

Comment on “Metallization of Fluid Nitrogen and the Mott Transition in Highly Compressed Low-Z Fluids”

The physical behavior and microscopic nature of highly compressed fluids continue to be unsolved and actively debated topics. The experimental data presented by Chau *et al.* on the electrical conductivity of nitrogen at high pressures are a welcome addition to the field. Unfortunately, in their desire to achieve a unifying picture of the behavior of low-Z fluids the authors oversimplify the interpretation of their data and *de facto* overlook the unique features of the systems they discuss.

The main hypothesis of the “low-Z systematics” introduced by Chau *et al.* is that nitrogen, hydrogen, and oxygen are completely dissociated in the shock reverberation experiments that lead to their metallization. This is hardly a reasonable assumption for oxygen. The results and analysis of electrical conductivity experiments presented in Ref. [1] indicate that metallization of fluid oxygen occurs in the molecular phase, and not in an atomic regime as stated in [2]. This conclusion is supported by recent *ab initio* simulations of fluid oxygen at the conditions of the shock reverberation experiments [3]. The simulations also reveal unique features of fluid oxygen under pressure, e.g., the role of the triplet spin state in the metallization transition and an unusual behavior of the molecular bond [3].

Complete dissociation of nitrogen at 80 GPa, the lowest pressure in the experiments of [2], is not, in fact, supported by previous work. The authors’ arguments are loosely based on two theoretical calculations but overlook their explicit caveats and disagreements with experiments. The quantum molecular dynamics simulations invoked in [2] report “noticeable disagreement from the second shock” experiments in the dissociation region [4]. It is therefore clear that any extrapolation of this work to the multiple-shock states relevant for the conductivity experiments has to be done with caution [4]. As additional evidence for an atomic state assumption the authors use a dissociation energy calculated by Ross [5] along with an empirical criterion introduced in [6]. However, by consistently following the treatment of [5], the first shock (14 GPa) and reshock (41 GPa) dissociation fractions corresponding to the 80 GPa final pressure can be estimated to about 10^{-10} and 3×10^{-3} , respectively. Since temperature reaches over 90% of its final value upon reshock, it is reasonable to assume that the fluid retains a significant molecular component. After all, even on the Hugoniot at 80 GPa and temperatures over 1.2 eV in both theoretical studies the fluid appears to be 30%–40% molecular [4,5].

A discussion of the hydrogen metallization experiments and Mott scaling analysis can be found in [7], where evidence is presented in support of a molecular fluid, in contradiction with the approach taken in [2].

We also point out several other inconsistencies of the “low-Z fluids systematics” presented in [2]. For example, we calculate a Mott scaling parameter of 0.27 for nitrogen at the metallization conditions defined in the Letter, in disagreement with the 0.35 value quoted by the authors. This comes simply from an average distance between atoms of 1.81 Å at a density of 3.9 g/cm³, and a Bohr radius (location of the maximum in the valence charge distribution $r^2\psi\psi^*$ averaged over the solid angle) of 0.91 bohr, Ref. [26] of [2]. The authors use of an empirical atomic radius meant to fit interatomic distances in a variety of crystalline compounds (see Ref. [25] of [2]) is puzzling and unnecessary. For example, the quoted reference gives a 0.5 bohr radius for hydrogen, in large disagreement with the accepted 1 bohr value. It should also be noted that although using zero pressure charge distributions to gain insight into the behavior at high pressure is perhaps reasonable, shifting the curves in the radial direction as done in Fig. 3 of [2] in order to compare their spatial extent is a rather meaningless exercise. Scaling all distributions to unity would allow the intended comparison and make it more apparent that the radial extent of hydrogen exceeds that of atomic nitrogen in contradiction with the statements by Chau *et al.*

Nitrogen is a complex system with one of the largest dissociation energies known in its diatomic state, a multitude of chemical bonding configurations, and a high pressure polymeric phase [8]. An accurate interpretation of electrical conductivity data for nitrogen around its high pressure metallization transition will probably need to account for this complexity.

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