

Sound velocity in colloidal SiO₂ suspensions

Peter R. Younger, George O. Zimmerman, C. E. Chase, and W. DrostHansen

Citation: *J. Chem. Phys.* **58**, 2675 (1973); doi: 10.1063/1.1679566

View online: <http://dx.doi.org/10.1063/1.1679566>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v58/i7>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Sound velocity in colloidal SiO₂ suspensions

Peter R. Younger and George O. Zimmerman

Department of Physics, Boston University, Boston, Massachusetts 02215

and

C. E. Chase*

Francis Bitter National Magnet Laboratory,† Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

W. Drost-Hansen

Laboratory for Water Research, Department of Chemistry, University of Miami, Coral Gables, Florida 33124

(Received 2 November 1972)

The velocity of sound in three colloidal suspensions of silica was measured in the temperature range between 10 and 75°C. The measurements show that the temperature dependence of the velocity is affected by the presence of the silica, but agreement between the observed values and classical theory, which considers the colloidal suspension made up of elastic particles, is poor. This suggests that the temperature and concentration dependence of the total hydrated SiO₂ particles is important.

The properties of water continue to attract attention because of the unresolved problem of its structure.¹ This interest has been heightened by reports of thermal anomalies in several properties of water, near interfaces. Ultrasonic measurements in pure distilled water have shown no anomaly in the velocity of sound as a function of temperature between 6 and 81°C.² However, it was suggested by one of us (D-H) that anomalies which have previously been reported might be due to spurious surface phenomena.³

Because of the large surface-to-volume ratio in a colloidal suspension, it was decided to measure the velocity of sound in such a medium. Ludox⁴ Colloidal Silica, supplied to us by DuPont, is an aqueous colloidal suspension of surface hydroxylated SiO₂. The repulsion of the negative surface charges insures the stability of the sol. The Ludox (TM) suspensions, on which the measurements were made, have a silica content of at least 49% by weight with solid, fully surface-hydroxylated silica particles 22–25 nm in diameter. This suspension will be referred to as “100% Ludox”. The suspension has a pH of 8.9 at 25°C.⁴

It was decided to employ an ultrasonic technique because the velocity u is simply related to the isothermal compressibility κ_T by the equation $\kappa_T = \gamma/\rho u^2$, where γ is the specific heat ratio and ρ is the density. (Unfortunately values for γ have not been reported in the literature for the Ludox suspensions. However, for our purpose this quantity is not required.) In addition, the velocity can be measured with a resolution of 20–30 ppm and thus might well serve as a sensitive detector of anomalous behavior. The measuring apparatus, shown in Fig. 1, consisted of a pair of x -cut quartz crystals, mounted in cylinders which kept

the crystals accurately parallel to each other as well as coaxial. The spacing between the faces was 8.601 ± 0.001 cm at 27°C. This apparatus was immersed in the fluid contained in a test tube; the test tube in turn was placed in a thermostat. The sample was held at a temperature between 4 and 10°C for at least 24 h before measurements were made. The purpose of this low temperature storage was to allow the water to reach an equilibrium state, with near maximal extent of water structuring. An immersion heater was used to raise the sample temperature at a rate of less than 10°C/h. Temperature uniformity was enhanced by use of a magnetic stirrer. A platinum resistance thermometer, mounted alongside the sample tube, was used to measure the temperature. The resistance was measured with a Wheatstone bridge built around a Princeton Applied Research Model JB-4 lock-in amplifier. This arrangement gave a temperature resolution of $\pm 0.02^\circ\text{C}$.

The sound velocity was measured by a pulsed phase-comparison technique previously described,^{5,6} in which the phase of a received echo is brought into a constant relationship with a continuously running master oscillator by means of a calibrated adjustable delay line. Measurements were made on the second received signal which occurred approximately 150 μsec after the transmitted pulse. The resolution of this apparatus at the operating frequency of 10 MHz is about 0.2 nsec, so that, in principle, velocity changes as small as ± 1 –2 ppm could be observed. In practice, however, various sources of error increase the uncertainty by about an order of magnitude. These errors have been treated in detail elsewhere.⁶

Changes in velocity were measured as a function of temperature for 100% Ludox suspension, Ludox diluted

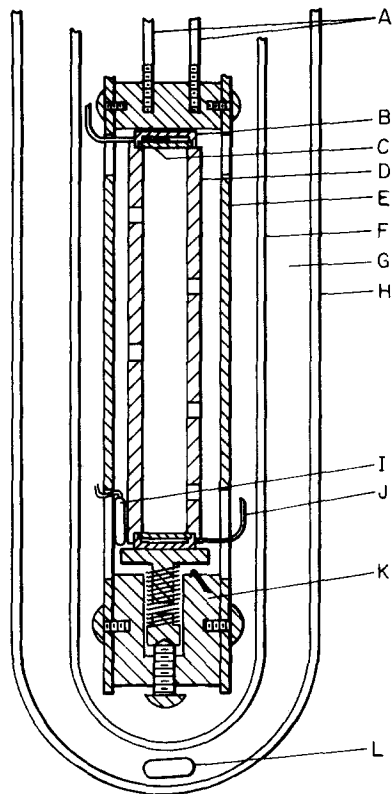


FIG. 1. Acoustic chamber: A. Support rod; B. Crystal holder; C. Quartz crystal; D. Crystal aligning cylinder; E. Outer support cylinder; F. Test tube; G. Water bath; H. Dewar flask; I. Platinum resistance thermometer; J. Coaxial leads; K. Adjustable spring clamp; L. Magnetic stirrer.

100 to 1 with distilled water and Ludox neutralized with sulfamic acid. The purpose of the sulfamic acid was to lower the pH to about 1.8, at which point the surface charges were neutralized and the silica particles uncharged.

The results of the measurements are shown in Fig. 2. The insert shows a portion of the graph of actual data points for 100% Ludox. The scatter is about 0.04 m/sec or about 25 ppm. To within this spread there is no indication of any anomalies in the temperature dependence of the sound velocity for any of the three cases studied. However, some interesting features are present. The temperature at which the velocity maximum is reached is lower in 100% Ludox and neutralized 100% Ludox than in pure distilled water. The velocity maximum for water is at 74°C,⁷ while for both of the above cases it is at about 65°C. This effect cannot be explained away by lack of thermal equilibrium; since the thermometer was outside the ultrasonic path, it was somewhat closer to the water bath than was the sample. Thus, if there were a difference between the sample temperature and the measured temperature, the sample would lag behind the thermometer reading

as the temperature rose. The effect of such a non-equilibrium situation would be to raise the apparent temperature of the maximum velocity, rather than to lower it. In addition, since the velocity maximum in diluted Ludox occurs at nearly the same temperature as that in distilled water (as it ought to do for large dilutions) it is believed that significant temperature errors were absent.

Figure 2 also shows that the temperature coefficient of the velocity of sound is different in the suspension than in pure water. The curves for all three forms of Ludox are somewhat steeper than observed for water.

Finally, the results of Fig. 2 are interesting in view of calculations by Herzfeld, who has considered the scattering of sound by small elastic spheres⁸ and the propagation of sound in such suspensions.⁹ The effect of suspended particles, of any shape, is to shift the velocity of sound by an amount

$$\Delta V/V = (V_l - V_{sus})/V_{sus} = \frac{1}{2}\beta\{[(\kappa_s - \kappa_l)/\kappa_l] + (\rho_s - \rho_l)/\rho_l\}, \quad (1)$$

where V , κ , and ρ are the sound velocity, compressibility, and density, respectively. The subscripts refer

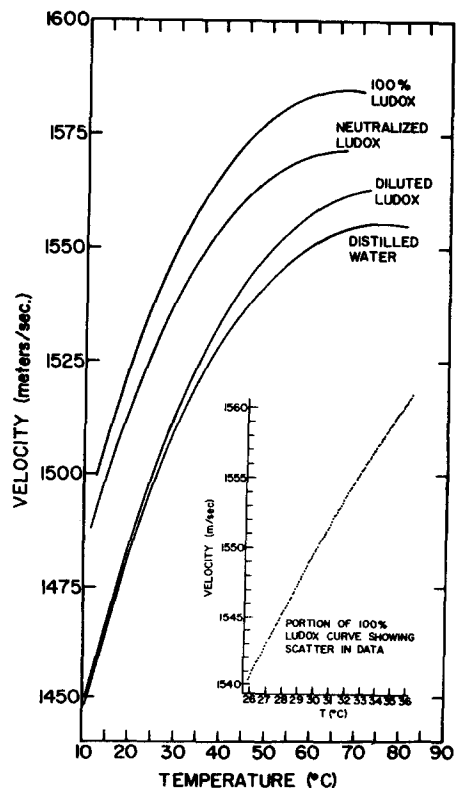


FIG. 2. Ultrasonic velocity as a function of temperature for the three cases studied. Curve for distilled water is from Ref. 2. A portion of the curve for 100% Ludox is included to show the scatter in the data.

TABLE I. Theoretical values of $\Delta V/V$ with properties of silica and water.

T (°C)	κ_s (vitreous) (10 ⁶ bar ⁻¹) ^a	κ_l (10 ⁶ bar ⁻¹) ^b	ρ_s (vitreous) (g/cm ³) ^a	ρ_l (g/cm ³) ^b	$\Delta V/V$
0	2.67 ₀	50.98	2.203	0.9999	0.0398
10	2.67 ₅	47.98		0.9997	0.0404
20	2.68 ₀	45.91		0.9982	0.0408
30	2.68 ₅	44.75		0.9957	0.0424
40	2.69 ₀	44.72	Assumed	0.9922	0.0438
50	2.69 ₅	44.12	constant	0.9881	0.0454
60	2.70 ₀	44.50		0.9832	0.0471
70	2.70 ₅	45.15		0.9778	0.0487
80	2.71 ₀	46.10		0.9718	0.0509
90	2.71 ₅	47.34		0.9653	0.0530
100	2.72 ₀	48.90	2.203	0.9584	0.0554

^a See Ref. 10.

^b See Ref. 11.

to the carrier fluid (l), the suspension (sus) and the solid material (s) forming the suspended particles. β is the fraction of space filled by the particles in the suspension. To a first approximation (for *dilute* suspensions) the change in velocity [Eq. (1)] due to the suspension of particles is dependent upon temperature, primarily through the temperature dependence of the compressibility and density of water.

Theoretical values of $\Delta V/V$ were calculated from the water and silica properties given in Table I. When the fill factor β is calculated from the densities of the two components it is found to be nearly constant over the whole temperature range of interest. Its value was taken as 0.312. The calculated values of $\Delta V/V$ vary from 4% at 0°C to 5.5% at 100°C for 100% Ludox. The effect is smaller by a factor of 100 for the diluted Ludox.

Figure 3 shows that the observed values of $\Delta V/V$ are generally in poor agreement with the theory. For the two more concentrated forms of Ludox, the effect is between 2% and 3% at low temperature and contrary to calculation decreases with increasing temperature.

For diluted Ludox, the calculated effect is small and is given by the difference of two large numbers; hence good agreement with experiment cannot be expected. However $\Delta V/V$ does increase with temperature in this case, but more rapidly than predicted by Herzfeld's theory.

The most interesting of the discrepancies noted above is that concerning the temperature coefficient of $\Delta V/V$. The Ludox particles have been treated as solid spheres suspended in bulk water. This treatment may well be greatly oversimplified. In view of the strong van der Waals forces existing at the surface of the Ludox par-

ticles it is not unreasonable to assume that a considerable amount of the liquid is bound to the colloidal quartz particles. In fact, with the assumed value of β , as much as 15% of the water could be contained in the

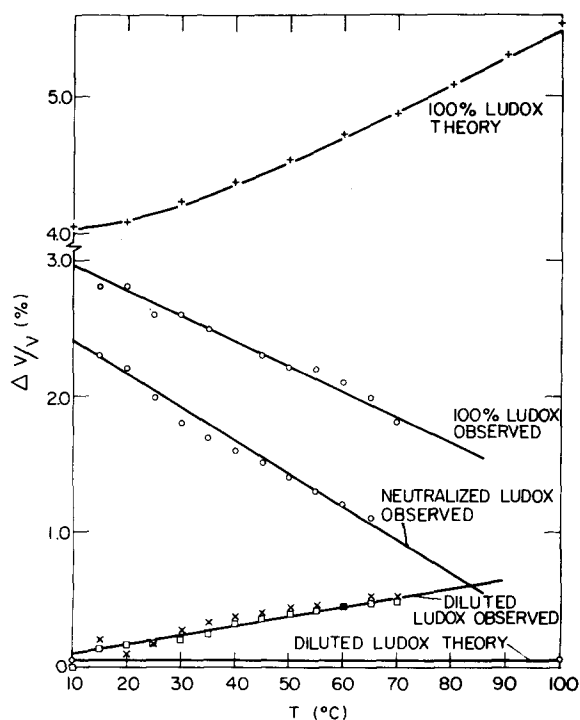


FIG. 3. Comparison between theoretical and observed $\Delta V/V$. Observed values of $\Delta V/V$ are found by comparison of measured values of the velocity with those of Ref. 2 in all cases except for the diluted Ludox points indicated by (\times). Here the comparison was with the results of Greenspan and Tschiegg.¹²

first two molecular layers surrounding the Ludox particles. The nature of these hydration hulls is of course uncertain, but the strong binding forces may cause the hydration structure to be more dense than the bulk water as in the case of the ice high-pressure polymorphs where densities may exceed 1.5 g/cm^3 .¹³ The hydration structure may also be relatively incompressible. The effect of this binding of the water would be to increase the effective radius of each quartz particle. The temperature dependence of the sound velocity in the presence of such hydrated particles would be quite different from that of the pure Ludox.

In order to consider these effects Eq. (1) is rewritten and differentiated with respect to temperature:

$$2 \frac{d}{dT} \left(\frac{\Delta V}{V} \right) = \frac{d\beta}{dT} \left[\frac{\kappa_{hs} - \kappa_l}{\kappa_l} + \frac{\rho_{hs} - \rho_l}{\rho_l} \right] + \beta \left[\frac{1}{\kappa_l^2} \left(\kappa_l \frac{d\kappa_{hs}}{dT} - \kappa_{hs} \frac{d\kappa_l}{dT} \right) + \frac{1}{\rho_l^2} \left(\rho_l \frac{d\rho_{hs}}{dT} - \rho_{hs} \frac{d\rho_l}{dT} \right) \right], \quad (2)$$

where it is necessary to introduce the notation κ_{hs} and ρ_{hs} for the average compressibility and density of the hydrated Ludox particles. The fill factor, β , is now considered a function of temperature.

The magnitude of the first bracketed expression depends greatly on the relative values of κ_{hs} and κ_l . If these two quantities are quite different, then this expression could be rather large. In the second bracketed expression the terms involving the derivatives of the pure liquid properties are on the order of $10^{-4}/^\circ\text{C}$ and are too small to account for the behavior of $\Delta V/V$. The effect of temperature on the hydration hulls may be the most important factor to be considered. If the hydration hulls were to break down with increasing temperature, then the fill factor β would correspondingly decrease. This effect alone could be large enough to cause the observed behavior. In addition, the temperature derivatives of κ_{hs} and ρ_{hs} might become large. Although these predictions are speculative they seem to provide the best clue to the nature of the observed

discrepancies. No immediate explanation can be offered of our observation that the large surface-to-volume ratio system of Ludox does not exhibit thermal anomalies. The absence of anomalous behavior is particularly surprising in view of the fact that many other quartz/water interfacial systems have revealed very notable thermal anomalies; see particularly the studies by Peschel and Adlfinger¹⁴ and Drost-Hansen.¹⁵

ACKNOWLEDGMENT

We wish to thank Dr. Ralph K. Iler of E. I. DuPont de Nemours and Company for providing us with the samples of Ludox and for suggestions about the measurements.

* During the performance of part of this work this author was Visiting Professor at the Department of Physics at Boston University.

† Supported by the National Science Foundation.

¹ For reviews see H. S. Frank, *Science* **169**, 635 (1970); L. Kavanau, *Water and Solute-Water Interaction* (Holden-Day, Los Angeles, 1964); D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford U. P., New York, 1969).

² W. Senghaphan, G. O. Zimmerman, and C. E. Chase, *J. Chem. Phys.* **41**, 2543 (1969).

³ W. Drost-Hansen, *Chem. Phys. Lett.* **2**, 647 (1968); *Ind. & Eng. Chem.* **61**, 10 (1969). For biological systems, see *Chemistry of the Cell Interface*, edited by H. D. Brown (Academic, New York, 1971), pp. 1-183.

⁴ Trade name. See technical bulletin, "Ludox Colloidal Silica," E. I. DuPont De Nemours and Co. (Inc.), Industrial and Biochemicals Dept., Wilmington, Delaware, 3M 11/69.

⁵ C. E. Chase, *Phys. Fluids* **1**, 193 (1958).

⁶ W. M. Whitney and C. E. Chase, *Phys. Rev.* **158**, 200 (1967).

⁷ M. Greenspan, C. E. Tschiegg, and F. Breckenridge, *J. A. S. A.* **28**, 500 (1956).

⁸ K. F. Herzfeld, *Phil. Mag.* **9**, 741 (1930).

⁹ K. F. Herzfeld, *Phil. Mag.* **9**, 752 (1930).

¹⁰ National Research Council, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (McGraw-Hill, New York, 1928), Vol. 3, p. 49 and Vol. 4, p. 20.

¹¹ *Handbook of Chemistry and Physics* (Chemical Rubber Company, Cleveland, 1963), 50th College Edition, p. F-5.

¹² M. Greenspan and C. E. Tschiegg, *J. A. S. A.* **31**, 75 (1959).

¹³ D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford U. P., New York, 1969).

¹⁴ G. Peschel and K. H. Adlfinger, *Z. Naturforsch. A* **26**, 707 (1971).

¹⁵ W. Drost-Hansen, *Proc. Solvay Conf.*, Brussels, June 1972 (to be published).