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The electrical resistivity of liquid hydrogen has been measured at the high dynamic pressures, densities and temperatures that can be achieved with a reverberating shock wave. The resulting data are most naturally interpreted in terms of a continuous transition from a semiconducting to a metallic largely diatomic fluid, the latter at 140 GPa (nine-fold compression) and 3000 K. While the fluid at these conditions resembles common liquid metals by the scale of its resistivity of 500 μΩ cm, it differs by retaining a strong pairing character, and the precise mechanism by which a metallic state might be attained is still a matter of debate. Some evident possibilities include: (i) physics of a largely one-body character, such as a band-overlap transition; (ii) physics of a strong-coupling or many-body character, such as a Mott–Hubbard transition; and (iii) processes in which structural changes are paramount.

Keywords: hydrogen; metallization of hydrogen; liquid metallic hydrogen; insulator–metal transition

1. Introduction

Hydrogen has been cited as the prototypical system for the study of the insulator–to–metal (IM) transition since Wigner & Huntington (1935) predicted that the insulating molecular solid could transform to a conducting monatomic solid at sufficiently high pressure at 0 K. That is, although solid molecular hydrogen is a wide bandgap insulator ($E_g = 15$ eV) at ambient conditions, at sufficiently high pressure the insulating diatomic solid is expected to transform to a conducting monatomic solid or the electronic energy bandgap E_g of the diatomic solid is expected to close, resulting in an IM transition. Since Wigner & Huntington's paper, predictions of the transition pressure of the former has varied from 25 (Wigner & Huntington 1935) to 2000 GPa (Alder & Christian 1960) at 0 K. To date this transition in the solid at low temperatures has not been observed by optical measurements in the range 190–260 GPa (Chen *et al.* 1996; Hemley *et al.* 1996; Ruoff 1996).

Metallization within the molecular solid phase by a band overlap mechanism is predicted to occur at pressures lower than is the case for the transition to the monatomic phase (Friedli & Ashcroft 1977), but the transition pressure is structure dependent (Garcia *et al.* 1990; Kaxiras *et al.* 1991; Chacham *et al.* 1992), and the structure at densities close to metallization at 0 K is not known. Extrapolation of recent pressure–volume data up to 120 GPa in the HCP phase yields a predicted dissociative transition of 620 GPa (Loubeyre *et al.* 1996). Both the monatomic and diatomic metallic solids have been predicted to be high-temperature superconductors (Ashcroft 1968; Richardson & Ashcroft 1997).

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Electrical conductivity measurements indicate that hydrogen becomes metallic (i.e. conducting†) at 140 GPa, nine-fold compression of initial liquid density, and 3000 K (Weir *et al.* 1996). Metallization is expected when pressure and density are sufficiently high that the electronic bandgap decreases from the value at ambient conditions of 15 eV down to approximately 0.25 eV, the temperature of these experiments. Extrapolation by means of the Simon equation of the melting curve of H_2 measured at low pressures (Diatschenko *et al.* 1985) gives a melting temperature of 1800 K at 140 GPa. Thus, as stated, metallization probably occurs in the high-temperature fluid.

Electrical conductivity has also been measured under single-shock compressions up to 20 GPa and 4600 K (Nellis *et al.* 1992). Those measurements showed that electronic conduction is thermally activated in the semiconducting fluid. Electrical conductivity experiments using explosively driven magnetic flux compression to isentropically compress liquid hydrogen have shown that the conductivity becomes greater than $1\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 200 GPa and 400 K (Hawk *et al.* 1978). Although this conductivity does not conform to metallic values, this experiment demonstrates that the electrical conductivity increases at high pressure and temperature. Shock Hugoniot and temperature data have also been measured (Nellis *et al.* 1983; Holmes *et al.* 1995; Da Silva *et al.* 1997).

Hydrogen is important for astronomy because its cosmological abundance is about 90 atomic percent, and the understanding of dense hydrogen is particularly important to planetary science. Jupiter and Saturn contain over 400 Earth masses, most of which is fluid hydrogen. Jupiter-size planets now being discovered close to nearby stars (Butler & Marcy 1996*a*, *b*; Mayor & Queloz 1995) probably contain massive amounts of hydrogen as well, and the interiors of these giant planets are likely to be at high pressures and high temperatures and in the fluid state (Zharkov & Gudkova 1992). Because of the large mass-diffusion coefficient and low thermal conductivity (Ross *et al.* 1981), magnetic fields are produced by the convective motion of electrically conducting fluid hydrogen by dynamo action (Stevenson 1983). Implications for Jupiter of recent measurements on dense hydrogen at high pressures and temperatures have been described elsewhere (Nellis *et al.* 1995, 1996).

Because of the high kinetic energy in the impactor (0.5 MJ), in a sense we are actually working at a confluence of high-energy and condensed matter physics. This energy is comparable to the total kinetic energy of all the protons and antiprotons in the beams in the Tevetron at the Fermi National Accelerator Laboratory. Here energy enables discovery of novel states of condensed matter, analogous to the discovery of novel states of subnuclear matter.

2. Finite temperatures

The distinguishing feature of these experiments is achievement of a stable hydrogen sample at 3000 K and 100 GPa pressures. It is desirable to look for the IM transition at higher temperatures because phenomena which inhibit metallization

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† There is some ambiguity in the definition of a metal. One possibility is the existence of a reasonably well defined Fermi-surface, while in 1996, the late Sir Nevill Mott wrote: 'I've thought a lot about 'what is a metal' [and] I think one can only answer the question at $T = 0$. Thus a metal conducts and a non-metal doesn't.' (P. P. Edwards, personal communication). However, in this paper we use an operational definition: a substance is metallic if the conductivity is in a 'typical' metallic range.

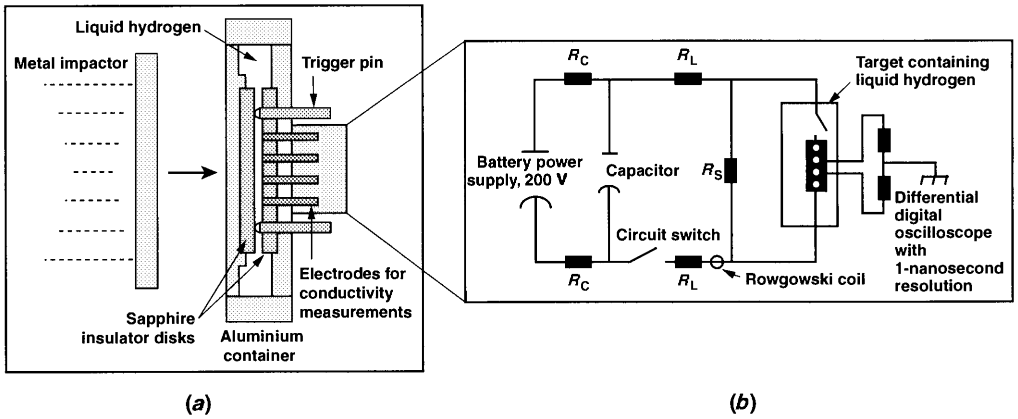

Figure 1. Schematic of electrical conductivity experiments on fluid metallic hydrogen. Four electrodes in (*a*) were connected to the circuit in (*b*). For conductivities lower than metallic, two probes were used. Trigger pins turn on the recording system. All cables are coaxial.

in the dense solid; namely, crystalline and orientational phase transitions (Ashcroft 1995*a*; Edwards & Ashcroft 1997), do not occur in the disordered fluid. However, because of the large mass-diffusion coefficient and chemical reactivity of hydrogen at high temperatures, it is essential to use a temperature pulse. The duration of this pulse should be sufficiently long to achieve equilibrium and sufficiently short that the sample cannot diffuse away nor react chemically before the experiment is completed. The approximately 100 ns duration of shock compression satisfies these criteria. Our temperature (equivalent to 0.3 eV) is relatively low for the electron distribution being probed because the energy gap at ambient pressure is 15 eV and the zero point energy of the molecule is 0.3 eV.

3. Experiment

Conditions of high pressures, densities and temperatures were produced by impact of a planar metal plate onto a cryostat containing liquid hydrogen. A two-stage light-gas gun was used to accelerate the impactor plate up to approximately 7 km s^{-1} (Jones *et al.* 1966). Hydrogen gas is used to accelerate the projectile because it has the highest sound speed of any gas and thus produces the highest impact velocity and pressure. The magnitude of the pressure generated by the impact is determined by the impact velocity (Mitchell & Nellis 1981*a*) and the Hugoniot equations of state of impactor and target (Mitchell & Nellis 1981*b*; Erskin 1994). To achieve highest densities and lowest temperatures at high pressures, the sample must have a relatively high initial density. High densities were achieved by using a liquid sample at 20 K (Nellis *et al.* 1983; Nellis & Mitchell 1980). We applied our previous techniques to measure electrical conductivities (Nellis *et al.* 1992; Radousky *et al.* 1986) to the configuration illustrated in figure (1).

The sample is 0.5 mm thick and 25 mm in diameter contained between two electrically insulating sapphire (single-crystal z-cut Al_2O_3) anvils, 2.0 mm thick and 25 mm in diameter. These are contained between two 2.0 mm-thick Al disks. Al is strong, ductile, and a good thermal conductor at 20 K, which facilitates condensing the sample from high-purity gas. Both H_2 and D_2 samples were used, depending on the final density and temperature desired. At the relatively high final temperatures achieved

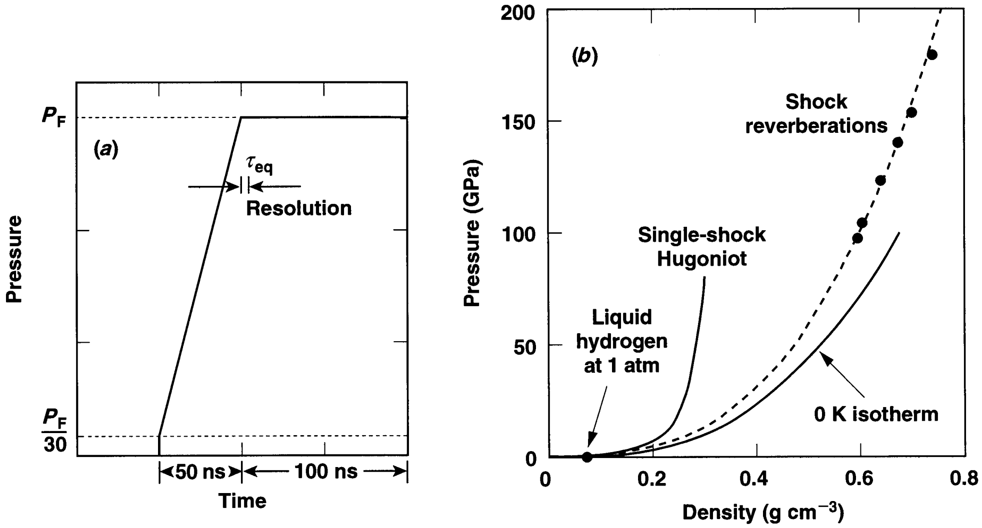

Figure 2. Effect of rise time on pressure-density states. (*a*) First pressure in hydrogen is *ca.* $P_f/30$, where P_f is incident shock pressure in Al_2O_3. Successive reverberations comprise a quasi-isentrope up to pressure P_f. This quasi-isentrope is represented by ramp over approximately 50 ns from $P_f/30$ up to P_f. After reverberation is complete, P_f is held for approximately 100 ns. If P_f were achieved in one jump, this state would be on single-shock Hugoniot. (*b*) Equation-of-state curves plotted as pressures versus density: 0 K isotherm, points reached by shock reverberations and single-shock Hugoniot. Initial point is liquid H_2 at 1 atm.

(approximately 3000 K), possible effects of different zero-point energies for hydrogen and deuterium are negligible. Stainless-steel electrodes exit the sample holder to the right. In the metallic phase four electrodes are used; two outer electrodes for current and two inner electrodes to measure potential difference. Two electrodes are used if hydrogen is in a state of poor conductivity. The electrical circuit for four-probe measurements is shown in figure 1*b*. Shock compression switches the hydrogen sample into the circuit when its conductivity becomes significant. Voltages were measured differentially with 1 ns time resolution. Current was measured with a Rowgowski coil. Typical currents were approximately 1 A and voltages were a few tens of mV. The resistance, R, is directly proportional to the resistivity, ρ, so that $R = C\rho$. To determine the cell constant C, steady-state three-dimensional current-flow simulations were performed to calculate R and ρ (Weir *et al.* 1996).

4. Thermodynamic states

This experiment achieves highly condensed matter relatively close to the 0 K isotherm by means of a reverberating shock (Yoo *et al.* 1989). The impact generates an initial pressure P_f in the Al_2O_3. When this shock reaches the liquid hydrogen, the pressure of the shock drops until the release pressure of sapphire matches the Hugoniot of liquid hydrogen. This drop is about a factor of 30 in pressure. The shock in hydrogen then reverberates back and forth between the sapphire anvils until the pressure reaches P_f, the pressure incident initially from the sapphire. Thus, the first wave in hydrogen is a weak shock and the total of the successive shock reverberations is a quasi-isentrope. This fast compression is near adiabatic and the temperature of hydrogen rises. This process causes a final temperature which is about an order of magnitude smaller than would be achieved by a single shock to the same final pressure.

The initial weak shock occurs in less than 10^{-12} s (figure 2*a*); the following quasi-isentrope takes approximately 5×10^{-8} s. The corresponding effect on the thermodynamics is illustrated in figure 2*b*. These various pressure-density states were calculated using the equation of state of Kerley (1983). Shock reverberation is necessary to reach metallization near 0.7 g cm^{-3}.

The densities and temperatures must be known to analyse the electrical conductivities. At present no means to measure them exist; they must be calculated. The densities and temperatures were calculated with two equations of state for hydrogen. One was developed by Kerley (1983) before recent shock data were available; it neglects molecular dissociation at the conditions in our experiments. The other is due to Ross, which is based on our recent shock temperature data and includes molecular dissociation (Holmes *et al.* 1995). The preferred values were those calculated with Ross' model, because it is based on recent data. The calculated final pressures in the hydrogen or deuterium agree to within 1% with the initial shock pressures in the sapphire calculated by shock impedance matching. Based on these calculations, the systematic uncertainties in calculated density and temperature are 5% and 20%, respectively.

5. Analysis of conductivity data

The experimental resistivity data are plotted as $\log(\rho)$ versus pressure in figure 3. The change in slope at 140 GPa is indicative of the transition to the metallic state. We analysed results in the semiconducting range, 93–135 GPa, by fitting the data to the dependence of conductivity for a thermally activated semiconductor:

$$\sigma = \sigma_0 \exp(-E_{\mathrm{g}}(D)/2k_{\mathrm{B}}T), \tag{5.1}$$

where σ is electrical conductivity, σ_0 depends on density, D, and relatively weakly on T, $E_{\mathrm{g}}(D)$ is the density-dependent mobility gap in the electronic density of states of the fluid, k_{B} is Boltzmann's constant and T is temperature.

Seven data points with error bars of 20–50% were fit to equation (5.1), the results being: $E_{\mathrm{g}}(D) = 1.12-(54.7)(D-0.30)$, where $E_{\mathrm{g}}(D)$ is in eV, D is in mol cm^{-3} (0.29–0.32 mol cm^{-3}) and $\sigma_0 = 66\ (\Omega\ \mathrm{cm})^{-1}$. Similar results are obtained using densities and temperatures calculated with Kerley's model (Weir *et al.* 1996). $\sigma_0 = 200$–$300\ (\Omega\ \mathrm{cm})^{-1}$ is typical of liquid semiconductors (Mott & Davis 1971). Since σ_0 is within a factor of three of the typical value, this result is reasonable. The theoretical rate of bandgap closure near metallization at 0 K of molecularly disordered HCP hydrogen is 40 eV (mol cm^{-3}) (Chacham *et al.* 1992), which is comparable to our value of approximately 60 eV (mol cm^{-3}) obtained by fitting. Thus, this slope is also comparable to what is expected. From our fit the gap $E_{\mathrm{g}}(D)$ and $k_{\mathrm{B}}T$ are equal at a density of 0.32 mol cm^{-3} and a temperature of approximately 2600 K (0.22 eV). In this region the energy gap is smeared out thermally, activation of electron carriers is complete, disorder is saturated in the fluid, and conductivity is expected to be weakly sensitive to further increases in pressure and temperature, provided the fluid does not change significantly. At 0.32 mol cm^{-3} the pressure is 120 GPa, which is close to the 140 GPa pressure at which the slope changes in the electrical resistivity (figure 3).

At pressures of 140–180 GPa the resistivity changes character; it is essentially

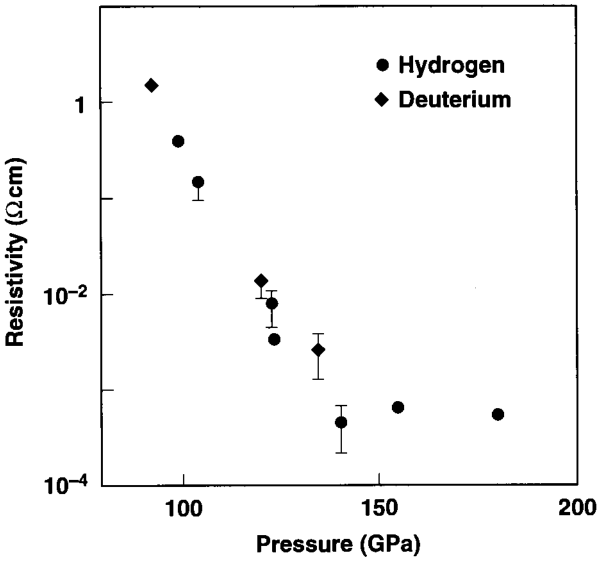

Figure 3. Logarithm of electrical resistivity of H_2 and D_2 plotted versus pressure. The slope change at 140 GPa is identified as the transition from semiconducting to metallic fluid.

constant at 500 $\mu\Omega$ cm, equivalent to a conductivity of 2000 $(\Omega\ \mathrm{cm})^{-1}$. This value is typical of the fluid (monatomic) alkali metals Cs and Rb at 2000 K undergoing the same transition (Hensel & Edwards 1996). Also, the minimum electrical conductivity of a metal is given by $\sigma = \frac{2}{3}\pi e^2 ha$, where e is the charge of an electron, h is Planck's constant and a is the average distance between particles (Mott & Davis 1971). In this case $a \sim D_{\mathrm{m}}^{-1/3}$, where D_{m} is the density of hydrogen at metallization. The calculated minimum metallic conductivity is 4000 $(\Omega\ \mathrm{cm})^{-1}$, which is in good agreement with the experimental value of 2000 $(\Omega\ \mathrm{cm})^{-1}$. Thus, fluid hydrogen becomes conducting at about 140 GPa and 3000 K via a continuous transition from a semiconducting to metallic fluid, in which the electronic activation energy is reduced by pressure to $k_{\mathrm{B}}T$.

An important point to keep in mind in what follows is this; though the characteristic time of the experiments are probably long enough to achieve equilibrium in a single phase, it is possible that the system has not reached its equilibrium phase should it happen that the system has just crossed a phase boundary.

6. Theoretical considerations

In hydrogen, at the conditions of the experiment, the confluence of thermal and quantum effects link the physics of dissociation and metallization, electronic and atomic ordering, and ionization and chemical (cluster) formation. Together these can lead to a remarkably rich phase diagram, most of which remains unexplored. The metallization experiment (Weir *et al.* 1996) reveals a new section of this phase diagram, and gives hints to its further structure, as shown in figure 4. Traditionally, theoretical interest has focussed on the change from a diatomic to a monatomic liquid or plasma, as well as the change from a metal to an insulator. In the new experimental regime now opened up, translational energies appear to match the vibron energies, and as such the metallization experiment may be probing both types of changes. With these confluences in mind we comment in turn on some interesting theoretical questions raised by the experiment, namely: (a) why does the

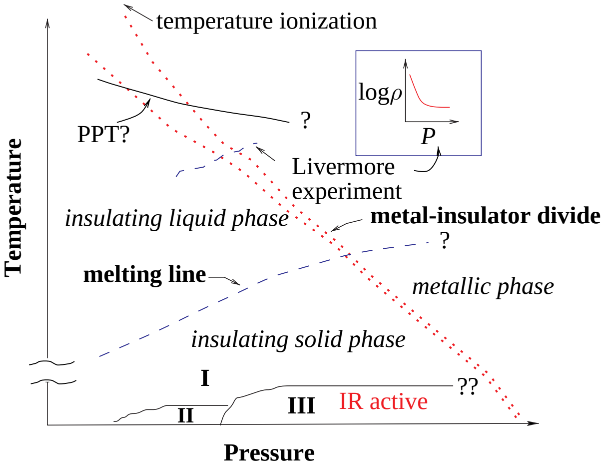

Figure 4. Schematic phase diagram. The metal–insulator transition in the liquid occurs at considerably lower pressure than the predicted transition in the solid. We suggest a metal–insulator band starting from the zero-temperature solid, and increasing in temperature with decreasing density as depicted above. At very low temperatures it will be sharp with the character of a thermodynamic phase transition. At the other extreme of low density and very high temperatures, the metallization will be by gradual transformation to a temperature ionized plasma. At zero temperature the metal–insulator transition is predicted to occur before (at lower density than) the diatomic–atomic transition. What happens at higher temperatures remains to be established. Possibilities include the crossing or merging of the lines, as well as their termination in one or two critical points. Recent theoretical predictions of a plasma phase transition (PPT) (Magro *et al.* 1995; Magro 1995; Saumon & Chabrier 1992) are schematically depicted as well. Also depicted in the figure is the Simon equation for the melting line, and the orientationally disordered (I) and ordered phases (II) and (III) found in the solid (Mao & Hemley 1994). We emphasize that this phase diagram is merely schematic; much still needs to be filled in.

resistivity, the primary measured quantity, take the value it does?; (b) why does the metal–insulator transition occur at a considerably lower pressure in the liquid than is predicted in the solid?; (c) what is the detailed mechanism of the metal–insulator transition?; and (d) what further experimental probes might clarify the situation?

7. The scale of resistivity in liquid metallic hydrogen

The fundamental approach to the transport properties of liquid metals is via the Kubo–Peierls–Greenwood theory, based on linear response of the system to a weak external field $E(t)$. The static conductivity $\sigma(0)$ is then given by

$$\sigma(0) \sim \int_0^\infty \langle j(0) j(t) \rangle \, dt, \tag{7.1}$$

where $\langle j(0) j(t) \rangle$ is a current–current correlation function for the many-electron system. If the self-energy of the electron system is sufficiently small (from all sources of interaction), then an expansion in the self-energy leads to an inversion of σ for the resistivity, and at lowest order this is equivalent to first-Born approximation within the Boltzmann semi-classical approach to transport. In the high-temperature limit it leads to the well known Ziman formalism (Ziman 1961; Faber 1972; Shimoji 1977) for degenerate electron systems, and this has been remarkably successful at predicting the resistivity of liquid metals to within about a factor of two, as well as trends seen in alloys, thermopower and the temperature dependence of the resistivity†. It requires as input the static structure factor $S(q)$ of the scattering system, an electron–ion interaction, and the assumption of an appropriate high-temperature limit.

To assess the applicability of this approach to the present problem, we may consider the case of liquid Si and Ge which prior to melting are not metals, though conduction by thermally excited carriers is evident. As fluids they are significantly under-coordinated (approximately 5–6) which reflects persistent covalent effects and hence interactions going beyond the pair model. In applications of the Ziman formalism to this problem, the tangible effects of remnant covalency are included only through the static structure factor $S(q)$; four electrons per ion are usually assigned to the conduction process (but see below).

In some ways, the situation for hydrogen can be considered physically similar to Si or Ge, only more extreme. It is, again, a fundamentally covalent (but not necessarily a network) system, and structurally it cannot be described just in terms of pairwise proton–proton interactions. The viewpoint taken from liquid Si (a metal) can be taken here if the state possesses a Fermi surface: in the application of the weak scattering formalisms covalency manifests primarily through $S(q)$ and in the specification of the fundamental excitations associated with the structure. As a first approximation (compare with the case for Si), two electrons per 'molecule' could be taken to participate in conduction, but with a significant density of states correction to be applied later. Given this fundamental picture essentially tied to the pairing picture of the solid, we proceed to investigate the resistivity of liquid metallic *molecular* H_2 (in the experimental metallization regime) starting with the Ziman expression (Ziman 1961; Faber 1972; Shimoji 1977). We express the resistivity ρ_L originating with a given type of carrier as

$$\rho_{\mathrm{L}} = m/n_{\mathrm{c}}e^2\tau, \tag{7.2}$$

where m is the carrier mass, n_c is the carrier density and τ is a measure of the relaxation time. In its simplest form the Ziman formalism gives (Louis 1997)

$$\rho_{\mathrm{L}} = \left(\frac{a_0\hbar}{e^2}\right)\frac{6\pi}{(n_{\mathrm{s}})(k_{\mathrm{F}})^2}\int_0^1 S(y)|v(y)|^2(y)^3\,\mathrm{d}(y), \tag{7.3}$$

where $y = q/2k_{\mathrm{F}}$ is the wave vector scaled by twice the Fermi wave-vector, n_s the number density of scatterers, $v(y)$ the screened coulomb potential, $S(y)$ the structure factor describing the proton–proton density fluctuations which scatter the carriers and $(a_0\hbar/e^2)$ can be viewed as the atomic unit of resistivity (it has the value of 21.7 μΩ cm).

The structural average required in the static structure factor appearing in (7.3) is not simple given the conditions of the experiment. In the first place translational energies appear well matched to rotational energies, and also to vibron energies. The kinematic transfer of energy from translational to vibrational degrees of freedom will be competitive with transference of translational energy to rotational energies. Accordingly, for this system the temperature and the density conspire in such a way that a standard averaging over rotational degrees of freedom prior to translational averaging is not secure. Second, orientational and translational entanglement leads

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† The resistivity of the liquid metallic state is often easier to calculate than that of the solid metallic state because in the former the scattering is dominated by density fluctuations while in the latter the scattering may come from a multitude of different sources such as defects, impurities, etc.

to considerable self-averaging in the determination of the static structure factor. Thirdly, it has to be emphasized that so far as the vibron excitations are concerned, the system is not at high temperatures, which affects both structural and scattering physics.†

In a naive approach using the usual free-electron density of states, and with the approximations introduced above for the structure factor $S(q)$, a resistivity of about 50 μΩ cm is found from (7.3), a significantly larger figure than obtained in previous calculations of monatomic H (Stevenson & Ashcroft 1974), but still considerably lower than the 500 μΩ cm measured experimentally (Weir *et al.* 1996). However, this is to be expected since in the one-electron picture we also anticipate a significant decline in the density of states at the Fermi energy‡.

If the band-gap has only just closed we expect a lowering of the density of states as compared with the full free-electron case which in turn can be linked to a significantly reduced effective carrier density. Equation (7.2) shows that a reduced number of carriers raises the resistivity¶; we also expect related multiple-scattering and other strong-coupling effects (see, for example, Kitamura & Ichimaru 1995) to be relatively important in this regime, and these effects also lead to higher resistivities.

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† In the usual application of the Ziman formalism, it is assumed that the temperature scale is such that $k_{\mathrm{B}}T \gg \hbar\omega$ for all excitations of interest in the system. While these conditions hold for translational and rotational energy scales, this is not true for vibrons. In fact, the temperature is quite closely matched to the vibron energies; a confluence that leads to the possibility of near resonant scattering processes. By taking fixed diatomic molecules we ignore the effect of vibrational excitation on the structure factor $S(k)$. We use an expression for the diatomic structure factor that includes the bond length of $1.4a_0$ and a Percus–Yevick structure factor with $\sigma = 0.29$ and $\eta = 0.29$ for the centre-of-mass–centre-of-mass part and as a first approximation neglects contributions from anisotropy (i.e. the free-rotation approximation (see, for example, Hansen & McDonald 1986)). The rotational and translational time-scales are about equal at this density, making the free-rotation approximation suspect. But even though simulations (Lenosky *et al.* 1997*a*, *b*; Pfaffenheller & Hohl 1997) give extremely short life-times for the 'molecules', a structure factor based on the static pair and free-rotation approximations does reasonably well (see, for example, Bunker *et al.* 1998).

The neglected vibrations lead to inelastic scattering effects. Baym (1964) showed that in this case the crucial quantitity is $S(\boldsymbol{k}, \omega)$, the dynamic structure factor for the protons defined by

$$S(\boldsymbol{k}, \omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} \langle \hat{\rho}(\boldsymbol{k}, t)\hat{\rho}^{\dagger}(\boldsymbol{k}, 0)\rangle,$$

where $\hat{\rho}(k)$ is the one-particle density operator for protons) the resistivity is then given by

$$\rho \sim \int_0^{2k_{\mathrm{f}}} q^3\, \mathrm{d}q |v(q)|^2 \int_{-\infty}^{\infty} (\mathrm{d}\omega/2\pi) S(\boldsymbol{k}, \omega)(\beta\hbar\omega/(\exp(\beta\hbar\omega) - 1)),$$

which reduces to the usual Ziman formula for $k_{\mathrm{B}}T \gg \hbar\omega$. The effect of the vibrations can be calculated and gives a correction to the static structure factor $S(q)$ proportional to q^2, but with a small enough prefactor (the same order as the correction for finite ion mass) to be ignored at this level of approximation.

‡ One reason for the success of the Ziman formalism is the so-called Edwards cancellation theorem which states that the d.o.s. corrections (as manifested in the effective mass) cancel out to first order (see, for example, Faber 1972; Shimoji 1977). However, in this case the Edwards cancellation theorem probably doesn't hold (see, for example, Itoh & Watabe 1984), and instead Mott's g^2 factor, where g is the ratio of the actual density of states to the free-electron value, must be included (Mott 1990). The minimum value of g is typically about 0.3, raising the resistivity by a maximum of about $1/g^2 \sim 10$.

¶ The mean-free path is roughly given by: $l = [174 \text{ a.u.}] \times [(rs/a_0)^2/\rho_\mu]$ (Ashcroft & Mermin 1976), which implies a mean free path of about 9 a.u. for a calculated resistivity of approximately 50 μΩ cm. Thus the Ziman formalism is self-consistent in that sense. A lower effective carrier density raises rs, so that in this approach the mean free path is still greater than the inter-molecular spacing for the larger (experimental) resistivities.

Thus by taking into account physics beyond the usual one-band picture our result of approximately 50 μΩ cm can only be seen as something of a lower bound. Since the overlap and related electron density is expected to increase with increasing density, this modified Ziman picture predicts that the resistivity at fixed temperature should continue to fall with increasing pressure so long as the liquid maintains its pairing correlations. We emphasize, however, that the pairs are in no sense permanent (again an analogy to fast exchange in liquid Si can be made) although they are long lived on *electronic* timescales and as such influence the electronic structure.

At present the experimental results have large error bars (20% in the metallic state) and are in too small a pressure range to confirm or falsify any predicted pressure dependence of the resistivity, but the actual value of the resistivity near metallization seems consistent with this picture, though this is not the only possible interpretation (see below).

8. The onset of the insulator to metal transition

At first sight the lower pressure and density of the metal–insulator transition in the liquid compared to the solid may seem surprising. One would expect the greater disorder (as compared with the solid) to delay the closing of the gap and the subsequent onset of metallization as is for example the case in Hg, another divalent pressure-induced metal–insulator transition (Kresse & Hafner 1997). However, a closer look at the origin of the band-gap in the solid phase reveals a more complex possibility which can be illustrated in the Pa3 structure, an isotropic solid which best mimics the high coordination and orientational averaging characteristics of the 'paired' liquid. The lower bands in such a structure can be represented by an equivalent face-centred cubic description (Ashcroft 1995*b*) where the principal Fourier components of the electron interaction with pairs are given by

$$V_{111} = (\tfrac{3}{4}\pi r_{\mathrm{s}}^3 a_0^3) S_0(111) v(111) \tag{8.1}$$

and

$$V_{200} = (\tfrac{3}{4}\pi r_{\mathrm{s}}^3 a_0^3) S_0(200) v(200). \tag{8.2}$$

Here S_0 is the structure factor per proton, and is given by

$$\begin{aligned} S_0(l,m,n) = \tfrac{1}{4}\{&\cos 2\pi\alpha(l+m+n) + (-1)^{m+n}\cos 2\pi\alpha(l-m+n) \\ &+(-1)^{l+m}\cos 2\pi\alpha(-l+m+n) + (-1)^{n+l}\cos 2\pi\alpha(l+m-n)\}, \end{aligned} \tag{8.3}$$

with $\alpha = d(r_{\mathrm{s}})/\sqrt{3a}$ ($2a$ being the separation, on average, between protons) and $v(K)$ is the Fourier transform for the screened potential of a single proton.

Increase of the temperature to ($k_{\mathrm{B}}T \sim \hbar\omega_{\mathrm{vib}}$) significantly excites the pairs into higher anharmonic vibrational states resulting in large amplitude spatial fluctuations. These in turn will lower the gap by a corresponding Debye–Waller factor, and given that the excursions are appreciable, the lowering can be significant. This can be demonstrated most easily by extending one of the four pairs in the Pa3 structure to a separation of $2d'$ ($2d' > 2d$) while the other basis pairs are kept fixed. From (8.3) the structure factor per proton for such a separation becomes

$$S(l,m,n) = S_0(l,m,n) - \tfrac{1}{2}\sin[\pi(\alpha'-\alpha)(l+m+n)]\sin[\pi(\alpha+\alpha')(l+m+n)], \tag{8.4}$$

which shows immediately that the gap will be reduced when the pair extends. This gives a strong hint of the likely effect of temperature, primarily to reduce the gap, and to promote an earlier transition from insulator (or semi-conductor) to metal. Note that a displacement arising with acoustic phonons can also contribute to this effect.

9. The physical characteristics of the insulator–metal transition

At the one-body level the general closing of the gap with increasing pressure and density appears well established, but what exactly happens upon close approach to the metal–insulator transition in hydrogen? Some possibilities now follow.

(a) Scenario 1: metal–insulator transition induced by one-body physics

In a continuous single-particle approach, the gap closes and progressively more and more carriers are excited into the conduction band; structurally this implies strong pairing correlations. Depending on the decline of this gap, the emerging conductivity can be significant. Experiments and theory converge on a consistent picture for hydrogen where the band-gap decreases with increasing pressure, both in the solid (Chacham *et al.* 1992; Mao & Hemley 1994) and liquid (Nellis *et al.* 1992) phases. In the solid, the concept of an indirect gap closing with increase of density in the paired phase is robust when calculated in various crystal structures and it also obtains under orientational disorder (Friedli & Ashcroft 1977; Kaxiras *et al.* 1991; Chacham *et al.* 1992); if generalized to the separation between mobility edges (Mott 1990), we expect it to carry through for the liquid phase as well†. Accordingly, under the assumption that the liquid remains largely paired, this view leads to a picture where the one-electron physics of the liquid may be similar to that of the solid; under pressure mobility edges are gradually approaching, and if this continues hydrogen will be transformed from a liquid semi-conductor to a liquid semi-metal. As pressure increases further the 'bands' overlap (mobility edges cross), and the effective carrier density continues to increase, eventually becoming degenerate‡.

The vibrational dynamics of the H_2 molecules imply an interesting possibility for the scale of conductivity in the semi-metallic regime (i.e. $k_BT \sim E_g$). If we assume that the electrons hop from pair to pair when close approach sufficiently increases orbital overlap, then their time-scale will be set by those translational excursions which bring molecules into sufficient proximity that wave-function overlap is especially effective (i.e. $\tau \sim 10^{-14}$ s). Together with a standard semiconductor picture invoked to estimate the carrier density (see, for example, Ashcroft & Mermin 1976, p. 575), this quickly leads to resistivities as low as approximately 700 $\mu\Omega$ cm for $E_g \sim 2k_BT$ (Louis 1997)!

Note, however, that the liquid phase corresponds to proton arrangements that are strongly disordered. If viewed at low temperatures, disorder can lead to states that lack diffusion, via Anderson-localization. The role of temperature is then to excite electrons from such states. Note, however, that the condition for Anderson

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† This in contrast to some narrow gap semi-conductors, or semi-metals like Bi, which would become a good metal upon a very slight distortion of the structure (see, for example, Ashcroft & Mermin 1976).

‡ The reader might wonder why we use language inspired by bands in this manifestly disordered system where the wave vector $\boldsymbol{k}$ is not at all a good quantum number. Although the concept of energy bands is not entirely correct here, it is well known that for many liquid metals the band structure of a solid with similar local coordination gives a good approximation of the electron physics of the liquid (Faber 1972), and so this is the sense in which we use the concept of bands here.

localization is similar to the condition for the Mott transition:

$$D_{\mathrm{m}}^{1/3} a^* \sim C, \tag{9.1}$$

where a^* is a measure of the localized orbital size, and C is typically about 0.3 (Mott 1990). Under the assumption that the Bohr radius for diatomic hydrogen is roughly the same as the Bohr radius of monatomic hydrogen, $D_{\mathrm{m}}^{1/3} a^* \sim 0.3$ at experimental metallization conditions.

(*b*) *Scenario 2: metal–insulator transition and the role of many-body physics*

Mott (1990) argued that a gap will never close continuously because upon restoration of residual many-body interactions, the formation of excitons which subsequently unbind upon further closing of the gap will lead to a jump in the conductivity. We expect in this case that the temperature of approximately 0.3 eV will be too high for the formation of excitons (see, for example, Halperin & Rice 1968) but this does not rule out some other type of correlation driven transition near band-gap closure. For example, the Hubbard U for monatomic hydrogen is about 17 eV (Mott 1990) while the free-electron band-width at experimental conditions is around 20 eV, which is probably an upper bound. Since the effects of disorder and correlation are expected to reinforce each other (Thouless 1979) the possibility of conductivity by thermal excitation across a declining Mott–Hubbard gap emerges. If we are in the regime where electron–electron interactions play an important role, the effect of spin becomes non-trivial. The twin effects of strong correlation and disorder as they influence the metal–insulator transition are not completely understood; they combine with some force in the hydrogen problem.

The highly successful semi-empirical Herzfeld polarization catastrophe criterion predicts that H_2 will become metallic only upon about 11-fold compression (Edwards & Sienko 1983; Ross 1972) (generally for ordered phases). However, we note that there is some ambiguity in the definition of the various quantities entering these criteria (for instance the meaning of local polarizability in the present environment), a problem that becomes even more acute for hydrogen where the fluid phase is involved.

(*c*) *Scenario 3: metal–insulator transition induced by structural change*

If simple pressure-induced band-gap closure in the paired state is preceded by significant structural change, metallization can also precede complete closure of this gap. Perhaps the best-known case of a metal–insulator transition driven by structural change is the metallic behaviour seen when melting the elemental semi-conductors such as Si and Ge (as discussed above). The change in band structure is driven by the change in local atomic structure, in this case a relatively small increase in coordination. In the case of hydrogen, structural change associated with, for example the rapid decline of pairing correlation, is a likely candidate. In the liquid phase, we have a direct parallel of the crystalline case discussed in § 8 above.

In fact, the Wigner–Huntington proposal (Wigner & Huntington 1935) itself falls into the class of MI transitions induced by structural changes. Here it was predicted that increasing pressure (at $T = 0$) could lead to dissociation in hydrogen, resulting in a structure with one electron per unit cell and concomitant metallic behaviour for paramagnetic states†. Even at relatively low densities, increasing the temperature

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† It is interesting that at their original predicted density, the monatomic solid would be close to a Mott–Hubbard insulator!

to regimes comparable with the dissociation energy will also rupture the H–H bond, possibly leading to metallic (conducting) behaviour. The case at hand is clearly much more subtle. At the extreme pressures of the shock experiment, the H–H bond is significantly weakened, but even at $r_s = 1.5$ (approximately nine-fold compression) the corresponding well depth continues to have a magnitude significantly larger than the temperatures achieved†. To date no evidence of static pressure induced dissociation in the solid has been observed, even at the significantly higher pressures of 250 GPa achieved by ultra pressure diamond anvil-cell techniques. Although the evidence above refers to zero-temperature solids in particular structures, increasing the temperature is not likely to change the well depth significantly.

At these extremely high densities and temperatures, the very concept of *dissociation* is nebulous. High temperatures will excite large amplitude stretching motion, leading for example to exchange of atoms from neighbouring pairs, or to the transient formation of new localized species (‘H_3’, etc.) and so standard chemical definitions are not unique. Perhaps it is better to speak of local coordination in a completely statistical sense, for example as the integral of the pair correlation function carried out to a certain distance. These changes in local coordination certainly lead to corresponding changes in the global electronic structure as pointed out in an interesting recent tight-binding (TB) molecular dynamics study by Lenosky *et al.* (1997*a*, *b*). Here ‘dissociation’ is defined by asserting that two atoms constitute a dimer if each forms the nearest-neighbour atom of the other. Atoms not identified as belonging to a dimer are then termed dissociated ‘monomers’. Interestingly, they find that states near the chemical potential have a large projection onto these ‘monomers’, and so by virtue of the Mott formula, for which resistivity scales as the inverse square of the density of states at the Fermi energy, the resistivity in their simulation scales inversely with the square of the average number of ‘monomers’. The mechanism they propose (similar to that suggested by Ross (1996)) in which the ‘dissociation’ plays a crucial role is a possible candidate for what might happen in liquid metallic hydrogen. However the large Hubbard U, included only indirectly through the effective parameters in TB, suggests that dissociation does not necessarily imply a conducting state. This may help explain why the TB conductivities found at low density and pressure are much higher than the experimental ones (Lenosky *et al.* 1997*a*, *b*).

Recently Pfaffenzeller & Hohl (1997) carried out Car–Parrinello *ab initio* molecular dynamics (AIMD) simulations on the metallic side of the M–I transition and find an even higher ‘dissociation fraction’. Because of the extremely short life-time of the pairs they term the metallic liquid ‘monatomic’, even though it retains significant pairing correlations. Their lowest density is slightly higher than the metallization density calculated for the experiments ($D_m = 0.4\ \mathrm{mol\ cm^{-3}}$ versus $0.32\ \mathrm{mol\ cm^{-3}}$) and they find a resistivity about a factor six smaller than the experiments. Simulating the metal–insulator transition with AIMD is difficult because the local density approximation (LDA) underestimates the gap, and the sensitivity on k-point sampling (see, for example, Edwards *et al.* 1995; Kohanoff *et al.* 1997) (the AIMD calculations

† Full *ab initio* LDA calculations of the pair potential in the solid phase at the liquid metallization densities give a well depth of about 3 eV, and also the correct vibron frequency of about 0.5 eV. These calculations also show very strong many-body effects making pair-potentials suspect (see, for example, Edwards & Ashcroft 1997). Even free H_2^+ is strongly paired with a dissociation energy of about 2.8 eV, a fact which helped motivate an earlier prediction of metallization in the molecular liquid (Ashcroft 1968). In the solid, vibron overtones have been measured up to pressures of 170 GPa (Chen *et al.* 1996; Hemley *et al.* 1996).

above use only one k-point) makes accurate large-scale simulations computationally intensive. Once again, the large Hubbard U implies that spin correlations may be important, necessitating AIMD simulations based on spin density functional theory instead of the usual paramagnetic ansatz.

But whether any of these these mechanisms describe the shock experiments (Weir *et al.* 1996) fully has yet to be established. The gap closes with increasing density even in an entirely diatomic phase, and if the TB or AIMD even slightly overestimate the 'dissociation', the metallization in the simulations will occur through the 'dissociation mechanism' instead of through a pure band-overlap scenario. In fact, as evidenced from comparison of pair correlation functions, the TB and AIMD results give a larger 'dissociation' fraction than the path-integral Monte-Carlo (PIMC) results of Magro *et al.* (Magro *et al.* 1995; Magro 1995). While PIMC includes the substantial zero-point motion of the protons which the TB and AIMD neglect, PIMC is usually carried out in a much smaller cell. Presently it is not clear which method is best suited to the experimental regime and the sensitive interdependence of dissociation and metallization physics coupled with a possible role for strong correlations will render an unambiguous interpretation of the simulations difficult.

Early predictions of finite-temperature pressure-induced metallization fall under the general rubric of *plasma phase transitions* (PPT)†. Most theories take a chemical approach, that is the species (bound states) are well defined, and this is at variance with the extremely short life-times predicted by simulations. Besides ignoring the possibility of band-overlap metallization, the chemical models are typically based on pair-potentials and a free-rotation approximation, both of which are ill-defined at these densities as we have noted. The most comprehensive chemical model calculations were carried out by Saumon & Chabrier (1992) who predict for the PPT a critical point at $T = 15310\,\mathrm{K}$ and a density of $D_\mathrm{m} = 0.18\,\mathrm{mol\,cm^{-3}}$, and at higher densities and lower temperatures an increasingly discontinuous transition between a diatomic insulating state and an ionized (conducting) monatomic phase (see also figure 4). In support of these chemical models, the physically based PIMC calculations (Magro *et al.* 1995; Magro 1995) also give rather similar results. On the other hand the TB simulations give a gradual transition to a more 'monatomic' phase. The metallization experiments appear just out of the range of the PPT predictions. To establish the existence of a PPT by shock experiments will also require a range of temperature and density data.

Clearly the experiments are in a very interesting regime; the interplay of thermal and electronic effects brings the system close to both the closing of the gap *and* the onset of pair fragmentation, the two being interconnected. Which occurs first will depend sensitively on the actual temperature and pressure and one could imagine different behaviours at different state points. For example at densities just below the proposed diatomic metal–insulator transition at 0 K one would expect a I–M transition of the band-overlap type while at higher temperature and lower densities structural change, if it exists, becomes more important. A definitive electronic interpretation of the Livermore shock experiments is still lacking, and could prove to be quite unlike the conventional explanations of transport properties of ordinary liquid metals.

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† The PPT was first proposed by Landau & Zeldovich (1943) for a somewhat different system. Since then the term PPT has been applied to a multitude of different transitions of the insulating–conducting type.

10. Future experimental probes

Considerations based both on a simple band-overlap scenario within the Ziman formulation, and the 'dissociation'-based mechanism proposed by Ross and Lenosky *et al.* (Lenosky *et al.* 1997*a*, *b*; Ross 1996), predict that the conductivity is high, but that it should drop with increasing density. Experiments going to higher pressure would therefore be of great interest. However, so also would shock experiments at about the same compression but lower temperatures. If the arguments given above are valid, then as depicted in figure 4, a boundary should be crossed (at fixed P) locating the I–M transition. One could also envisage that at even higher pressures, the I–M transition would be at low enough temperature to be within reach of static pressure techniques such as diamond anvil cells†.

The transition to a conducting state in hydrogen may be quite unusual. The tenacity with which H retains its pairing, an effect driven largely by exchange, can be manifested even in a metallic environment and at quite high temperatures. Though covalent, this ensuing state is not of a network character as in molten Si (or Ge), but a rapid exchange of pairs (akin to the fast exchange proceeding in Si and Ge) may be proceeding. It is an interesting and perhaps novel state of matter, which now merits considerable further study.

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† Heating of hydrogen can cause diamond anvils to fail, but at high enough pressures the metal–insulator transition should occur at temperatures that may be low enough to avoid this failure.

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Discussion

R. L. Johnston (*School of Chemistry, University of Birmingham, UK*). Isn't part of the problem that we are using words such as 'molecules' in a regime where they may not be applicable? Professor Nellis has said that these dimers are very short lived and undergoing large amplitude vibrations. Wouldn't another way of describing this system be as a dynamic system undergoing 'sticky' collisions (as in soft sphere collisions)?

W. J. Nellis. Yes there is a language issue here. The term 'molecule' implies permanency, i.e. a molecule is long-lived on electronic time scales. Since we are talking about 'molecules' whose lifetimes are only a few vibrational periods, a better term is 'transient pair'. The vibrational period of H_2 is 7 fs.

C. N. R. Rao (*Indian Institute of Science, Bangalore, India*). (i) I am afraid that Professor Nellis has not clearly stated the state of hydrogen in the metallic regime. Is it molecular or atomic? As a chemist, I would prefer atomic species, even possibly the presence of H^+ and H^-. In any case, the atoms/molecules must be ionized to produce charge carriers. Does he prefer H_2^+ or H^+?

(ii) Is the carrier concentration 10^{23} or 10^{21}? 10^{21} is what one finds in low density metals and oxides at the metal–non-metal boundary. If it is 10^{23}, then H atoms ionizing (producing 2e for H_2) would explain the high carrier density.

W. J. Nellis. (i) The whole idea of distinct independent chemical species is questionable in this regime due to the high densities and the continuous exchange of protons between transient pairs. This in turn obscures the definitions of 'ionization' and 'dissociation fraction'. Thus the exact nature of this unusual fluid needs to be determined. However, with this caveat in mind, we estimate from thermodynamic considerations that about 5% of the molecules are dissociated into monomers. Some of the transient pairs and the monomers so formed are probably neutral. Based on tight binding molecular dynamics simulations of Lenosky *et al.*, we estimate that at the densities and temperatures of metallization the major constituent is the transient pair. The protons in all the species are exchanging on the timescale of 10^{-14} s. All of these species form a mixture with a common electronic density of states and common electronic excitation energy in the semiconducting fluid. The relative contribution of conduction electrons from transient pairs (H_2^+) or monomers (H^+) depends on their relative contributions to the density of states at the Fermi level and that remains to be determined.

(ii) The concentration of electronic carriers at the Fermi level of the metal is *ca.* 10^{22} cm^{-3}.

D. P. Tunstall (*School of Physics and Astronomy, University of St Andrews, UK*). Please could Professor Nellis indicate what regions, on the T-P phase diagram, he thinks one can access by changing the initial conditions.

W. J. Nellis. By changing the initial conditions, I estimate that we can sample pressures in the range 50–300 GPA and temperatures in the range 1000–10 000 K.

H. von Löhneysen (*Institute of Physics, University of Karlsruhe, Germany*). Concerning the question of dimers versus monomers at the non-metal–metal transition: is it feasible to perform optical measurements to look for rotational transitions of H_2? At these high temperatures and pressures ortho–para conversion to higher rotational states should perhaps become significantly fast to occur during the short time scale of the experiment.

W. J. Nellis. Unfortunately, at present it is not possible to perform optical experiments on metallic fluid hydrogen. Although we begin with transparent single-crystal sapphire anvils, the high rate deformations produced by the reverberating shock wave turns the anvils into opaque polycrystalline alumina.

P. P. Edwards (*School of Chemistry, University of Birmingham, UK*). (i) Could Professor Nellis provide a brief summary of the evolution of his project at Lawrence Livermore, i.e. from its begining to the present day experimental situation?

(ii) A general observation might be that the ‘metallization process’ in a range of liquid elements occurs at a consistently lower density (pressure) than that of the corresponding solid element. I suppose that the metallization of elemental hydrogen by Professor Nellis is the most spectacular example of this. Could he comment on this?

(iii) I suppose, related to the above point, is the chemical observation that the liquid Periodic Table of the Elements (at their melting points) contains more metals than the corresponding solid Periodic Table!

(iv) What are the prospects for pressure-induced metallization of fluid lithium hydride, LiH?

W. J. Nellis. (i) We began to measure physical properties of cryogenic liquids in 1976. I designed the sample holders and cryogenics to use liquid hydrogen and helium so that any liquid with a boiling point of 4 K or higher could be studied. In the early 1980s. A. C. Mitchell and I measured the Hugoniot equation-of-state of liquid H_2 and D_2 in the range 2–80 GPa. At that time we were told by a theoretician that there was no point in going to higher shock pressures because we would find nothing interesting. We then focussed our attention on other liquids, such as He and N_2. In the mid 1980s a graduate student joined the group and tried measuring electrical conductivities of liquid hydrogen under single-shock compression. We could only do about three of these experiments per year and for the first two years, none of these experiments were successful because of cryogenic vacuum leaks. Eventually I learned that a crucial step in the assembly had been dropped. An acid etch, which had been used to clean Al surfaces prior to gluing together our cryogenic holders, had been dropped for environmental reasons. After finally learning the source of the problem, the student graduated. A few years later, A. C. Mitchell returned to Lawrence Livermore National Laboratory and we restarted the conductivity experiments. After safely reinstating the acid etch, single-shock hydrogen conductivity experiments became successful. In the early 1990s, Mitchell and I did five such experiments and determined the electronic energy gap of singly shocked hydrogen. To analyse these data we used calculated temperatures. In 1992, N. C. Holmes and I began optical experiments to measure the temperatures of shock-compressed hydrogen. The results showed that the calculated temperatures we used previously up to 20 GPa were correct but at 83 GPa the measured temperatures are lower than expected if the hydrogen molecule does not dissociate. This was the first indication that hydrogen does not remain totally molecular under the conditions we can achieve. In 1991 S. T. Weir, Mitchell and myself began the series of experiments to measure the electrical conductivity of hydrogen up to 180 GPa using a reverberating shock wave. We spent three years doing ten experiments and a year analysing the data. In 1995 we announced that we had made metallic hydrogen. Weir began this project as a postdoc and now works elsewhere in the Laboratory. Mitchell has retired. A new postdoc has started work on these experiments.

(ii) Yes, metallization pressures are often lower in the liquid than in the solid. For example, solid I_2 becomes metallic at 16 GPa at room temperature. Liquid I_2 becomes metallic at 3 GPa and 1000 K. Si at room temperature becomes metallic at a few tens of GPa. Simply melting Si at 1 bar produces the metallic state.

(iii) In many cases melting causes non-metals to become metallic. One example is Si. I want to emphasize, however, that our belief that hydrogen is in the fluid phase is based on extrapolation of measured melting curves up to *ca.* 400 K and on theoretical calculations. Melting temperatures at 100 GPa pressure have yet to be measured and there are unresolved theoretical issues. Thus, the phase of metallic hydrogen still needs to be determined.

(iv) We have no plans to try to metallize LiH.

D. E. Logan (*Physical and Theoretical Chemistry Laboratory, Oxford University, UK*). Dr Nellis remarked that concurrence with the 'Mott criterion' for a metal–insulator transition—namely $n^{1/3}a_{\mathrm{H}} \sim 0.25$—shows the importance of electron correlation in dense hydrogen. The latter may well be true, but cannot be inferred from the Mott criterion—which in practice is satisfied for virtually any material undergoing an MIT and by, itself, gives no hint of the underlying mechanism(s).

W. J. Nellis. I agree. $n^{1/3}a_{\mathrm{H}}$ is just a ratio of the effective Bohr radius to the distance between particles supplying electrons. As such it gives no hint of the underlying mechanism(s). However, I believe that at this high-density many-body effects occur at metallization.

It is important to calculate theoretically the metal–insulator transition at finite temperature. To do so requires a definition of the M–I transition at finite temperature. At present there is no generally accepted definition. This is very important in hydrogen at high pressures and temperatures.

A long-standing problem in hydrogen at high pressures and high temperatures is whether or not the plasma phase transition exists. Theoretical work is needed in this area. However, no first-order phase transition has ever been observed in a fluid at the high pressures and temperatures achieved by shock compression. The reason is thermal smearing. The prediction of the plasma phase transition is model dependent. For these reasons, I do not believe that the plasma phase transition exists.