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Speeds of Sound in Fluid Ammonia to 3.8 GPa and 680 K

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Speeds of sound in fluid ammonia have been measured by Impulsive Stimulated Scattering, to a pressure of 3.8 GPa and along isotherms of (297, 476, and 680) K. Speeds are compared with previous measurements and with predictions of equations of state.

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1. Introduction

Few studies of thermophysical properties of fluid ammonia have encompassed pressures in excess of 1 GPa. Measurements of density have been made to pressures of 0.95 GPa and 473 K,[1] 0.95 GPa and 723 K,[2] and 1.0 GPa and 320 K.[3] The solid−fluid line of equilibrium has been followed up to pressures of (1,[4] 2,[5] and 2.4) GPa.[6] Densities[7,8] and temperatures[9] of shock-compressed ammonia have been reported to ~60 GPa. Additionally, measurements of speed of sound have been published to 1 GPa and 320 K.[3] Here we report speeds of sound measured in the diamond-anvil cell up to pressures of 3.8 GPa and temperatures of 680 K. Comparison is made with previously obtained data and with published equations of state (EOS).

2. Experimental

Speeds of sound were measured with Impulsive Stimulated Scattering[10] with a typical precision of 0.2 % and systematic errors which are believed to be less than 0.1 %. The acoustic wavelength was held at 2.5 μm, with frequencies ranging from (1 to 1.8) GHz.

Ammonia was purchased from Linde Gas with a stated purity of > 99.99 %. A diamond-anvil cell was placed in a closed container, flushed with ammonia gas at room temperature, then brought to 195 K at which temperature the supplied gas condensed and filled the cell.

Measurements were made along nominal isotherms of (297, 476, and 680) K. Temperatures were obtained with chromel−alumel thermocouples and varied less than 1 K during any run. Two separate thermocouples and factory-calibrated readers (Omega Engineering) gave the same value to ± 1 K, and this is assumed to be the accuracy of the measurement. Pressures were obtained with included chips of either ruby[11] (up to ~476 K) or samarium-doped SrB_4O_7[10,12] with precisions of ~0.02 GPa. During different runs, the chips were placed either in direct contact with the fluid or separated from it by a thin, gold barrier. With a borate pressure gauge, or ruby at room temperature, addition of the gold barrier had no discernible effect. However, at 476 K, speeds of sound were seen to be greatly reduced when the ammonia was in direct contact with ruby; no attempt was made to repeat these measurements, and the data were discarded.

At 680 K, a second phase slowly began to appear in the cell, identified as N_2 from the Raman spectrum. (Presumably, H_2, which was not observed, escapes by diffusion through the Inconel 718 gasket, and a gold liner placed between the ammonia and gasket did not prevent dissociation.) The fluid at this temperature therefore contains an unquantified admixture of dissolved nitrogen. The apparent consistency of the results of two different, affected runs, one of which exhibited saturation in N_2 and the other of which did not (there was no observable second phase at the time data were taken), leads me to believe that the consequent change in speed was similar in size to other experimental errors; however, these data should be treated with caution.

Table 1. Measured Pressure *P*, Temperature *T*, Speed of Sound *w*, and Calculated Density[14] ρ of Fluid Ammonia

P/GPa	T/K	w/km·s^{-1}	ρ/kg·m^{-3}
0.78	297	2.942	824.4
0.78	297	2.932	824.4
0.62	297	2.741	800.5
0.74	298	2.903	818.3
0.37	298	2.376	751.8
0.70	297	2.836	812.9
0.88	297	3.023	837.5
0.97	297	3.113	848.4
1.09	477	2.954	793.6
1.43	474	3.280	836.1
1.55	476	3.375	848.2
2.20	476	3.788	904.9
2.22	479	3.797	905.7
1.35	680	2.982	[a]766.6
1.35	680	2.970	[a]766.6
1.48	679	3.084	[a]783.4
2.44	679	3.740	[a]876.5
3.75	679	4.342	[a]960.7
3.14	678	4.103	[a]925.7
3.08	678	4.072	[a]922.2
2.92	678	4.000	[a]911.8

[a] At 680 K, the ammonia contained nitrogen (see text) in amounts which might have affected the speeds of sound.

3. Results and Discussion

Speeds of sound, w (see Table 1), are plotted against pressure in Figure 1. Speeds given by Mills et al.[3] around 297 K are systematically higher than the current measurements by ~0.03 km·s^{-1}, slightly more than their stated uncertainty of ± 0.02 km·s^{-1}. Their EOS for ammonia, contained in the same paper, is based on data taken only to ~320 K and is not suitable for use above that temperature.

Two other EOS have been published for ammonia, that of Haar and Gallagher[13] and of Tillner-Roth.[14] The first was fit only to PVT data and gives poor approximations to caloric properties at high pressure (e.g., at 297 K, the predicted specific heats are negative above 0.83 GPa). Its results are given by

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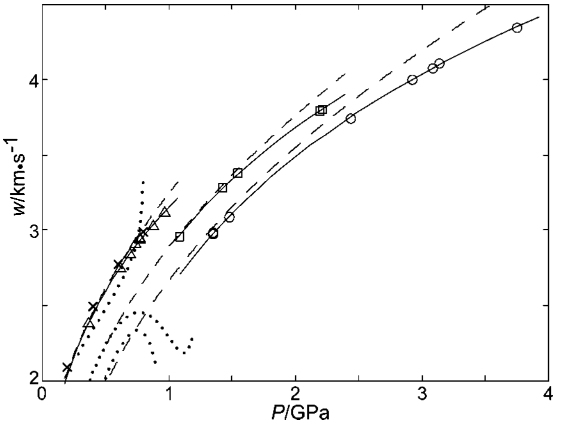

Figure 1. Speed of sound, *w*, is plotted against pressure: Δ, this work, 297 K; □, this work, 476 K; ○, this work, 680 K; ×, ref 3 interpolated to 297 K by way of their EOS; —, straight line fit of measured *w* to calculated[14] *ρ*; - - -, ref 14; •••••, ref 13.

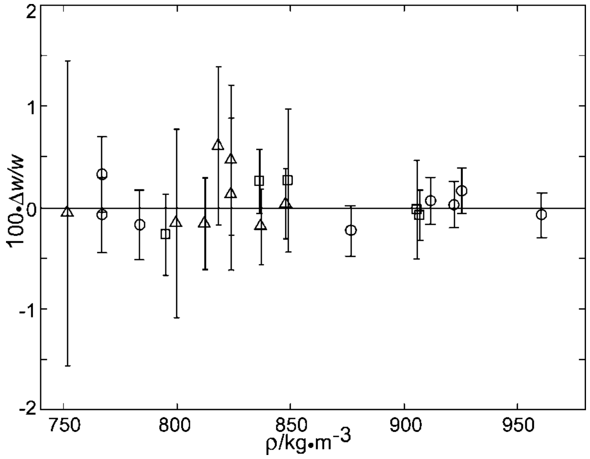

Figure 2. Fractional deviations $\Delta w = w(\text{exptl}) - w(\text{calcd})$ of the experimental speed of sound (this work) plotted against density. Calculated values are from straight lines fit to the measured *w* as functions of *ρ* (the latter from ref 14): Δ, 297 K; □, 476 K; ○, 680 K. Error bars represent combined, expanded uncertainties and, especially at lower pressures, are dominated by the uncertainty in pressure.

dotted lines in Figure 1. The EOS of Tillner-Roth yields a good representation of the measured volumes up to 1 GPa, within 2 % of ref 1 and 1.5 % of ref 2 (those authors' stated uncertainties are 0.5 % and 0.8 %, respectively); remarkably, it predicts volumes within probable errors of ref 3 at (298 and 320) K ($4 \cdot 10^{-8}$ $\text{m}^3 \cdot \text{mol}^{-1}$ and 2 MPa, or about 0.2 % combined error), data to which it was not fit. This EOS also matches the measured speeds of sound reasonably well at our lower pressures while progressively overestimating them as pressure is increased (dashed lines in Figure 1). Overestimated speeds of sound indicate an underestimation of compressibility and thus density at higher pressures. This observation is confirmed by direct comparison with published densities along the shock Hugoniot (not shown) and is due to several terms in the EOS which are known[15] to be poorly suited for extrapolation to high densities or temperatures.

For either liquids or highly compressed gases, plots of speeds of sound against density commonly yield straight lines.[16] To the extent that the EOS of Tillner-Roth gives an adequate account of densities, this relation also holds for ammonia. We see in Figure 2 that deviations from such fits are within estimated errors in the data. In contrast, speeds calculated from the EOS of Tillner-Roth do not give straight lines when plotted in the same manner.

Note Added after ASAP Publication: This paper was published ASAP on July 24, 2008. Figures 1 and 2 were transposed. The revised paper was reposted on July 29, 2008.

Literature Cited

(1) Tsiklis, D. S.; Semenova, A. I.; Tsimmerman, S. S. Molar Volumes and Thermodynamic Properties of Ammonia at High Pressures. *Russ. J. Phys. Chem.* **1974**, *48*, 106–107.
(2) Harlow, A.; Wiegand, G.; Franck, E. U. The Density of Ammonia at High Pressures to 723K and 950 MPa. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 1461–1465.
(3) Mills, R. L.; Liebenberg, D. H.; R., L.; Pruzan, P. Equation of State of Fluid NH3 from P-V-T and Ultrasound Measurements to 12 Kbar. *Mater. Res. Soc. Symp. Proc.* **1984**, *22*, 43–50.
(4) Mills, R. L.; Liebenberg, D. H.; Pruzan, P. Phase Diagram and Transition Properties of Condensed Ammonia to 10 Kbar. *J. Phys. Chem.* **1982**, *86*, 5219–5222.
(5) Hanson, R. C.; Jordan, M. Ultrahigh-Pressure Studies of NH3. *J. Phys. Chem.* **1980**, *84*, 1173–75.
(6) Grace, J. D.; Kennedy, G. C. The Melting Curve of Five Gases to 30 Kb. *J. Phys. Chem. Solids* **1967**, *28*, 977–982.
(7) Dick, R. D. Shock Compression Data for Liquids. III. Substituted Methane Compounds, Ethylene Glycol, Glycerol, and Ammonia. *J. Chem. Phys.* **1981**, *74*, 4053–4061.
(8) Mitchell, A. C.; Nellis, W. J. Equation of State and Electrical Conductivity of Water and Ammonia Shocked to the 100 GPa (1Mbar) Pressure Range. *J. Chem. Phys.* **1982**, *76*, 6273–6281.
(9) Radousky, H. B.; Mitchell, A. C.; Nellis, W. J. Shock Temperature Measurements of Planetary Ices: NH3, CH4, and "synthetic Uranus. *J. Chem. Phys.* **1990**, *95*, 8235–39.
(10) Abramson, E. H.; Brown, J. M. Equation of state of water based on speeds of sound measured in the diamond-anvil cell. *Geochim. Cosmochim. Acta* **2004**, *68*, 1827–1835.
(11) Mao, H. K.; Xu, J.; Bell, P. M. Calibration of the ruby presssure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **1986**, *91*, 4673–4676.
(12) Datchi, F.; LeToullec, R.; Loubeyre, P. Improved calibration of the SrB_4O_7: Sm^{2+}optical pressure gauge: Advantages at very high pressures and high temperatures. *J. Appl. Phys.* **1997**, *81*, 3333–3339.
(13) Haar, L.; Gallagher, J. S. Thermodynamic Properties of Ammonia. *J. Phys. Chem. Ref. Data* **1978**, *7*, 635–792.
(14) Tillner-Roth, R.; Harms-Watzenburg, F.; Baehr, H. D. Eine neue Fundamental-gleichung fur Ammoniak *20th Deutschen Kälte-und Klimatechnischen Vereins (DKV)*; Nuremberg, 1993; pp 167−181.
(15) Span, R.; Wagner, W. On the Extrapolation Behavior of Empirical Equations of State. *Int. J. Thermophys.* **1997**, *18*, 1415–1443.
(16) Shaner, J. W.; Hixson, R. S.; Winkler, M. A.; Boness, D. A.; Brown, J. M. Birch's Law for Fluid Metals In *Shock Waves in Condensed Matter-1987*; Schmidt, S. C., Holmes, N. C., Eds.; North-Holland: Amsterdam, 1988; pp 135−138.

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