Ordered Ground States of Metallic Hydrogen and Deuterium

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Metallic hydrogen and metallic deuterium are both predicted to be liquids in their ground states over a wide range of densities. They may be described as quantum liquid metals, but since the proton and deuteron fluids obey Fermi-Dirac and Bose-Einstein statistics, respectively, their physical properties can be markedly different. In both there is the likelihood of superconductivity through the usual coupling via the density fluctuations of the ions. But in addition the deuteron fluid admits of the possibility of Bose condensation and may develop superfluid order. Finally, the protons may themselves pair at extremely low temperatures.

1. INTRODUCTION

Under conditions of modest compression and temperature hydrogen and deuterium form diatomically ordered insulating states. This familiar situation changes radically at very high densities where the dense phases of these systems undergo an insulator-metal transition to conducting states. Though this is expected on very general grounds, what cannot yet be foretold with any degree of certainty is the nature of the resulting high density phases, where the many possibilities that might be expected differ in energy by exceedingly small amounts. Perhaps the most interesting aspect of both metallic hydrogen and metallic deuterium is that they seem to fall securely within the class of quantum solids and liquids [1]. Combined with their specifically metallic character, this places them in the somewhat rare category of quantum metallic solids (or as we shall see later, liquids). This in itself is noteworthy: however, at low temperatures there can be long-range ordering in both the electronic and ionic systems, and these too are imbued with unusual characteristics.

The purpose of this article is to discuss the physical attributes of some of the more physically distinct ordered states of metallic hydrogen and metallic deuterium at T = 0 and nearby. In many respects the experimental fabrication of these metals still represents one of the major goals of high pressure physics. As noted by Ginzburg [2], the production and understanding of new materials and substances is a fundamental challenge. In this context the metallization of hydrogen has been and continues to be as difficult as it is fundamental. The conditions required for its attainment involve serious problems associated with the ultimate strengths of materials. Thus the spirit of this report is very much directed to 'what might be' and in cataloging the remarkable properties below one is nevertheless very conscious of the fact that the ease of theoretical conjecture bears here, apparently, an inverse relationship to difficulty of experimental reality. With this cautionary remark in mind, we shall see that the inferences that can be made from relatively well accepted principles lead to some interesting predictions. These depend in a striking way on the quantum statistics of the systems under consideration and for this reason, among others no doubt, both common isotopes of hydrogen are worthy of detailed experimental examination in the high pressure context.

2. THE FUNDAMENTAL HAMILTONIAN

We begin by considering a neutral assembly of electrons (e) and protons or deuterons (i = p or d), under conditions of density that span, on the one hand, the normal condensed insulating phases of identifiable molecules and on the other high density phases exhibiting metallic properties. This range of densities can be conveniently expressed in terms of the fundamental linear measure, \( r_s = (3/4\pi n_e a_0)^{1/3} \) where \( n_e \) is the single-particle density for the electrons averaged over the system. From the known density of condensed hydrogen and deuterium at 1 atmosphere, we find \( r_s \approx 3.07 \). The states we shall be describing below, however, are characterized by \( r_s \ll 1 \). (Observe the experimental requirement of volume compressions leading to some interesting predictions. These depend in a striking way on the quantum statistics of the systems under consideration and for this reason, among others no doubt, both common isotopes of hydrogen are worthy of detailed experimental examination in the high pressure context.

Let the electrons in the system have a set of coordinates \( \mathbf{r}_e \), and the protons or deuterons (which we refer to as ions) have the set \( \mathbf{r}_i \). Then all of the phases that we will consider are described by a fundamental Hamiltonian

\[
\hat{H} = \hat{H}(\mathbf{r}_e, \mathbf{r}_i).
\]  

All of the interactions in the system are strictly Coulombic. We consider only charge
neutral ensembles of fixed number so that the thermodynamic functions are well defined. If \( v_c(k) = 4\pi\epsilon_k^2/k^2 \) then for a macroscopic ensemble of volume \( \Omega \), \( \mathcal{H} \) takes the form

\[
\mathcal{H} = \hat{T}_e + \frac{N}{2\Omega} \sum_{k\neq 0} v_c(k)(N^{-1}\rho_e^c(\mathbf{R}_e^{0})(-\mathbf{k})^{-1}) - \hat{T}_i + \frac{N}{2\Omega} \sum_{k\neq 0} v_c(k)(N^{-1}\rho_i^c(\mathbf{R}_e^{0})(-\mathbf{k})^{-1}) - \frac{N}{\Omega} \sum_{k} v_c(k)\rho_e^c(\mathbf{R}_e^{0})(-\mathbf{k})^{-1}.
\]

The first two terms (2a) of \( \mathcal{H} \) represent a well-known problem: they constitute the standard Hamiltonian of \( N \) interacting electrons of mass \( m \) and total kinetic energy \( \hat{T}_e \) whose single particle density operators have Fourier components \( \rho_e^c(\mathbf{R}_e^{0}) \). They move in a uniform compensating background at average charge density \( \langle \rho_e^c \rangle \). Similarly (2b) represents the Hamiltonian of \( N \) protons or deuterons of mass \( m_i \), whose kinetic energy is \( \hat{T}_i \), and whose density components are \( \rho_i^c(\mathbf{R}_i^{0}) \). They also move in a uniform compensating background with average charge density \( -eN/\Omega \). With appropriate boundary conditions, (2a) and (2b) are themselves Hamiltonians for distinct and well-defined problems. However, in the system under consideration they are coupled, and coupled strongly, by the attractive interaction described by (2c). In the thermodynamic limit, which we assume, the average of (2c) in states of fixed \( N \) is removed by the requirements of charge neutrality. Unlike the Hamiltonians that one might imagine writing down for other simple metallic systems, (2) is exact. There are no residual uncertainties stemming from the necessity of constructing a pseudopotential, for example.

The Hamiltonian summarized in (2) has considerable symmetry.

3. NORMAL GROUND STATES

We are especially interested in ordered states of the system described by (2). But first we briefly describe the expected normal states and their origin. Let \( \psi^0 \) be the ground state wavefunction for the electron-proton or electron-deuteron assembly. Then the determination of the ground state energy requires us to evaluate

\[
\langle \psi^0 | \mathcal{H} | \psi^0 \rangle = \langle \mathbf{R}_e^{0} | \mathbf{R}_i^{0} \rangle \langle \psi^0 | \mathbf{R}_e^{0} \rangle \langle \psi^0 | \mathbf{R}_i^{0} \rangle.
\]

Since \( (m/m_p)^3 = 0.153 \) and \( (m_0/m_e)^3 = 0.128 \), it is a reasonable starting point for such a goal to factor the dependence on electronic and ionic degrees of freedom the adiabatic form:

\[
\psi^0 | \mathbf{R}_e^{0} \rangle \psi^0 | \mathbf{R}_i^{0} \rangle \psi^{0*} | \mathbf{R}_e^{0} \rangle \psi^{0*} | \mathbf{R}_i^{0} \rangle
\]

where \( \psi^0 \) is the ground state wavefunction for the instantaneous configuration \( (\mathbf{R}_e, \mathbf{R}_i) \) of the ionic system (whose ground state, in turn, is described by \( \psi^{0*} \)). If the electron system remains in its ground state or close to it then it follows that the motion of the protons, or deuterons, is described by the Hamiltonian

\[
\mathcal{H}(\mathbf{R}_i^{0}) = \langle \psi^0 | \mathbf{R}_e^{0} \rangle \langle \mathbf{R}_e^{0} | \mathbf{R}_i^{0} \rangle \langle \psi^0 | \mathbf{R}_e^{0} \rangle \langle \psi^0 | \mathbf{R}_i^{0} \rangle.
\]

The electronic degrees of freedom are clearly integrated out, but the result of this procedure, and hence of the resulting ionic motion, very much depends on the nature of these electronic states (whether itinerant or localized, for example). The characteristics of these states depend on density, as noted. Near \( r_s = 3.1 \) hydrogen and deuterium form well-defined diatomic molecular states (whether itinerant or localized). In principle, these units should be distinguished according to the states of the ionic spins. The matter of ortho-para differences will not concern us further in the low density phases.) A physically acceptable choice for \( \psi^0 \) for such states is a product of \( (N/2) \) two-electron functions each localized about the mean molecular coordinate. The electron functions in this choice are thus identified by site and this form for \( \psi^0 \) therefore conflicts with the basic requirements of overall antisymmetry. This difficulty is overcome in practice by introducing into (5) phenomenological short range potentials which are generally taken as pairwise functions of the relative intermolecular separations. At longer range, a product state based on an assumption of little overlap leads, as is well known, to fluctuating dipole forces in lowest order. Thus when combined with the Pauli repulsion (short range) terms we arrive at the familiar picture of a system of interacting molecules with pairwise interactions (not necessarily spherically symmetric) between them. The ionic Hamiltonian can therefore be recast in the form

\[
\mathcal{H}(\mathbf{R}_i^{0}) = \hat{T}_i + \frac{1}{2} \sum_{m, m'} (\mathbf{R}_m - \mathbf{R}_{m'}) + \cdots
\]

where \( m \) and \( m' \) denote molecular coordinates, and \( \hat{t} \) is a pair-potential.

If the density is such that the two-particle functions seriously overlap, then terms beyond simple pair interactions displayed in (6) will become important, beginning with the dipole-dipole term. At still higher densities the overlap becomes so large that the very starting point of the description, the assumption of well-defined localized two-electron states, ceases to have any physically justifiable validity. Under such conditions the density of electrons near the boundaries of the Wigner-Seitz cells has become an appreciable fraction.
of the average density $\bar{n}$, and in these circumstances it is more appropriate to characterize the electron band states by band structure. In a very general sense the details of the electron band structure must still reflect the geometrical arrangement of the protons or deuterons. Thus, for example, we may think of a set of bands which continue to display at high density the basic diatomic ordering so characteristic of the low density system. For crystalline arrangements an integral number of bands are normally filled, but this paradigm of insulating configurations can itself revert to metallic behavior through the mechanism of band overlap. That such overlap can occur with diatomic ordering being preserved has been known for some time [3,4]. The corresponding conducting state is a forerunner of the more complete dissociative transition to a metal which, in crystals, for example, is expected to be represented by relatively simple structures (Bravais lattices are the simplest).

If metallization by band overlap is the correct mechanism, then the most interesting question concerns the density (and hence pressure) at which this occurs. To address this question, one requires a sequence of band structure calculations as a function of density for various separations $2d$ of the ions in the basis. Correspondingly one also requires a sequence of total energy calculations for both insulating and metallic phases. The metallic phases have been treated by a variety of methods including Wigner-Seitz techniques [5-9], localized orbital techniques [10-15], expansion methods [16-22] (in which (2c) (above) is treated as a perturbation) and density functional techniques [23]. The latter have the particular advantage that, in principle, they can treat metallic and molecular phases on the same footing with the errors of the method entering largely on a systematic basis. The combination of the results of this method with those of band structure calculations [4] leads to a prediction for band overlap metallization at around 1.8 Mbar; complete dissociation in a static model does not appear to occur until much higher densities ($r_s \approx 1.1$), the corresponding pressure being quite dependent on the energies bound up in the ionic degrees of freedom and determined by (6). The motion of the ions is thus important. It is also extremely important in determining the possible states of long-range order of the metallic state once it is formed. This motion is again determined by an effective ionic hamiltonian obtained by integrating out the electron degrees of freedom. For itinerant states appropriate to the metal the result is

$$\hat{H} = \hat{T}_i + E_0(r_s) + \frac{1}{2} \sum_i \hat{S}(\hat{R}_i, \hat{r}_i) + \ldots$$

(7)

where $E_0(r_s)$ is a term depending on volume arising from paramagnetic electron-gas energies, and $\hat{S}$ is a screened pair-potential for the ions. We note that provided $r_s$ is held fixed, the problem of solving for the motion of the ions is not essentially different from the equivalent problem in the insulating context.

4. ORDERED STATES

The description just given will determine the major contributions to the total energy of the system. The states we now discuss will involve ordering energies that are trivial in comparison. The states to be described are summarized in Table I.

If hydrogen and deuterium are both in crystalline phases in their high density metallic manifestations then, with one possible exception, it is unlikely that the fact that one is a Fermion system while the other a Boson will lead to any marked physical distinctions. The

<table>
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Table I: States of order of electron, proton, and deuteron systems resulting from equation (6) and broken symmetry. The entries identified by (*) might well include magnetically ordered states.
exception concerns ground state vacancies [24] and defects that may occur in highly quantum systems. The spectrum of vacancy waves might then be quite different. However, the presumption that the metals are indeed crystalline, even in their ground states, is itself not at all well founded [1]. One can see that this might be the case by noting that a typical zone boundary phonon for the ions will have a frequency typical of an ionic plasma frequency, or an energy per ion of about 

\[ \hbar \omega_p \approx 2.5r_s^{-3/2}(m/m_i)^{1/4} \text{ Ry.} \]  

(8)

For protons, for example, this amounts to 0.014 Ry at \( r_s = 2.0 \) and 0.04 Ry at \( r_s = 1.0 \). These energy differences per ion (typically milliRydbergs) characteristic of different static structures [22]. For another way, there is sufficient zero point energy in the ionic degrees of freedom to cause continuous rearrangement between a variety of common crystal structures. Though this argument is qualitatively correct, in practice it is necessary to treat electron and ionic degrees of freedom self-consistently [23]. Nevertheless, by direct simulation methods [1], it can be established that the conclusion to which one is being led, namely that liquid-like ground states may be energetically preferred, is in fact confirmed, at least over a specified range of densities. If the ground state is a liquid, however, then the quantum statistical differences between hydrogen and deuterium become extremely important.

4.1. Liquid Metallic Hydrogen

Even if the density is such that metallic hydrogen is a (quantum) crystal, the melting point is expected to be very low [31]. It has been pointed out that crystalline forms of metallic hydrogen are likely to be superconductors with high transition temperatures [26-28]. Consequently, for crystalline states we can also imagine that metallic hydrogen will be a superconductor at least up to its melting point. If we now assume that the lack of crystallinity is not inimical to superconductive pairing (and the existence of amorphous or glassy superconductors certainly gives support to this view) then we can conclude that metallic hydrogen will order, even as a liquid, into a superconducting state. The question is whether the transition temperature is lower or higher than in the corresponding crystal and whether the standard theory can be applied. The answer to the latter is that it can: to obtain \( T_c \) we need to solve the Eliashberg equations for the gap function and to find the temperature at which the gap is just suppressed by a pairing breaking term. To carry out this procedure, the Eliashberg function of electric polarization potential (30). It can be obtained from memory function techniques, for example, but is most easily given by a generalization of the RPA like form:

\[ \chi(q, \omega) = \frac{\chi^0(q, \omega)}{1 - f(q, \omega)\chi^0(q, \omega)} \]  

(9)

where \( \chi^0(q, \omega) \) is the response function for non-interacting protons and \( f(q, \omega) \) is the so-called polarization potential [30]. It can be obtained from the reasonable assertion that it is a continuous function with the appearance of a screened Coulomb interaction at long range, and a constant value at short range. The constant is fixed by the calculated sound speed as \( q \to 0 \). From (9) and from the electron-proton interaction \( \chi(q) \) we obtain the Eliashberg function according to

\[ a^2 F(\omega) = N(0) \int_0^{2k_F} \text{d}q (q/2k_F)^2 |\chi(q)|^2 \chi'(q, \omega)/\pi. \]  

(10)

This is the required input for the gap function \( \Delta(\omega) \), the solution of the Eliashberg equations [31] is relatively straightforward. The resulting transition temperature is \( \sim 10^2 \) K and is a fairly strong function of density [29]. These temperatures do indeed exceed the melting temperature in certain density ranges so that the assumption that a liquid superconducting state exists appears to be substantiated.

It is worth noting that if the density is such that metallic hydrogen is in a liquid state, but the temperature is such that the system is normal, the properties of this 'normal' state are still rather remarkable. For it then constitutes a two-component Fermi liquid (H and D) in the high density limit and the other (the protons) in the low density limit. Both Fermi liquids have identical Fermi surfaces but very different Fermi temperatures \( T_F \) and \( T_p \). The standpoint of experimental detection of a (static) pressure generated phase of metallic hydrogen, it is also important to understand the properties of this phase. This can be achieved most easily through a straightforward generalization of Landau Fermi liquid theory to two (charged) components, both for equilibrium properties [32] and transport properties [33]. One of the most striking equilibrium properties is the appearance of a giant linear specific heat at low temperatures. This is a manifestation of the high density states of the proton Fermi liquid and is in marked contrast to the normal \( T_3 \) phonon behavior expected when the system freezes.

The transport properties are no less dramatic. To study these one begins with a two-component generalization [33] of the Landau Fermi liquid theory, which can be used to describe the momentum, space, and time development of the electron and...
proton quasi-particle distribution functions. It is possible to obtain closed form expressions for the electrical conductivity, thermal conductivity, viscosity \( \eta \), and spin diffusion coefficients. As \( T \to 0 \) all of these quantities diverge because of the phase-space considerations controlling the scattering. The electrical resistivity, in particular, vanishes as \( T^0 \), again in marked contrast to the solid where, in the absence of impurities, it would vanish as \( T^\alpha \). Most importantly, the transport coefficients of the liquid are found to be at least a factor \( (m_e/m_p)^2 \) smaller than in the corresponding solid metal (and in the case of the resistivity, the inverse of the conductivity, the factor can approach 10^8).

Finally, in a fluid phase of metallic hydrogen, the Fermi temperature of the protons is \( \sim (m_e/m_p)T_F \) where \( T_F \) is the Fermi temperature of the He Electrons. For \( r_s \sim 1-2 \), \( T_F \sim 10^4 K \).

As noted above, there are effective (screened) interactions \( \phi \) between the protons which have a repulsive region at short range, and an attractive and oscillatory region at long range [1]. Given this form of the interaction and with the example of He^2 before us, it is possible that at extremely low temperatures the protons become unstable toward pairing. The temperature at which such a protonic superfluid will form will be in the neighborhood of \( 10^{-3} T_F \). Whether the potential is sufficiently repulsive at short range to favor p-wave over s-wave pairing has yet to be determined.

4.2. Liquid Metallic Deuterium

A possible low temperature liquid metallic phase of deuterium represents a system with "mixed statistics," the electrons constituting a Fermi liquid, as before, but the deuterons belonging to the class of spin-1 Bosons. Unlike helium (spin-zero Bosons) the presence of the additional spin degree of freedom leads to a new branch in the quasi-particle spectrum even though there are no explicitly spin-dependent terms in the Hamiltonian [2]. The dispersion of the branch follows a \( k^2 \) behavior at small \( k \) [35], and therefore differs in an essential way from the linear type of dispersions so characteristic of phonon-like quasi-particle excitations. There are thus 3 separate types of elementary excitations: the "phonons," the spin excitations, and electron-hole pairs. The system is quite unusual [36] and certainly contrasts markedly with, say, He^3-He^4 mixtures.

At low temperatures we may certainly expect, as with metallic hydrogen, that electron pairing can occur through the density fluctuations of the ions. The crucial difference is that \( \lambda(q,\omega) \) (see equation (9)) now reflects the boson character of the ionic system. Again the approach is very similar: \( \lambda \) is constructed with the polarization-potential model [30] and the Eliashberg equations again solved. The resulting transition temperatures are somewhat lower than in metallic hydrogen [37], but still in the neighborhood of \( 10^4 K \).

At even lower temperatures a potentially more interesting ordering can occur in liquid metallic deuterium. This is a superfluid transition associated with the Bose-condensation anticipated for the spin-1 system. At \( r_s = 1.5 \) an estimate based on non-interacting Bosons anticipates \( T_{bc} \sim 30^0 K \) for this system. This suggests the rather intriguing possibility that we have a charged system in which the electrons display superconducting order while at the same time the deuterons display superfluid order. If it exists it is difficult to imagine a more remarkable state of condensed matter. At the very least it raises a number of interesting theoretical issues, for example, whether or not it is valid to describe the system with a two-fluid hydrodynamical picture, and whether or not persistent deutron currents will actually exist, that is to say, whether combined superfluidity and superconductivity is stable.

The transport properties of the system are expected to be unusually rich in their possible temperature dependences. This is because in setting up the appropriate kinetic equations for the three types of quasi-particles it is recognized that their associated statistics have considerable bearing on the standard phase-space arguments determining the scattering characteristics. To give but one example, if the temperature exceeds both \( T_{bc} \) for the deuterons and \( T_c \) for the electrons, then the low temperature behavior of the electrical resistivity is expected to be linear in the temperature [36] rather than quadratic as is the case for the normal electron-proton fluid. The reason is that the phase space limitation on the scattering cross-section imposed by the Fermi-Dirac distribution of the protons is essentially removed when the protons are replaced by deuterons. A further consequence is that the magnitude of the low temperature resistivity of normal liquid metallic deuterium should greatly exceed that of liquid metallic hydrogen. As \( T \) falls below \( T_{bc} \) the deuterons will Bose condense and this transition should be manifest in the electrical transport properties, both in critical behavior near \( T_{bc} \) itself and in the form of the transport coefficients well below \( T_{bc} \) [36]. In particular, the manner in which electrons cause excitations between the condensed (approximately in one subspace of the spins) and the excitation gas (in the remaining subspaces) should be particularly interesting.

It was remarked above that the Hamiltonian (2) has considerable symmetry. In the macroscopic manifestations of (2) this symmetry is broken, the resulting states possessing physical properties that may be unique among the elements. The states we have discussed are probably only the simplest that can be imagined. There may be more complex possibilities involving magnetic order.
Acknowledgments. This work has been supported by NASA under Grant NGR 47-007. I also wish to thank Drs. J. Oliva and J. Jaffe for many enlightening discussions throughout the continuing course of this work.

References

[37] J. Jaffe and N. W. Ashcroft, to be published.