for krypton, and 221 for xenon) and the value from the solidification density of a soft-sphere fluid[42] $\rho(\epsilon/kT)^{1/4}=0.813$ for the temperatures corresponding to the triple point of each simple liquid.

Bulk viscosity was not given close to solidifica-

TABLE IV. Values of viscosities obtained from soft-sphere molecular dynamics.

	η_s (mPa s)	η_v (mPa s)	$\frac{\eta_v}{\eta_s}$
Argon corresponding temperature 130 K	0.237	0.0152	0.06
Krypton corresponding temperature 144 K	0.338	0.0233	0.07
Xenon corresponding temperature	0.383	0.029	0.075

TABLE V. Comparison of viscosities obtained from experiment and from Lennard-Jones molecular dynamics for LVK's state. LVK(864), results obtained by Levesque, Verlet, and Kurkijarvi (Ref. 10) for a system of 864 particles; L(108), results obtained by Levesque (Ref. 43) for a system of 108 particles; L(256), Ref. 43, but for 256 particles; L(864), Ref. 43, but for 864 particles; Ha, results obtained by Hoover *et al.* (Ref. 12) from a zero-frequency extrapolation; Hb, results obtained by Hoover *et al.* (Ref. 12) under lower-frequency conditions; the force constant of the Lennard-Jones (6—12) potential are (Ref. 8) for argon $\sigma = 3.405$ Å and $\epsilon/k = 119.8$ K, for krypton $\sigma = 3.60$ Å and $\epsilon/k = 171$ K, and for xenon $\sigma = 4.10$ Å and $\epsilon/k = 221$ K.

		η_s $(\sigma^2/\sqrt{m\epsilon})$	η_v $(\sigma^2/\sqrt{m\epsilon})$	$\frac{\eta_v}{\eta_s}$
Experiment	Argon	3.33	1.66	0.5
	Krypton	3.25	1.0	0.3
	Xenon	3.62	1.1	0.3
Molecular dynamic	LVK(864)	4.03	1.05	0.26
	L(108)	2.97	1.13	0.38
	L(256)	2.92	0.89	0.30
	L(864)	3.85	1.04	0.27
	H a	3.18	1.55	0.48
	b	2.70	1.10	0.40

tion. The values available at high densities (Table IV) are about ten times smaller than the experimental ones, so the ratio does not have the usual value.

Thus the soft-sphere model, in spite of its aspect which is less schematic than that of hard spheres, does not enable one to account really well enough for the behavior of real fluids. At high densities, the particles of such a soft-sphere fluid undergo an almost permanent repulsive action which in their movement makes them dependent on each other and thereby increases kinetic momenta exchanges. In comparison with the hard-spheres model, this results in an increase in the shear viscosity. Moreover, this repulsion also contributes to a high relaxation in relation to pressure variations, i.e., to a very short relaxation time to which corresponds a bulk viscosity much smaller than that of rigid spheres. The essential contribution of this model with respect to hard spheres is at the temperature-dependency level, but for the potential energy the absence of an attractive well makes it inadequate, especially at high densities, which is also the case for the hard-sphere model. What is more, the bad value of the ratio η_v/η_s eliminates any possibility of a perturbation theory by fitting the parameters σ and ϵ as a function of the physical conditions: i.e., density and temperature.

C. Lennard-Jones fluid

The work near the triple point by Levesque, Verlet, and Kurkijarvi[10] (LVK) has become a reference for this model. This is why many other studies have been carried out at the same density $n\sigma^3 = 0.8442$ and temperature $kT/\epsilon = 0.722$. With the usual parameters σ and ϵ/k the state of LVK is acceptable only for argon, and it is found to be closer to the triple point than if the Lennard-Jones fluid data are taken into account. One would be tempted to consider that in such a restricted area as the one around the triple point, parameter fitting and simulation for the Lennard-Jones two-body interaction model are not reliable enough for such a state correspondence to be significant. So, in the present case, no attempt has been made to approach reality with questionable specific fittings. It is considered that LVK's state was near the triple point for all three liquids, which is fully justified since the respective data, experimental and calculated, are of relatively low accuracy and do not present any noticeable variation in the temperature range on the order of 10 K above the triple point.

Table V presents a comparison of results obtained for η_s and η_v: (i) with the Green-Kubo (GK) method by LVK over 864 particles and more recently by Levesque[43] over 108 and 256 particles and (ii) with the method called nonequilibrium from an isothermal oscillating shear and a dilation compression.[12]

With regard to the ratio η_v/η_s, given the limited accuracy, the agreement can be considered as good since the orders of magnitude are identical and the values lie within the same uncertainty limits. η_v/η_s

values given by GK for a large number of particles tend to be a little low especially if we consider that LVK's state is farther away from the triple point than our measurements. This is due to a too-great shear viscosity which in turn results from the prolongation of the stress autocorrelation function, i.e., the well-known "long-time tail" already mentioned in the case of hard spheres. Results at zero frequency by Hoover *et al.*[12] are to be considered with more reservations, because of the added uncertainty of an extrapolation, than those obtained at various frequencies and which yield an almost constant $\eta_v/\eta_s = 0.38 \pm 0.02$. For the experimental checking of a frequency effect on the viscosities to which Hoover alludes, it would necessitate measurements at minimum frequencies of a few tens of gigahertz for simple liquids (ten times the frequency range usually accessible with Brillouin spectroscopy).

In order to consider the values for η_s and η_v in detail, we expressed our experimental data for argon, krypton, and xenon in reduced units with the usual values for ϵ/k and σ parameters (used in Table V). One notes immediately that these viscosities are not really in a corresponding state. This is not surprising since this is also the case for the states themselves. Krypton and xenon are in better agreement than argon with the GK results, especially at the bulk viscosity level. This could lead one to assume that the strong repulsion in r^{-12} for the Lennard-Jones potential which brings about a strong bulk modulus and low bulk viscosity at high density is better adapted to these atoms which one can consider as having a denser electronic structure than argon. An overestimation of shear viscosity in the case of GK calculation applied to big systems was observed by Alder for hard spheres (systems with 108 and 500 particles). There is no predominant influence of the potential form (presence of an attractive well and more realistic repulsion) on this effect. However, in the case of hard spheres, the differences with respect to reality were sufficiently homogeneous (good ratio η_v/η_s) so that it could be hoped to improve the results by a perturbation theory. For the Lennard-Jones fluid, the situation is different; in the present case for example, an acceptable agreement for bulk viscosities would no longer be respected if the parameters were modified in order to improve the shear viscosity agreement. In this sense we agree with Vermesse's and Levesque's conclusions who carried out GK calculations for three different interactions including the Lennard-Jones model.[44] Compared to those obtained for krypton their results show that none of these was really adapted, and it is thus impossible to apply a perturbation theory to the Lennard-Jones fluid.

To conclude, it is possible to say that whatever the refinements and the accuracy of the calculations, the real potentials for two bodies are insufficient at high densities. It would be advisable, therefore, for the introduction of three-body contributions to intervene at the potential form level, or, for example, in a more phenomenological manner at path level, by taking into account supplementary particles and the incidence of perturbation type on stress tensor autocorrelation functions.

VI. CONCLUSION

Stokes's assertion that "there is no reason why a motion of dilation uniform in all directions should give rise to a viscous force or cause the pressure to differ from the statistical pressure corresponding to the density" has been experimentally invalidated. On the contrary, Hoover *et al.* recently wrote: "the bulk viscosity describes the irreversible resistance, over and above the reversible resistance given by the isentropic bulk modulus to changes of volume." This has been verified by our experiment since bulk viscosity exists for simple liquids, not subject to absorption by relaxation. Enskog's theory was able to predict this property, but computer simulation brings it closer to reality and accounts for the decrease of the η_v/η_s ratio near solidification which we have been able to demonstrate experimentally. The direct dependence of the bulk viscosity on molecular interaction would be interesting to study in detail, but this will be difficult as one is actually limited both practically by the degree of precision which can be experimentally attained and theoretically by the need to use more elaborate interaction models.

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[*] Associé au Centre National de la Recherche Scientifique, *N*° 21.

[†] Groupe de Dynamique des Phases Condensées, laboratoire associé au Centre National de la Recherche Scientifique, *N*° 233.

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