FINAL SCIENTIFIC REPORT

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Recipient: University of Washington

Project Title: Viscosities of Dense Fluids

Principal Investigator: Evan Abramson

Executive Summary

The accurate modeling of both detonations and detonation initiation is contingent upon an accurate knowledge of the viscosities of hot, highly compressed fluids. Current practice is to derive these necessary parameters from molecular dynamics code. In the regime of high densities to which it is being applied such code remains substantially untested by comparison with experiment. This project has produced the first reliable, experimental data concerning such viscosities. Measurements were made on the major explosive products, water, nitrogen and carbon dioxide, to a maximum pressure of ~80,000 atmospheres and temperature of 400°C. The acquired data are intended primarily for the modeling of modern high explosives, but will also be relevant to the study of planetary physics and of high-pressure chemical synthesis.

Goals and Accomplishments

Our goals were to make measurements of the viscosities of water, nitrogen and carbon dioxide, up to temperatures of ~900K and the resulting melting pressures. To do so instrumentation was to be developed, composed of a videomicroscope, a tilt/rotation stage, and a cell capable of the desired high temperatures and pressures; an auxiliary loading vessel for fluid carbon dioxide was also to be built. All the goals were met with the exception that we were only able to reach temperatures of 700K without consistently destroying a diamond upon decompression (each high-pressure cell comprises two diamonds) and we therefor limited our experiments to that temperature. A new cell designed for the higher temperatures is now available, but was not tried before the grant ran out.

Project Activities

technical approach

Fig. 1. The speed of a small sphere, rolling in a high-pressure diamond-anvil cell, and surrounded by a viscous fluid, is monitored with a videocamera.

Fig. 2. Six fields from a videotape show a sphere rolling in a diamond-anvil cell. The immobile object at the top is a piece of ruby used as a pressure gauge.

Viscosities were measured with a rolling-ball technique in which a small (30-60 μm diameter) platinum sphere is allowed to roll down the inner diamond surface of the inclined cell, the speed of transit being recorded in video images (Figs 1 and 2). The speeds, $\mathbf{v}$, are given by:

$$\mathbf{v} = \left[\frac{2\gamma R^2 (\rho_S - \rho_F) g}{9} \right] \frac{\sin \theta}{\eta} - \frac{F_r}{6\pi\eta R} \quad (\text{Eq. 1})$$

Here, R , ρ_s , ρ_r , g , θ and η are, respectively, the sphere's radius, sphere's density, density of the fluid, gravitational acceleration, incline angle to the horizontal and shear viscosity. The first term may be simply derived from equation of the Stokes drag with the gravitational force along the inclined plane, taking into account a measurable, constant factor, γ , due to wall effects. F_r is an additional, speed independent, rolling friction. Typically, speeds are measured at several different values of θ . The slopes of the straight lines are inversely proportional to the viscosities, the constant of proportionality being determined by calibration against fluids of known viscosity (Fig. 3).

In general, the absolute accuracy of measurements is difficult to assess due to the possibility of unknown and systematic errors. Measurements of viscosity, in particular, can be significantly in error due to small, unanticipated (or poorly understood) variations in the geometry of the viscometer as pressure or temperature is raised. Here, we have undertaken to repeat the measurements several times, with different loads and different spheres. Since the speed of roll of the spheres is roughly proportional to the square of the diameter (Eq. 1), and clearances are different for each load, obtaining the same calculated viscosities from two spheres of different diameter provides a very pleasing and convincing argument for the absence of systematic error. In Fig. 3 it is shown that two spheres give the same results (at two pressures in water) while rolling

Fig. 3. Speed of roll is plotted against the sine of the tilt angle for two different spheres rolling in water at 0.3 and 1.5 GPa. Although the loads (and pressure cells) are different, and the spheres differ in their speeds at any given angle, the calculated viscosities are identical at both pressures.

Fig. 4. Viscosities of water along several isotherms (ABRAMSON, 2007). Previous data: (x) (HARLOW, 1967) and (+) (DUDZIAK and FRANCK, 1966). Positions on the primary Hugoniot are marked with stars.

at speeds which differ by roughly a factor of two.

water

Reliable measurements of the viscosities of water were of particular interest because several previous attempts to measure them in the shocked fluid had yielded extremely contradictory results, differing by as many as six orders of magnitude depending on the experimental technique used (HAMANN and LINTON, 1969; KIM, 1984; MINEEV and ZAIDEL, 1968). Several explanations had been

offered for these discrepancies, but absent a reliable value for the viscosity there had been no resolution of the problem (MILLER and AHRENS, 1991). Our new data for water are shown in Fig. 4. It is clear that viscosities along the Hugoniot are close to constant, the tendency toward increased viscosity with higher densities being offset by the rising temperatures. These new data corroborate the analysis of Hamman and Linton (1969), while precluding the extreme viscosities reported by others.

nitrogen

Viscosities of nitrogen (ABRAMSON and WEST-FOYLE, 2008) are shown in Fig. 5. The curves in the figure are fits to a modified free-volume equation (ABRAMSON, 2005; COHEN and TURNBULL, 1959; TURNBULL and COHEN, 1970) and represent the data to within 4%, from the gas phase to the highest densities achieved ($\sim 5\times$ critical).

These data were subsequently used to test a hypothesized universal correlation between a reduced viscosity and reduced excess (residual) entropy which had been suggested (GROVER et al., 1985; ROSENFELD, 1977) on the basis of early molecular dynamic simulations of structureless particles. A plot of these variables for several real systems is shown in Fig. 6. Nitrogen, a molecule which is almost spherical, lies close to the predicted line. Also shown are previous, moderate pressure data for argon along with several higher pressure, supplemental points taken in our own laboratory, as well as data from expanded (high temperature) alkali metals under their own vapor pressures. It appears that the observed relationship is quite general. Simulations of argon (BASTEA, 2003) performed at Lawrence Livermore for extreme pressures (52 GPa) and temperatures (3000K) also fall satisfactorily close to the real data, suggesting a reasonable accuracy of calculation.

Fig. 5. The viscosities of supercritical nitrogen (ABRAMSON and WEST-FOYLE, 2008). The inset shows previous data up to 373K (Vermeese, 1969; Golubev and Kurin, 1974).

Fig. 6. Reduced viscosities of argon (ABACHI et al., 1980; TRAPPENIERS et al., 1980) and two alkali metals (SHPIL'RAIN et al., 1985) are plotted along with the nitrogen data. The data lie close to the hypothesized universal curve (dashed line). Also shown are simulations of argon (BASTEA, 2003).

Fig. 7. Viscosities of carbon dioxide. The curves represent a simultaneous fit of all the data to a modified free-volume expression with four free parameters. The smaller, black circles represent previous data taken up to 0.45 GPa

carbon dioxide

Viscosities of carbon dioxide are shown in Fig. 7. The curves again represent a modified free-volume equation.

Since carbon dioxide is not a structureless molecule, it was expected that when plotted as reduced viscosity against reduced residual entropy it would not fall along the same line as previous systems (Fig. 6). Nonetheless, as seen in Fig. 8, the two variables are

Fig. 8. Reduced viscosity is plotted against reduced residual (or excess) entropy. Data are from this study (lighter symbols) and van der Gulik (1997) (vdG, bold symbols); additionally, the formulation of Fenghour et al. (1998) is used to give values at the triple point, and two points at 673K and 1000K extrapolated to pressures beyond their available data (FWV, bold symbols). The straight, solid line is drawn through the 308K data. The dotted line represents Rosenfeld's suggestion for a fluid of structureless particles. Shown in the inset are isotherms of density (g cm^{-3}) plotted against reduced residual entropy for the equation of state used (Giordano et al., 2006) (solid lines); the dashed line represents a 673K isotherm which would cause the 673K reduced viscosities to fall on the same straight line as the other data in the main figure.

still highly correlated by a straight line. Interestingly, the only data that deviate from this correlation are the few points at highest pressures and 673K. In the inset to Fig. 8 a plot of density and entropy shows clearly that this deviation is due to a deficiency in the equation of state used to calculate entropy; the 673K isotherm deviates considerably from the pattern of the other isotherms. On the other hand, a hypothesized 673K isotherm, constructed to cause the 673K viscosity data to fall on the same line as all the rest, does comport well with the pattern of the others.

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Publications deriving from this award

- Abramson E. H. (2007) Viscosity of Water Measured to Pressures of 6 GPa and Temperatures of 300°C. *Physical Review E* **76**, 051203-1-6.
- Abramson E. H. and West-Foyle H. (2008) Viscosity of Nitrogen Measured to Pressures of 7 GPa and Temperatures of 573K. *Physical Review E* **77**, 41202-1-5.
- Abramson E.H. (2009) Viscosity of Carbon Dioxide Measured to a Pressure of 8 GPa and Temperature of 673K. *Physical Review E (submitted for publication)*