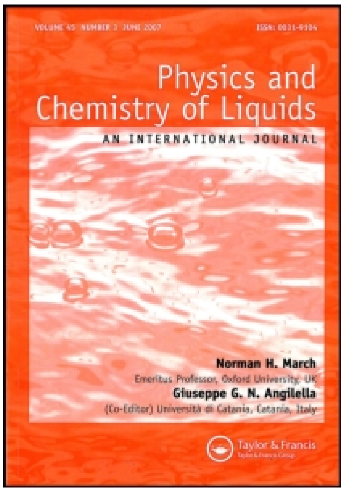

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Polyatomic molecular liquids under extreme compression: facts, models, and a few predictions

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LETTER

Polyatomic molecular liquids under extreme compression: facts, models, and a few predictions

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Early work by Siringo, Pucci and March (Phys. Rev. B, **37**, 2491 (1988)) studied solid I_2 under high pressure at $T=0$. Their conclusion was that insulating crystalline I_2 at low pressures eventually transformed into a molecular metal. This has subsequently been confirmed experimentally. Later studies by Weir *et al.* (Phys. Rev. Lett., **76**, 1860 (1996)) on solid H_2 under pressure point in the same direction, though in the solid phase the metallic state has still not been achieved at low temperatures. However, in the liquid phase, an insulating metallic transition has been proposed, as in solid iodine, again on the basis of experimental high-pressure studies. Here, attention is shifted to some polyatomic molecules, such as the 10-electron series H_2O, NH_3 and CH_4. Particular attention is focused on the measured Hugoniots of the polyatomic molecular liquids.

Keywords: polyatomic molecular liquids; Hugoniots; molecular dissociation

1. Background

We have already indicated in the Abstract the interest in the solid I_2 and H_2 built from diatomic molecules. In I_2, it has been established, as predicted by Siringo *et al.* [1,2], that under sufficiently high compression the insulating solid I_2 at low pressures is transformed into a metallic phase, in which an I_2 bond length, distinct from the crystal lattice spacing, is still observed in diffraction experiments. For solid H_2, as far as we are aware at the time of writing, no metallic transition has yet been conclusively observed at the highest pressures currently attainable in the laboratory. However, for liquid H_2, Weir *et al.* [3] have reported a metallic phase induced by high compression.

Our aim here is to focus attention on some polyatomic molecular liquids, subjected to high compression. However, to date the relevant experimental data appears to have come from Hugoniot studies of shock compressed liquids, some data on specifically CH_4 and CO_2 being summarised below in Figures 1 and 2, respectively [4]. Such data will then be compared and contrasted with NH_3 and H_2O.

To conclude this brief background, it is relevant to stress that fingerprints of the strength of the intermolecular interactions in liquids such as H_2O are to be found in the

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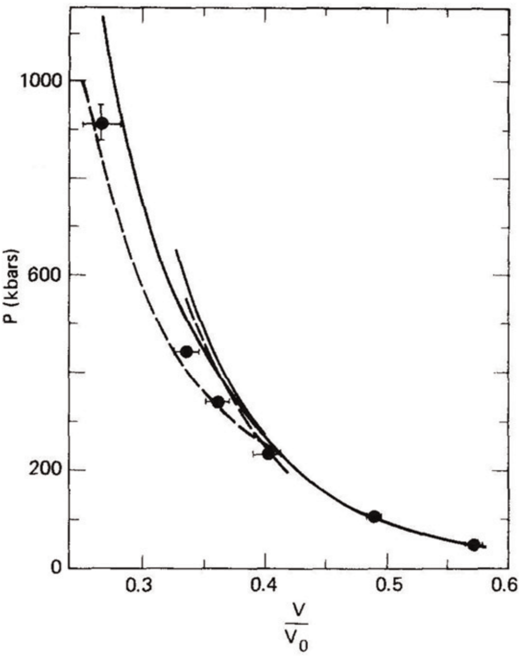

Figure 1. Liquid CH_4 Hugoniots, in form of pressure (kbar) *vs.* compression V/V_0. (Redrawn from [4].)

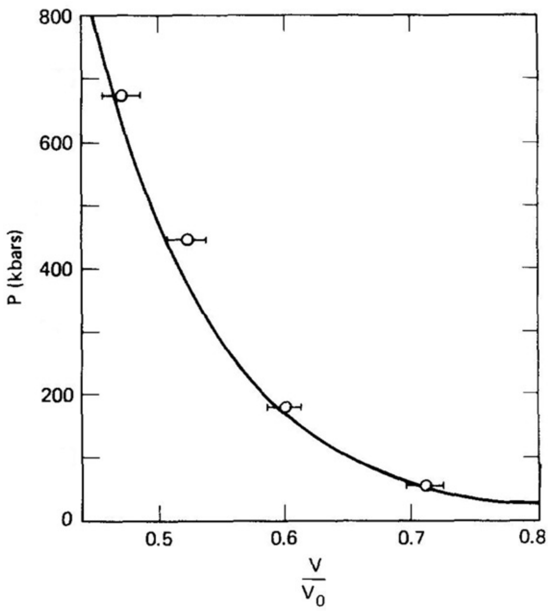

Figure 2. Liquid CO_2 Hugoniots, in form of pressure (kbar) *vs.* compression V/V_0. (Redrawn from [4].)

Table 1. Values of critical temperature T_c and critical pressure p_c for some of the molecular fluids discussed in the text [5,6].

Liquid	T_c (K)	p_c (atm)
H_2	33.26	12.8
N_2	126.16	33.5
I_2	785.16	116.0
H_2O	647.26	218.3
NH_3	405.66	112.5
CH_4	191.06	45.8
CO_2	304.16	72.9

values of the critical temperatures T_c [5]. Thus, we felt it was of interest to record in Table 1 some critical constants, namely temperature and pressure, for five of the six molecular liquids referred to in this Letter.

2. Dissociation of molecules induced by shock compression

Nellis and Mitchell [7] have studied the molecular liquids N_2 and O_2 up to 900 kbar (90 GPa). These authors emphasise that shock energy may be absorbed by (i) electronic excitations or (ii) molecular dissociation. The experiments of Nellis and Mitchell were analysed further in the study of Ross and Ree [4]. Ross and Ree give a theoretical treatment of liquid N_2 Hugoniots based on repulsive forces between molecules. This agrees with the early experimental results of Zubarev and Telegen [8], and also with the work of Nellis and Mitchell [7] up to a pressure of 400 kbar. However, Ross and Ree note a sharp divergence above this pressure between theory and experiment. They conjecture that this is a consequence of dissociation of the N_2 molecule. However, for liquid O_2 Hugoniots, Figure 2 of Ross and Ree [4] shows that their theoretical results leave more open the question of molecular dissociation than for N_2, though near 650 kbar pressure there is a clearly observable discrepancy between the shock compression data and the Ross–Ree model. These latter workers obtain a similar level of agreement for the polyatomic liquid CO_2.

But for the polyatomic liquid CH_4, the pressure *versus* compression data indicate (Figure 4 in [4]) that results for the completely dissociated molecule somewhat above 200 kbar (and 2000 K) fit the experimental data of Nellis and Mitchell convincingly.

3. Summary and future directions

We have first noted in solid I_2 the transition at high pressure from a molecular insulator to a molecular metal [1,2]. In solid H_2, to our knowledge, the transition to a metallic phase has not been conclusively observed at the time of writing, although Weir *et al.* [3] have measured metallic conductivity in the liquid phase of H_2 at a pressure of 140 GPa.

In this letter, our focus has been on the behaviour of polyatomic molecular liquids at high compression. However, the available data bearing on an important issue such as molecular dissociation is on Hugoniots. From these earlier experiments, it seems clear that in a liquid built from the 'almost spherical' molecule CH_4 the Hugoniot data, as analysed by Ross and Ree [4], is consistent with molecular dissociation at around 230 kbar and temperature $\sim$2300 K. We have compared these data with the Hugoniots measured subsequently by Mitchell and Nellis [9] on the liquid phases built from the polyatomic molecules NH_3 and H_2O. It is to be stressed here that the experimental results on liquid ammonia and on water are comparable to the earlier data of Nellis and Mitchell [7] on liquid CO_2. To date, for these polyatomic molecular liquids, there is no evidence that one needs to include dissociation to understand the behaviour of the Hugoniots, which is in marked contrast to liquid methane.

Of course, it may be that the highest pressures generated so far to compress CO_2, NH_3 and H_2O are not sufficient, when combined with the appropriate temperatures (see also Table 1), to cause molecular dissociation. It would seem that further higher pressure studies on these three polyatomic molecular liquids would be of considerable interest in what we believe is a future area of considerable interest for high-pressure physics.

Acknowledgements

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