Chapter 3

Metallization of Fluid Hydrogen

3.1 Introduction to Metallic Hydrogen

3.1.1 Some background on dense hydrogen

Hydrogen, out of it the Universe evolved,
every atom and leaf, marine iguana

and apricot-smelling chanterelle. But my, my,
what alchemy: nondescript H_2

–Diane Ackerman[1]–

Hydrogen, a deceptively simple mixture of electrons and protons in equal concentration, is commonly thought of as a group I element, a correspondence which helped motivate the classic 1935 paper by Wigner and Huntington[1] in which they predicted that pressures above about 25 GPa would be sufficient to break the diatomic bond, leading to one electron per unit cell, and within a standard band-theory picture, metallic behavior. Since then hydrogen has often been viewed as

[1] Taken from "Jupiter", in *The Planets A Cosmic Pastoral*, Diane Ackerman, William Morrow and Company Inc. New York (1976)

the prototypical (MIT) system and has been intensely studied; experiment and theory revealing a remarkably rich phase behavior.

A joint intertwining of strong Coulomb interactions and quantum mechanics produces a robust molecule[2], and in the solid phase heroic attempts to metallize it and to eventually rupture the bond have not yet been successful. Instead, at low temperatures, solid paired hydrogen undergoes a number of phase transitions with increasing density, each of which seems to open the energy gap in such a way that it stays insulating up to 10-fold compression[2, 3, 4] and pressures an order of magnitude higher than originally predicted by Wigner and Huntington.

This persistence of pairing suggests that hydrogen is perhaps better described as a group VII element[5], with one electron short of a filled shell. Like the halogens, it condenses into a diatomic insulating solid, and, as was predicted 20 years ago[6, 7], it can become metallic in the diatomic phase by a band overlap transition. Iodine is a good example of this; it becomes metallic by a band-overlap transition at about 16Gpa[8], before the diatomic bonds are broken at slightly higher pressures.

The quest for metallic hydrogen has been motivated in part by the hope that understanding the (MIT) in this "simple" system would lead to new understanding of the phenomenon in more complex materials. However, hydrogen is far from a simple material. Instead, experiments consistently surprise, leading repeatedly to an overhaul of theoretical models. There are several reasons for this: first, hydrogen has no core-electrons, there is no pseudo-potential to soften the electron-ion interaction from its bare Coulomb form, and so higher order scattering effects quickly become relevant. Second, the low mass of the protons implies substantial zero-point motion (around $0.25eV$ per proton at 10-fold compression) which is difficult

[2] The energy required to separate the free molecule into atoms is $\sim 4.5eV$.

to treat theoretically. Mainly for these two reasons (there are more) dense hydrogen research consistently stretches the limits of our calculations and theoretical models, resulting in a deeper and more complete understanding of the theory of rarefied and condensed matter.

Besides the fundamental interest as a model system, dense hydrogen is crucial to the understanding of the giant planets. For example Jupiter and Saturn contain almost 400 earth masses of hydrogen, most of which is in a dense (hot) fluid phase. Details of the MIT transition can profoundly influence theories of the interior of these planets. For example, convective motion in metallic hydrogen produces large, observable magnetic fields through a dynamo effect[9], and the recent experiments demonstrating metallization of fluid hydrogen[10] have interesting implications for the interior of Jupiter[11]. Also, Jupiter-size planets now being discovered close to nearby stars[12] 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 therefore in the fluid state[13].

3.1.2 What (When) is a metal?

..., instead of having a cosy arrangement in which each ion has its 'own' electron bound tightly to it, we have a sort of communist society ..."

–J.M. Ziman[3]–

The electrical resistivity of the elements can range anywhere from $\rho =\sim 1\mu\Omega cm$ for copper to $\rho \sim 10^{18}\mu\Omega cm$ for sulphur, 18 *orders of magnitude!*, arguably one the largest natural variation of any material property at normal equilibrium con-

[3] J.M Ziman in *Electrons in Metals: A Short Guide to the Fermi Surface*, London, Taylor and Francis (1964)

ditions[4] Materials with low resistivity are typically called metals, materials with high resistivity are typically called insulators. With that the question: *"What is a metal?* would seem closed, but this optimistic assessment breaks down when external conditions such as temperature, pressure or composition are are varied: many materials transform from metals to insulators and vice-versa under the action of varying an external parameter. These metal-insulator transitions have spectacular consequences for the resistivity, they have been described as "turning copper into wood"[5], but the phenomenon remains poorly understood, still standing as one of the premier intellectual challenges of our day. In the words of P.P. Edwards and M.J. Sienko; "The two questions: 'What is a metal?' and 'When does a metal transform to an insulator?' are indeed inseparable"[14].

The traditional understanding of "What is a metal?" is based on a one-electron approximation (band-theory) and crystalline order. In fact, "the conductivity of a perfect periodic crystal is infinite"[6], the electrons are in stationary Bloch states, with all effects of the periodic lattice taken into account. Certain symmetries may also preclude conductivity: If there are for example two electrons per unit cell and thus no readily accessible states for conduction, a material is a perfect insulator[15]. At the level of band-theory (and at $T = 0$) all matter is classified into perfect metals and perfect insulators. For metallic systems any residual resistivity must therefore arise through deviations from perfect crystallinity: phonons, defects, grain-boundaries etc.., and one intuitively expects greater disorder to induce larger resistivities.

In the light of this, the recent shock-compression experiments of Nellis et al[10],

[4] If we extend this point to compounds, fused quartz has a resistivity even higher than sulphur, namely $10^{26} \mu\Omega cm$!

[5] C.N.R. Rao, private communication to P.P. Edwards

[6] See [57] page 215. Of course this holds for partially filled bands only.

which claim to metallize hydrogen in the (disordered) fluid state at pressures and densities for which the (periodic) solid is still in the insulating phase, are all the more surprising. This new fluid state straddles the borders of plasma physics and solid-state physics, as well as the borders of the classical statistical mechanics of a correlated molecular liquids and the quantum physics of correlated electron liquids. A theoretical discussion of these experiments will necessarily explore and illuminate multiple aspects of the twin questions "What is a metal" and "When is a metal", and this forms the focus of the present chapter.

3.1.3 Short historical retrospective on the metal-insulator transition and the definition of a metal*

"He [Sommerfeld] didn't even care terribly much why electrons were free, which I thought was a very important thing to know"

–H. A. Bethe†

A few years after J.J. Thompson's 1897 discovery of the electron, P. Drude[20] put forth the first theory capable of describing metallic behavior from quasi-microscopic concepts, albeit within a completely classical kinetic picture. The first successful application of quantum mechanics to conduction electrons was the semi-classical electron theory developed by Sommerfeld in 1927[21] who applied the new quantum statistics to the old Drude theory. However, as the quote by Bethe at the beginning of this section shows, Sommerfeld did not discuss why the electrons were free, i.e. why the system was metallic. In that same year however, P. Bridgman considered the question of high density in a paper entitled "The Breakdown of Atoms at High

* Much of this section was taken from references[17],[14], and [19].

† Interview with Bethe, as recorded by T.H. Kuhn in *Archive for the History of Quantum Physics* (New York, Copenhagen, Berkeley and Minneapolis) and referenced in[17].

Pressures"[22]. Stimulated by his discovery of the change of certain properties of potassium under high pressure, he postulated that not only high temperature, but also high pressure (i.e. high density) could cause the breakdown of atoms to an electrical gas of electrons and protons. The next year, F. Bloch[23] proposed this theory of the quantum state of independent electrons in a crystalline potential, and soon thereafter A.H. Wilson proposed his theory of why crystals were metals or insulators based on band structure[24]. However, as he himself later wrote[25]: "Bloch's theory had in fact proven too much. Before his paper appeared it was difficult to understand the existence of metals. Afterwards it was the existence of insulators that required explanation. This problem had been by-passed because it was taken for granted that insulators were merely bad conductors rather than non-conductors, the difference between metals and insulators being a quantitative and not a qualitative one. This concept I now challenged."

The considerations above are all based in some way on a picture of independent non-interacting electrons. That view was first seriously challenged at a 1937 conference in Bristol, where de Boer and Verwey presented data that convincingly showed that the Wilson theory of metals and insulators gave incorrect results when applied to NiO[26]. Peierls pointed out that this was most likely related to neglect of the electron-electron interactions, and this inspired Mott to consider ideas beyond the simple Bloch-Wilson band-theory of independent electrons and propose his theory of a correlation induced metal-insulator transitions (now called the Mott-transition)[27]. Some years later, Anderson proposed that sufficiently perturbing crystalline symmetry by disorder could also lead to localization within a model of non-interacting electrons and a MIT as well[28].

These quantum pictures are basically $T = 0$ statements, and the difference between a metal and an insulator is crystal clear, "a metal conducts and a non-metal doesn't"[15]. At finite temperatures the definition of a metal becomes more ambiguous. For systems that are insulating at $T = 0$, but which have small gaps, the raising of the temperature thermally excites more and more electrons into conductive states so that the conductivity becomes temperature dependent. Even more spectacular variations in conductivity occur happen as the temperature is raised high enough provoke a structural change. For example upon melting, Si has a large conductivity jump to a value similar to that of many metals. In fact, the periodic table of melted elements includes more highly conductive materials than the usual periodic table at standard conditions. Thus although the $T = 0$ definitions are clean and well defined, they don't apply well at the finite temperatures usually encountered in nature. An operational definition could be that a metal is a material with a conductivity in the "metallic range", although this would also include plasmas where the electrons are thermally stripped from their parent atoms. To differentiate between non-degenerate plasmas and degenerate systems, a useful definition would be that metals are materials (solid or liquid) with a reasonably well-defined Fermi-surface[‡]. For this chapter, we shall hold to a combination of the last two definitions: namely we shall call our material (hydrogen) metallic when it has a conductivity in a "typical" metallic range, but is still at conditions where the electrons are expected to be mostly degenerate[§]

[‡] which is strictly defined at $T = 0$ only, but still measurable at finite temperatures far below the Fermi temperature

[§] That is, we assume a Fermi-surface, even if it cannot be directly measured (yet).

3.2 Description of the Livermore Experiment

... I experienced retrospective fear and at the same time a kind of foolish pride, at having confirmed a hypothesis and having unleashed a force of nature. It was indeed hydrogen, therefore: the same element that burns in the sun and stars, and for whose condensation the universes are formed in eternal silence.

–Primo Levi¶–

The Livermore experiments[10] were carried out with a two-stage gas-gun which accelerates an impactor plate up to $\sim 7km/s$[29]! Needless to say, the plate impact on a cryostat containing liquid hydrogen produces extremely high transient pressures, in fact pressure and temperature conditions extreme enough for the metallization of hydrogen. In contrast to the diamond-anvil cell techniques which produce static pressures and remain at low temperatures[2, 3, 4], this dynamic shock technique simultaneously raises the pressure and temperature. The novel aspect of the Livermore experiments is their use of a reverberating multiple shock technique which keeps the final temperature much lower than traditional single shock techniques do[30]. Important also in this is an initial state at low temperatures – hence the cryostat. The result is megabar pressures but at temperatures where the electrons are still degenerate. (see [10, 31] and figure 3.1 for more details).

The compressed state of hydrogen only exist for about 200 ns, short on chemical and phase-transition timescales, but long enough on molecular time-scales to achieve thermodynamic equilibrium in a single phase, and also very long on the time scale of present day modern electronics. An important point to keep in mind is that the system may not have reached its equilibrium phase should it happen that the system has just crossed a phase boundary. On the other hand, because of its high chemical reactivity and large mass-diffusion coefficient it is essential to have a temperature

¶ Primo Levi in *The Periodic Table*, Schocken Books, New York, (1984), p 28.

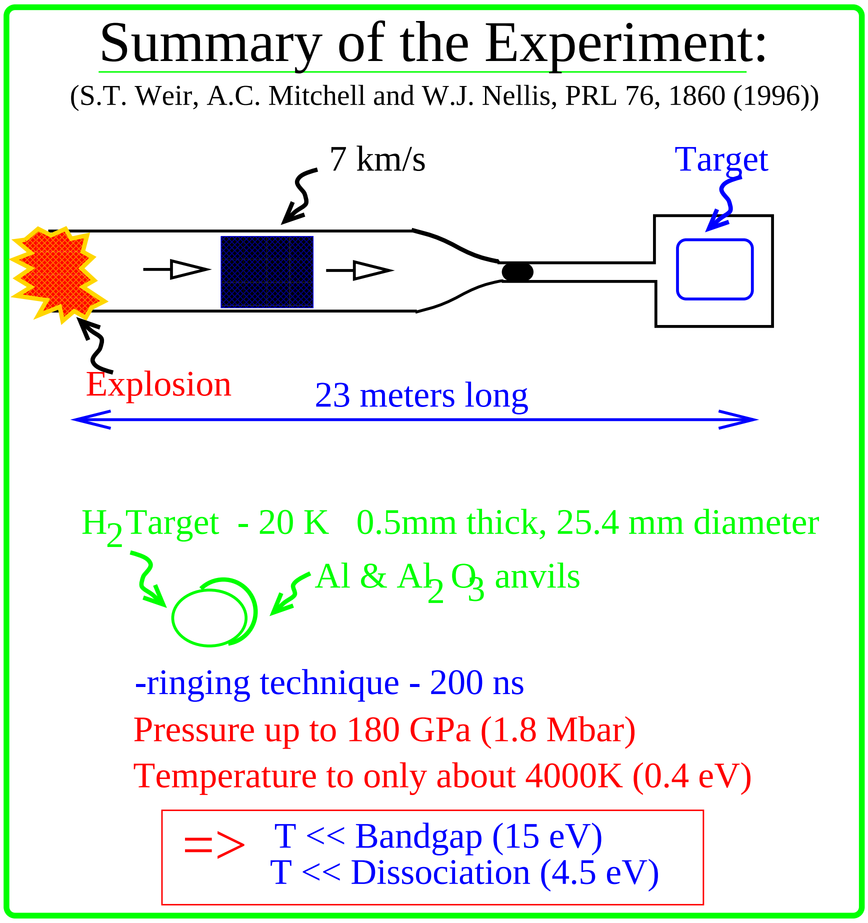

Figure 3.1: **Schematic of the Livermore Experiment**
A two-stage light-gas gun was used to accelerate the impactor plate up to $\sim 7km/s$[29]. The initial energy source which drives the impactor is caused by gunpowder (although the initial thrust is not quite as spectacular as the explosion shown in the figure above). The cryogenic hydrogen sample is 0.5 mm thick and 25 mm in diameter, at an initial temperature of 20 degrees K, and contained between two sapphire anvils, which are in turn contained between two aluminum disks. The density mismatch between the sapphire and the hydrogen causes the multiple shocks. This arrangement can lead to pressures of over 180 GPa, and concomitant temperatures around $3000K$. These conditions are maintained for about 200 ns, after which the whole cryogenic and measuring apparatus disintegrates under the extreme pressure. Within this short time window (but still long on molecular timescales), fast electronics coupled with a four-probe measurement scheme is used[10] to directly measure the resistivity.

pulse. In fact, this temperature pulse should be short on the chemical time-scales, but long enough to achieve thermodynamic equilibrium, precisely the conditions achieved by the shock compression technique!

Pressures, which are directly available through shock impedance matching, and resistances, which are directly measured, are the only directly assessible quantities, densities, temperatures etc... must all be calculated. Nellis et al[10] used two equations of state, one was developed by Kerley[32] before recent shock data were available; it neglects molecular dissociation, and another is due to Ross and was based on earlier shock experiments. It explicitly includes molecular dissociation[33]. Based on these calculations, they claim systematic uncertainties in calculated density and temperature of 5% and 20%, respectively, and they plot the experimental resistivity data as $\log(\rho)$ versus pressure. The change in slope at 140 GPa is indicative of the transition to the metallic state (see figure 3 of [31]). When these results were plotted in the semiconducting range, 93-135 GPa, and fit to the conductivity of a a thermally activated semiconductor:

$$\sigma = \sigma_0 \exp(-E_g(D)/2k_B T), \tag{3.1}$$

where σ is electrical conductivity, σ_0 depends on density D and relatively weakly on T (typically as $T^{3/2}$), $E_g(D)$ 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, the seven data points with error bars of 20 to 50% were fit to Eq. (1), the results being: $E_g(D) = 1.12 - (54.7)(D - 0.30)$. $E_g(D)$ is in eV, D is in mol/cm^3 $(0.29 - 0.32\ mol/cm^3)$, and $\sigma_0 = 66\ (\Omega cm)^{-1}$. Similar results are obtained using densities and temperatures calculated with Kerley's model[10]. σ_0 =200-300 $(\Omega cm)^{-1}$ is typical of liquid semiconductors[34]. Full GW calculations predict a theoretical rate of $40eV/(mol/cm^3)$[35] for bandgap closure near metallization at 0

K in a molecularly disordered hcp hydrogen. This is comparable to the fluid value of $\sim 60eV/(mol/cm^3)$ obtained by fitting to equation 3.1, so that $E_g(D)$ and k_BT are equal at a density of 0.32 mol/cm^3 and a temperature of $\sim 2600K$ $(0.22eV)$. 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. Interestingly, the measured resistivity flattens out (rather like Iodine), at pressures of 140 to 180 Gpa to a value around $500\mu\Omega cm$, equivalent to a conductivity of $2000(\Omega cm)^{-1}$, which is typical of the fluid (monatomic) alkali metals Cs and Rb at 2000 K undergoing the same transition[36].

3.3 General 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, ionization and chemical (cluster) formation. Together these lead to a remarkably rich phase diagram, most of which remains experimentally unexplored. The metallization experiment[10] reveals a new section of this phase diagram, and hints to its further structure, as shown in Fig. (3.2).

Traditional 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 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?

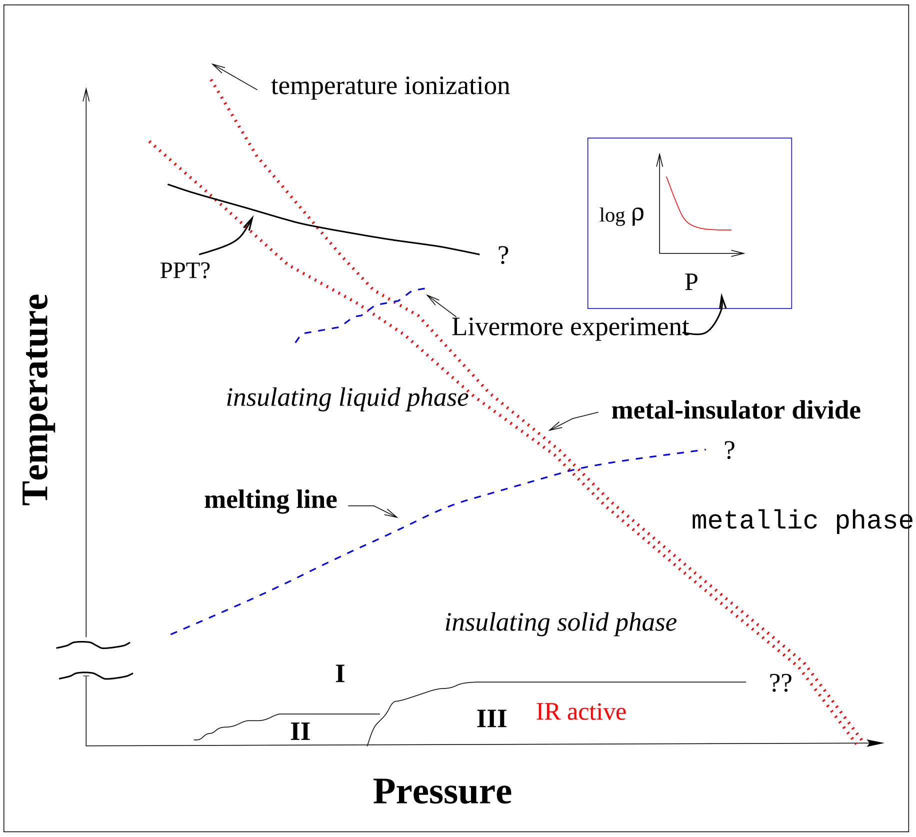

Figure 3.2: **Schematic Phase Diagram of Hydrogen**

The MIT in the liquid occurs at considerably lower pressure than is predicted for the transition in the solid. We suggest a metal-insulator band (not necessarily a sharp transition) 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)[37, 38, 39] 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[2]. We emphasize that this phase diagram is merely schematic; it is just a plausible guide and much still needs to be filled in.

3.4 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 $\sigma(\omega = 0)$ is then given by:

$$\sigma(0) \sim \int_0^\infty < j(0)j(t) > dt \tag{3.2}$$

where $<< j(0)j(t) >>$ is a current-current correlation function for the many-electron system, and $<<>>$ is an average over electron states and atomic configurations. 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 [40, 41, 42] 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[43]. 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 (5 to 6 fold) 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 $S(q)$; 4 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 plausible Fermi surface: in the application of the weak scattering formalisms covalency manifests itself 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 [40, 41, 42]. We express the resistivity ρ_L originating with a given type of carrier as:

$$\rho_L = \frac{m}{n_c e^2 \tau}, \tag{3.3}$$

where m is the carrier mass, n_c is the carrier density, and τ is a measure of the relaxation time. In its simplest high temperature[||] form the Ziman formalism gives:

$$\rho_L = \left(\frac{a_0 \hbar}{e^2}\right) \frac{6\pi}{(n_s)(k_F)^2} \int_0^1 S(y)|v(y)|^2 (y)^3 d(y), \tag{3.4}$$

where $y = q/2k_F$ 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

[||] In this case the temperature is high compared to acoustic phonon type modes that determine inter-pair motion, but less than the optic intra-pair vibron type modes so that we are dealing with a diatomic structure factor $S(q)$.

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 $21.7\mu\Omega cm$).

The structural average required in the static structure factor appearing in (3.4) 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. Secondly, orientational and translational entanglement leads 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[44] and scattering[45] 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 $\mu\Omega cm$ is found from (3.4), a significantly larger figure than obtained in previous calculations of monatomic H[46], but still considerably lower than the 500 $\mu\Omega cm$ measured experimentally[10]. 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[47].

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 (3.3) shows that a reduced number of carriers raises the resistivity[48]; we also expect related multiple-scattering and other strong-coupling effects[49] to be relatively important in this regime, and these effects also lead to higher resistivities. Thus by taking into account physics beyond the usual one-band picture our result of $\sim 50\mu\Omega cm$ 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).

3.5 The Onset of the Metal Insulator 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[50]. However, a closer look at the origin of the bandgap 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-centered cubic description[51] where the principal Fourier components of the electron interaction with pairs are given by

$$V_{111} = (3/4\pi r_s^3 a_0^3) S_0(111) v(111) \tag{3.5}$$

and

$$V_{200} = (3/4\pi r_s^3 a_0^3) S_0(200) v(200). \tag{3.6}$$

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

$$\begin{aligned} S_0(l,m,n) = \frac{1}{4}\{\cos 2\pi\alpha(l+m+n) \quad &+ \quad (-1)^{m+n}\cos 2\pi\alpha(l-m+n) \\ &+ \quad (-1)^{l+m}\cos 2\pi\alpha(-l+m+n) \\ &+ \quad (-1)^{n+l}\cos 2\pi\alpha(l+m-n)\} \end{aligned} \tag{3.7}$$

with $\alpha = d(r_s)/\sqrt{3a}$ ($2a$ 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 ($k_BT \sim \hbar\omega_{vib}$) 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 4 pairs in the Pa3 structure to a separation of $2d'$ ($2d' > 2d$) while the other basis pairs are kept fixed. From (3.7) the structure factor per proton for such a separation becomes

$$S(l,m,n) = S_0(l,m,n) - \frac{1}{2}\sin[\pi(\alpha'-\alpha)(l+m+n)]\sin[\pi(\alpha+\alpha')(l+m+n)], \quad (3.8)$$

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.

3.6 The Physical Characteristics of the Metal-Insulator 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:

3.6.1 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[35, 2] and liquid[52] 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[7, 53, 35]; if generalized to the separation between mobility edges[54], we expect it to carry through for the liquid phase as well[55]. 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[56].

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 semi-conductor picture invoked to estimate the carrier density (see e.g. p 575 of [57]), this quickly leads to resistivities as low as $\sim 700\mu\Omega cm$ for $E_g \sim 2k_BT$! (recall that the experimental value is $\sim 500\mu\Omega cm$.)

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. The condition for Anderson localization is similar to the condition for the Mott transition; namely:

$$D_m^{1/3} a^* \sim C, \tag{3.9}$$

where a^* is a measure of the localized orbital size, and C is typically about 0.3[54]. Under the assumption that the Bohr radius for diatomic hydrogen is roughly the same as the Bohr radius of monatomic hydrogen, $D_m^{1/3} a^* \sim 0.3$ at experimental metallization conditions. However, as emphasized by T.V. Ramakrishnan: “The main conclusion from the above discussion of criteria [eq (3.9)] for the metal-nonmetal transition is that it is not possible to decide on a particular mechanism from the agreement of the parameters for the transition with the value predicted. Only the detailed physical behavior of the system can help distinguish between various possibilities”**

** T.V. Ramakrishanan in [18], p42.

3.6.2 Scenario 2: Metal-insulator transition and the role of many-body physics

Mott[54] 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 lead to a jump in the conductivity. We expect in this case that the temperature of $\sim$ 0.3 eV will be too high for the formation of excitons[58] 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[54] 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[59] 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 $\sim$ 11 fold compression[60] (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.

3.6.3 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 likewise precede complete closure of this gap. Perhaps the best known case of a metal-insulator transition driven by structural change is the metallic behavior seen when melting the elemental semiconductors 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 section VIII. above.

In fact, the Wigner-Huntington proposal[1] 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 behavior for paramagnetic states[61]. Even at relatively low densities, increasing the temperature to regimes comparable with the dissociation energy will also rupture the H-H bond, possibly leading to metallic (conducting) behavior. 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 $r_s = 1.5$ (~ 9 fold compression) the corresponding well depth continues to have a magnitude significantly larger than the temperatures achieved[65]. To date no evidence of static pressure induced dissociation in the solid has been observed, even at the significantly higher pressures of $350 GPa$ achieved by ultra pressure diamond anvil-cell techniques[4]. 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 neighboring pairs, or to the transient formation 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.[66]. Here "dissociation" is defined by asserting that two atoms constitute a dimer if each forms the nearest neighbor 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[67]) 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[66].

Recently Pfaffenzeller and Hohl[68] 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 ($D_m = 0.4 mol/cm^3$ vs. $0.32 mol/cm^3$) and they find a resistivity about a factor 6 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[69] (the AIMD calculations 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[10] 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 over-estimate 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.*[39]. 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)[37]. 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 and Chabrier[38] who predict for the PPT a critical point at $T = 15310$ K and a density of $D_m = 0.18\ mol/cm^3 (rs \sim 2)$, and at higher densities and lower temperatures an increasingly discontinuous transition between a diatomic insulating state and an ionized (conducting) monatomic phase (see also Fig. (3.2)). In support of these chemical models, the physically based PIMC calculations[39] 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 behaviors 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.

3.7 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.*[66, 67], 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 Fig. (3.2), 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[70].

3.8 Conclusions

Depending on temperature, 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.

Bibliography

[1] E. Wigner and H.B. Huntington, J. Chem Phys. **3**, 764 (1935).

[2] H-K. Mao and R.J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).

[3] H. N. Chen, E. Sterer, and I. F. Silvera, Phys. Rev. Lett. **76**, 1663 (1996).

[4] A. L. Ruoff, in *High Pressure Science and Technology*, edited by W. Trzeciakowski (World Scientific, Singapore, 1996), pp. 511-516; C. Narayana, H. Luo, J. Orloff and A. L. Ruoff, *Solid Hydrogen at 351 GPa: Still the Reluctant Alkali*, Cornell preprint (1997).

[5] N. W. Ashcroft, Physics World **8**, 43 (1995).

[6] D.E. Ramaker, L. Kumar, and F.E. Harris, Phys. Rev. Lett. **34**, 812 (1975) (note that this reference has no bands in it).

[7] C. Friedli and N.W. Ashcroft, Phys. Rev. B **16**, 662 (1977).

[8] A.S. Balchan and H.G. Drickamer, J. Chem. Phys. **34**, 1948 (1961), B.M Riggelman and H.G. Drickamer, J. Chem. Phys. **38**, 2721 (1963)

[9] D. J. Stevenson, Rep. Prog. Phys. **46**, 555 (1983).

[10] S.T. Weir, A.C. Mitchell and W.J. Nellis, Phys. Rev Lett. **76**, 1860 (1996), S.T. Weir and W.J. Nellis, *ibid* ..., and .S.T. Weir, A.C. Mitchell and W.J. Nellis, manuscript submitted to Phys. Rev. B.

[11] W. J. Nellis, M. Ross, and N. C. Holmes,Science **269**, 1249 (1995); W. J. Nellis, S. T. Weir, and A. C. Mitchell, Science **273**, 936 (1996).

[12] R. P. Butler and G. W. Marcy, Astrophys. J. **464**, L153 (1996); R. P. Butler and G. W. Marcy, Astrophys. J. **474**, L115 (1996); M. Mayor and D. Queloz, Nature **378**, 355 (1995).

[13] V. N. Zharkov and T. V. Gudkova, in *High-Pressure Research: Application to Earth and Planetary Sciences*, Y. Syono and M. H. Manghnani, Eds., (Terra Scientific Publishing Co., Tokyo, 1992), pp.393-401.

[14] P.P. Edwards and M.J. Sienko, Intern. Rev. Phys. Chem **3**, 83 (1983).

[15] As late as 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, private communication).

[16] *Symposium on The Beginnings of Solid State Physics*. Proc. R. Soc. Lond. A 371, 1-177 (1980).

[17] L.H. Hoddeson and G. Baym in [16].

[18] *Metallic and Non-Metallic States of Matter* (Taylor and Francis, London (1985)), ed. by P.P. Edwards and C.N.R. Rao.

[19] D.E. Logan and P.P. Edwards in [18].

[20] Annalen der Physic, **1**, 566 and **3**, 369 (1900).

[21] The results were announced at the 1927 Volta conference and accepted almost immediately[17].

[22] P.W. Bridgman, Phys. Rev. **29**, 188 (1927).

[23] F. Bloch, Z. Phys **52**, 555 (1928), *ibid* **57**, 545 (1929).

[24] A.H. Wilson, Proc. R. Soc. A **133**, 358 (1931). *ibid* **134**, 277 (1931).

[25] A.H. Wilson in [16], p45.

[26] J.H de Boer, and E.J.W. Verwey, Proc. R. Soc. **49**, 59 (1937).

[27] N.H. Mott in [18].

[28] P.W. Anderson, Phys. Rev **109**, 1492 (1958).

[29] A. H. Jones, W. M. Isbell, and C. J. Maiden, J. Appl. Phys. **37**, 3493 (1966).

[30] C. S. Yoo, G. E. Duvall, J. Furrer, and R. Granholm, J. Phys. Chem. **93**, 3012 (1989).

[31] W.J. Nellis, A.A. Louis and N.W. Ashcroft, to appear: Phil. Trans. Roy. Soc. A. (1997)

[32] G. I. Kerley, in *Molecular-Based Study of Fluids*, edited by J. M. Haile and G. A. Mansoori (American Chemical Society, Washington, 1983), pp. 107-138.

[33] N. C. Holmes, M. Ross, and W. J. Nellis, Phys. Rev. B **52**, 15835 (1995).

[34] N. F. Mott, Phil. Mag. **24**, 2 (1971).

[35] H. Chacham, X. Zhu, and S.G. Louie, Phys. Rev. B **46**, 6688 (1992).

[36] F. Hensel and P. P. Edwards, Phys. World, April, **43** (1996).

[37] The PPT was first proposed by L. Landau and G. Zeldovich, Acta. Phys. Chim. USSR, **18**, 194 (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.

[38] D. Saumon and G. Chabrier, Phys. Rev. A **46**, 2084 (1992).

[39] W.R. Magro, D.M. Ceperley, C. Pierleoni and B. Bernu, Phys. Rev. Lett. **76**, 1860 (1995), W.R. Magro, PhD thesis, University of Illinois (1995).

[40] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

[41] T.E. Faber *Introduction to the Theory of Liquid Metals* (Cambridge University Press, Cambridge 1972).

[42] M. Shimoji, *Liquid Metals* (Academic Press, London 1977).

[43] 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...

[44] In the usual application of the Ziman formalism, it is assumed that the temperature scale is such that $k_BT >> \hbar\omega$ 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 for the hard sphere system with $\sigma = 0.29$ and $\eta = 0.29$ for the center-of-mass-center-of-mass part and as a first approximation neglects contributions from anisotropy (i.e. the free-rotation approximation (see e.g. J-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, (Academic Press, London 1986))). The rotational and translational time-scales are about equal at this density, making the free-rotation approximation suspect. But even though simulations[66, 68] 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 A. Bunker, S. Nagel, R. Redmer and G. Röpke, Phys. Rev. E (1997), to appear).

[45] The neglected vibrations lead to inelastic scattering effects. Baym (G. Baym Phys. Rev **135**, A1691 (1964)) showed that in this case the crucial quantitity is $S(\vec{k},\omega)$, the dynamic structure factor for the protons defined by:

$S(\vec{k},\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} < \hat{\rho}(\vec{k},t)\hat{\rho}^{\dagger}(\vec{k},0) >$

where $\hat{\rho}(k)$ is the one-particle density operator for protons) the resistivity is then given by: $\rho \sim \int_0^{2k_f} q^3 dq |v(q)|^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\vec{k},\omega) \frac{\beta\hbar\omega}{(\exp(\beta\hbar\omega)-1)}$ which reduces to the usual Ziman formula for $k_B T >> \hbar\omega$. 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.

[46] D. J. Stevenson and N. W. Ashcroft, Phys. Rev. A **9**, 782 (1974).

[47] 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[41, 42]). However, in this case the Edwards cancellation theorem probably doesn't hold (see e.g. M. Itoh and M. Watabe, J. Phys. F **14**, L9 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[54]. The minimum value of g is typically about 0.3, raising the resistivity by a maximum of about $1/g^2 \sim 10$.

[48] The mean-free path is roughly given by: $l = [174 a.u.] \times [(rs/a_0)^2/\rho_\mu]$[57], which implies a mean free path of about $9a.u.$ for a calculated resistivity of $\sim 50\mu\Omega cm$. 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.

[49] See for example H. Kitamura and S. Ichimaru, Phys. Rev. E, **51**, 5006 (1995).

[50] G. Kresse and J. Hafner, Phys. Rev. B, **55**, 7539 (1997).

[51] N.W. Ashcroft in *Elementary Processes in Dense Plasmas,* ed by S. Ichimaru and S. Ogata, (Addison Wesley, 1995).

[52] W. J. Nellis, A. C. Mitchell, P. C. McCandless, D. J. Erskine, and S. T. Weir, Phys. Rev. Lett. **68**, 2937 (1992).

[53] E. Kaxiras, J. Broughton and R.J. Hemley, Phys. Rev. Lett. **67**, 1138 (1991).

[54] N. Mott, *Metal Insulator Transitions* (Taylor & Francis, London 1990).

[55] 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 e.g. [57]).

[56] The reader might wonder why we use language inspired by bands in this manifestly disordered system where the wave vector **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[41], and so this is the sense in which we use the concept of bands here.

[57] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York 1976).

[58] See e.g. B.I. Halperin and T.M. Rice, Solid State Physics **21**, 116 (1968).

[59] D. J. Thouless in *Ill-Condensed Matter* edited by R. Balian, R. Maynard and G. Toulouse (North Holland, Amsterdam 1979).

[60] P.P. Edwards and M. Sienko, Chemistry in Britain **19**, 39 (1983), M. Ross, J. Chem. Phys **56**, 4651 (1972).

[61] Its interesting that at their original predicted density, the monatomic solid would be close to a Mott-Hubbard insulator!

[62] N.W. Ashcroft, Phys. Rev. Lett. **21**, 1748 (1968).

[63] C. F. Richardson and N. W. Ashcroft, Phys. Rev. Lett. **78**, 118 (1997).

[64] R. J. Hemley, H. K. Mao, A. F. Goncharov, M. Hanfland, and V. Struzhkin, Phys. Rev. Lett. **76**, 1667 (1996).

[65] 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, B. Edwards and N.W. Ashcroft, unpublished). Even free H_2^+ is strongly paired with a dissociation energy of about 2.8eV, a fact which helped motivate an earlier prediction of metallization in the molecular liquid[62]. In the solid, vibron overtones have been measured up to pressures of 170 GPa[3, 64].

[66] T.J. Lenosky J.D. Kress, L.A. Collins, I Kwon, Phys. Rev. B **55**, 11907 (1997). T.J. Lenosky J.D. Kress, L.A. Collins, I Kwon J. Quant. Spect. Radiat. Trans (1997), to appear.

[67] M. Ross, Phys. Rev. B **54**, R9589 (1996).

[68] O. Pfaffenzeller and D. Hohl, Preprint 1997.

[69] See for example B. Edwards, N.W. Ashcroft and T.J. Lenosky, Euro. Phys. Lett. **34**, 519 (1996) and J. Kohanoff *et al.* Phys. Rev. Lett. **78**, 2783 (1997).

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