Mass-Radius Relationships for Exoplanets II: 
Grüneisen Equation of State for Ammonia

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ABSTRACT

We describe a mechanical equation of state for NH$_3$, based on shock wave measurements for liquid ammonia. The shock measurements, for an initial temperature of 203 K, extended to 1.54 g/cm$^3$ and 38.6 GPa. The shock and particle speeds were fitted well with a straight line, so extrapolations to higher compressions are numerically stable, but the accuracy is undetermined outside the range of the data. The isentrope through the same initial state was estimated, along with its sensitivity to the Grüneisen parameter. Mass-radius relations were calculated for self-gravitating bodies of pure ammonia, and for differentiated ammonia-rock bodies. The relations were insensitive to variations in the Grüneisen parameter, indicating that they should be accurate for studies of planetary structure.

*Subject headings:* ammonia, shock, equation of state, planetary structure
1. Introduction

Ammonia, $\text{NH}_3$, is a common molecule in ice giant planets, which appear to be found widely throughout the galaxy (Schneider 2011). The equation of state (EOS) of ammonia is therefore important for our understanding of planetary structures and their evolution, potentially to pressures of order 1 TPa for the base of the ice-rock interface in icy exoplanets. An accurate EOS for ammonia is also needed for studies of hypervelocity impacts, such as meteoroid collisions with ice giants. Furthermore, ammonia is a simple prototype for bonds occurring in chemical explosives, for which densities from up to around twice that of zero-pressure solids are of interest for shock initiation and detonation.

Although shock compression experiments have been performed on ammonia to pressures of several tens of gigapascals (Marsh 1980), the only equation of state readily available is SESAME 5520 (Holian 1984), based on National Bureau of Standards gas phase data (Haar & Gallagher 1978), and is tabulated to a maximum density of 0.765 g/cm$^3$, which is barely greater than the zero-pressure density for liquid ammonia. Quasistatic compression experiments have been performed in which the density and sound speed were measured along isotherms (Abramson 2008; Li et al 2009), but the highest pressures reported have reached only a few gigapascals.

2. Empirical Grüneisen equation of state

Shock experiments have been reported previously in which the shock and particle speeds $u_s$ and $u_p$ were measured for a range of shock pressures, for liquid ammonia at an initial temperature of 203 K (Marsh 1980) (Fig. 1). The uncertainties in $u_s$ and $u_p$ were approximately 1%. These data can be fitted by a straight line fit

$$ u_s = c_0 + s_1 u_p $$

(1)
with

\[ c_0 = 2.00 \pm 0.13 \quad (6.7\%) \]
\[ s_1 = 1.511 \pm 0.039 \quad (2.6\%) , \]

where the standard errors shown are from the residual fitting error, neglecting the uncertainty in measurement. The experimental measurements exhibited a slightly curved trend, but the number of points was not great enough to justify a higher-order fit. Solving the Rankine-Hugoniot equations for a steady shock (Zel’dovich & Raizer 1966) using the fitted parameters rather than the individual shock measurements, the highest shock pressure was 38.6 GPa, giving a mass density of 1.54 g/cm³. The observed sound speed in liquid ammonia at 203 K is 1.9535 km/s (Bowen & Thompson 1968), which is consistent with the extrapolated Hugoniot data. (Fig. 1)

Various universal EOS have been proposed for different classes of material. It is interesting to compare with the ‘universal liquid EOS’ of Woolfolk et al (1973), whose only material-specific parameter is the sound speed at zero pressure. This EOS does not reproduce the shock data for ammonia, which is softer and more linear than the universal EOS (Fig. 1).

The fit to the shock Hugoniot can be used to predict the mechanical equation of state, using the Hugoniot as a reference curve (McQueen et al 1970)

\[ p(\rho, c) = p_r(\rho) + \Gamma(\rho) \left[ c - e_r(\rho) \right] \quad (2) \]
\[ p_r(\rho) = \frac{c_0^2 \rho_r (\rho - \rho_r)}{[\rho + s_1 (\rho - \rho_r)]^2} \quad (3) \]
\[ e_r(\rho) = e_0 + \frac{1}{2} p_r(\rho) \left( \frac{1}{\rho_r} - \frac{1}{\rho} \right) \quad (4) \]

where \( \rho_r \) is the initial density on the reference curve, and \( p_r(\rho) \) was derived for zero initial pressure, as here. Other experiments are required to determine \( \Gamma(\rho) \), such as sound speed
Fig. 1.— Principal shock Hugoniot of liquid ammonia (initial temperature 203 K): experimental measurements and least-squares fit. The point at zero particle speed is the observed sound speed, which was not included in the fit. The curve labelled WCS is the Woolfolk-Cowperthwaite-Shaw universal liquid equation of state, whose sole fitting parameter is the sound speed at zero pressure.
measurements on the Hugoniot, a shock Hugoniot from a different initial state, or ramp compression. However, $\Gamma$ can be estimated from the slope of the shock Hugoniot as $2s_1 - 1$, which is accurate for cubic crystals (Skidmore 1965). Thus $\rho_r = 0.725 \text{ g/cm}^3$ and $\Gamma \approx 2.022$.

Given the mechanical EOS, the isentrope through any state can be calculated by integrating the $-p\,dv$ work numerically (Swift 2008). Isentropes calculated from Grüneisen EOS fitted to shock data typically behave unphysically at high compression, where the assumption that the Grüneisen parameter is a function of density only breaks down. For the ammonia fit, the breakdown occurred at a mass density of 2.145 g/cm$^3$. The isentrope was well-behaved to several terapascals, though its accuracy was undetermined. The isentrope should be reasonably accurate at least up to the peak compression in the shock data, which equates to 22.1 GPa on the isentrope. To investigate the sensitivity to the Grüneisen parameter, isentropes were calculated for the nominal value above, and for values 10% lower and higher. With this variation in $\Gamma$, the pressure varied by 10% at 20 GPa, rising to 25% at 500 GPa. (Fig. 2)

3. Mass-radius relationships

Mass-radius relationships were calculated using the deduced EOS, for a self-gravitating body comprising pure ammonia and also for differentiated bodies consisting of a rocky core and an ammonia mantle, using the numerical methods described previously (Swift et al 2011). Separate mass-radius curves were constructed for the nominal and perturbed values of the Grüneisen parameter. In all cases, the temperature at the surface was taken to be 203 K, to match the initial state in the shock experiments. The rocky core was modeled using an EOS for basalt, SESAME 7530 (Barnes & Lyon 1988), as was done previously (Swift et al 2011).
Fig. 2.— Principal isentrope of liquid ammonia (initial temperature 203 K) deduced from mechanical equation of state fitted to principal shock Hugoniot, showing sensitivity to assumed Grünseisen parameter.
The variations in $\Gamma$ made a negligible difference to the mass-radius relations. At high masses, the mass-radius relation for pure ammonia asymptoted to a power-law behavior $R = \alpha M^\beta$ with $\alpha = 1.4395 \pm 0.0005$ and $\beta = 0.32889 \pm 0.00004$. For an incompressible material,

$$M = \frac{4}{3} \pi r^3 \rho_0,$$

(5)

giving $\beta = 1/3$. The difference in the fitted value is small but significant; $\alpha$ is considerably less than the incompressible value of $(\frac{4}{3} \pi \rho_0)^{-1/3}$. The mass-radius relation was also deduced using the SESAME EOS, which matched that from the Grüneisen EOS up to 0.1 $M_E$, above which point the extrapolation beyond the bounds of the table gave unphysical behavior. (Figs 3 to 5)

The planetary radius for pure ammonia did not exhibit a maximum within the range of masses investigated. The range of compressions explored by the shock experiments was equivalent to the central pressure in bodies of pure ammonia up to around 2/3 $M_E(1.5 R_E)$. However, the mass-radius relation is accurate for significantly larger bodies, because the mass and volume are dominated by matter at much lower pressures until the average density exceeds 1.5 $g/cm^3$ or so: approximately 4 $M_E$, 2.5 $R_E$, and a core pressure of 100 GPa. The relation may be accurate for even larger bodies, but it has not been validated by EOS experiments.

4. Conclusions

The relation between shock and particle speeds in liquid ammonia appears linear to within the scatter in the data up to pressures of at least 39 GPa. A Grüneisen mechanical equation of state was constructed using the principal Hugoniot of initial state zero pressure and 203 K as a reference, and estimating the Grüneisen parameter $\Gamma$ from the slope of the Hugoniot. Isentropes were calculated through the same state, the sensitivity to $\Gamma$ rising
Fig. 3.— Mass-radius relation deduced from equation of state for liquid ammonia (surface temperature 203 K), also showing relation for incompressible material and least-squares fit to the relation, which is dominated by high pressure behavior.
Fig. 4.— Variation of central pressure with mass, for liquid ammonia (surface temperature 203 K).
Fig. 5.— Mass-radius relations for differentiated ammonia-rock bodies. The percentages are the mass fraction of ammonia in the body.
with pressure.

Mass-radius relations were calculated for self-gravitating bodies consisting of ammonia, and differentiated ammonia-rock mixtures. The mass-radius relations were insensitive to variations in \( \Gamma \), indicating that the relations should be reliable for comparison to planetary measurements, to central pressures substantially above those reached in the shock experiments.

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