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# Hydrogen at high density

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## Abstract

The physics of dense hydrogen can be developed starting with separate proton and electron (or deuteron and electron) plasmas and formally introducing the coupling between them. If this coupling is treated beyond linear response in the interacting electron gas the dominant pairing features of low-density hydrogen are captured. Progression of effective proton–proton pair interactions, especially with respect to the domain of repulsive behaviour in relation to cell size, and the overall scale of zero-point energy, indicates the possible onset of a near ground-state fluid above a critical density. This fluid will be metallic and unusually different in its properties when compared to more conventional liquid metals. Further assessment of the quantum aspects of such a state suggests the need for a more general analytical approach to the hydrogen problem and one possible route is via scaling relations.

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## 1. Introduction

The standard plasma problem for protons (charge  $+e$ , mass  $m_p$ ) in a macroscopic volume  $V$  (in which a uniform charge density  $-e(N/V) = -e\bar{\rho}$  has also been established) has the Hamiltonian

$$\hat{H}_p = \hat{T}_p + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_p^{(2)}(\mathbf{r}, \mathbf{r}') - 2\hat{\rho}_p^{(1)}(\mathbf{r})\bar{\rho} + \bar{\rho}^2 \} \quad (1)$$

where  $v(r) = e^2/r$  and  $\hat{T}_p$  is the kinetic energy operator. Here  $\hat{\rho}_p^{(1)}(\mathbf{r})$  is the single-particle density operator for protons and  $\hat{\rho}_p^{(2)}(\mathbf{r}, \mathbf{r}') = \hat{\rho}_p^{(1)}(\mathbf{r})\hat{\rho}_p^{(1)}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\hat{\rho}_p^{(1)}(\mathbf{r})$  is the corresponding two-particle density operator. Normal plasma conditions will require  $k_B T > e^2/(V/N)^{1/3}$  and  $k_B T > \{e^2/(V/N)^{1/3}\}(m_e/m_p)/(V/Na_0^3)^{1/3}$ . States of the plasma that are not translationally invariant are discussed by DeWitt *et al* in the present proceedings [1].

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The electron gas problem (charges  $-e$ , masses  $m_e$ ) has a Hamiltonian of exactly the same form, namely

$$\hat{H}_e = \hat{T}_e + \frac{1}{2} \int_V \mathbf{dr} \int_V \mathbf{dr}' v(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') - 2\hat{\rho}_e^{(1)}(\mathbf{r})\bar{\rho} + \bar{\rho}^2 \} \quad (2)$$

with one- and two-particle density operators paralleling the proton forms, but with a background charge density  $+e(N/V) = +e\bar{\rho}$ . Fermi liquid states will require  $(V/Na_o^3)^{1/3} \sim 1$  ( $a_o = \hbar^2/m_e e^2$ ) and also  $k_B T < \{e^2/(V/N)^{1/3}\}/(V/Na_o^3)^{1/3}$ . This will also be the regime of interest in the hydrogen problem which is obtained by taking equal values for  $\bar{\rho}$  in (1) and (2) and then augmenting  $\hat{H}_e + \hat{H}_p$  by the Coulomb interactions which arise when the two assemblies defining (1) and (2) occupy a common volume,  $V$ . Thus

$$\hat{H} = \hat{H}_e + \hat{H}_p + \int_V \mathbf{dr} \int_V \mathbf{dr}' v(\mathbf{r} - \mathbf{r}') (\hat{\rho}_p^{(1)}(\mathbf{r}) - \bar{\rho})(\hat{\rho}_e^{(1)}(\mathbf{r}') - \bar{\rho}) \quad (3)$$

which is rotationally and translationally invariant in the thermodynamic limit. By replacing the protons (Fermions,  $s = 1/2$ ) with deuterons (Bosons,  $s = 1$ ), implying a fundamental change in quantum statistics, the corresponding Hamiltonian for deuterium is

$$\hat{H} = \hat{H}_e + \hat{H}_d + \int_V \mathbf{dr} \int_V \mathbf{dr}' v(\mathbf{r} - \mathbf{r}') (\hat{\rho}_d^{(1)}(\mathbf{r}) - \bar{\rho})(\hat{\rho}_e^{(1)}(\mathbf{r}') - \bar{\rho}). \quad (4)$$

The importance of the coupling in (3) and (4), even in the Fermi liquid regime of densities for (2), can be seen by noting that the problem represented by (1) has an energy/proton dominated by the Madelung energy and in the ion-sphere approximation this is  $-(9/5)/r_s$ , where  $(4\pi/3)r_s^3 a_o^3 = V/N$  (energies will be given in atomic units). Accounting for kinetic energy and exchange (but omitting correlation) the corresponding energy of (2) is  $3(9\pi/4)^{2/3}/5r_s^2 - 3(9\pi/4)^{1/3}/2\pi r_s$  and in the absence of the coupling a stabilizing density for a metallic state would occur at  $r_s \sim 1.62$ , or with an average separation between protons of  $\sim 3.2a_o$ . The latter is to be compared with  $1.4a_o$  in a molecule in the ground state of molecular hydrogen, where  $r_s \simeq 3.13$ . The evident pairing tendencies attributable to electron-proton coupling terms remain exceedingly strong, even in highly compressed hydrogen. When this is viewed in terms of effective interactions controlling the pairing of protons, the fact that separations in proton pairs are so different from average separations inferred from density will be seen to play an important role in arguing the existence of a possible near ground-state liquid phase at pressures sufficiently high to also ensure a metallic state.

It will also be important to remember that at one atmosphere the zero-point energy, per proton, amounts to 1450 K. This energy is localized in optic-like modes, but can become translational, and further enhanced, at a depairing transition. It may be compared immediately with the proton plasmon energy which sets the scale for proton dynamical energies in crystalline hydrogen (for example, energies typifying longitudinal acoustic phonons as will appear below). In atomic units this energy is  $\hbar\omega_p = (m_e/m_p)^{1/2} 2\sqrt{3}/r_s^{3/2}$ , and for normal densities it would already yield a plasmon with an energy equivalent to 2300 K, while at 10-fold compression it rises to 7300 K. These are substantial energies, and they imply that the proton dynamics depart noticeably from classical expectations. The tenacity of the quantum characteristics of the protons is also illustrated by the thermal de Broglie wavelength  $\lambda_T$  for protons, which as a fraction of  $r_s a_o$  can be written as

$$\lambda_T/r_s a_o = 32.85/r_s \{T(\text{K})\}^{1/2} \quad (5)$$

where the temperature  $T$  is in kelvin. Thus if the temperature is taken, for example, as 1500 K, and  $r_s$  is 1.55 (eight-fold compression, or megabar conditions) the ratio in (5) is 0.55, and is clearly too large to ensure classical conditions, even at what might reasonably be assessed

as an elevated temperature. For the sake of comparison it may be noted that the equivalent quantity for  $^4\text{He}$ , at its normal density, is 2.1 but for a temperature that is just 4 K. Adiabatic separation of electron and proton timescales is also a difficulty as may be seen from the magnitude of the Born–Oppenheimer parameter governing possible separation of proton and electron timescales; this is  $(m_e/m_p)^{1/4} = 0.153$  (and 0.128 for the deuteron case).

The properties of the macroscopic phases originating with Hamiltonians (3) and (4) and under normal conditions have been extensively reviewed by Silvera [2]. Maksimov and Shilov [3] have provided a more recent review of high pressure properties. What follows will be focussed on the physical nature of the states of hydrogen close to 13-fold compression (current experimental capabilities, at low temperatures, already being close to 12-fold compression).

## 2. Crystal stability in dense hydrogen

For structures that are themselves Bravais lattices, hydrogen will take up a metallic state. Structural preference can then be examined using response methods, beginning with linear response and a uniform interacting electron gas described by (2) to which the protons couple (by (3)). In particular, the stability of crystalline states relative to fluid can first be examined at this level by determining the manifestation of zero-point effects on the static structure  $S_p(\mathbf{k})$  factor for protons which is involved directly in the ground-state energy in terms originating with the proton–proton interaction in (4). However, it also emerges indirectly through the coupling terms in (4) when the adiabatic approximation is invoked and electron response is developed to linear order in proton fields. The coupling term then contributes to the ground-state energy per proton an amount

$$\frac{1}{2} \int_{0+} \frac{d\mathbf{k}}{(2\pi)^3} |v(k)|^2 \chi^{(1)}(k) S_p(\mathbf{k})$$

where  $\chi^{(1)}(k)$  is the linear response function of the interacting electron gas (see below) and  $S_p(\mathbf{k})$  is given by

$$S_p(\mathbf{k}) = (1/N) \langle \hat{\rho}_p^{(1)}(\mathbf{k}) \hat{\rho}_p^{(1)}(-\mathbf{k}) \rangle - N \delta_{\mathbf{k},0}. \quad (6)$$

Here

$$\hat{\rho}_p^{(1)}(\mathbf{k}) = \int_V d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \hat{\rho}_p^{(1)}(\mathbf{r}) = \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_{jp})$$

(the  $\{\mathbf{r}_{jp}\}$  being the set of proton coordinates). For what follows the statistical average of  $\hat{\rho}_p^{(1)}(\mathbf{k})$  is denoted by  $\rho_p^{(1)}(\mathbf{k})$ . If the corresponding average of  $\hat{\rho}_p^{(2)}(\mathbf{r})$  is  $\rho_p^{(2)}(\mathbf{r})$ , then the relationship between the static structure factor and the average two-particle density  $\langle \hat{\rho}_p^{(2)}(\mathbf{r}, \mathbf{r}') \rangle = \rho_p^{(1)}(\mathbf{r}) \rho_p^{(1)}(\mathbf{r}') g^{(2)}(\mathbf{r}, \mathbf{r}')$ , with  $g^{(2)}$  the two-particle correlation function, is

$$S_p(\mathbf{k}) - 1 = \left\{ (1/N) \rho_p^{(1)}(\mathbf{k}) \rho_p^{(1)}(-\mathbf{k}) - N \delta_{\mathbf{k},0} \right\} + \frac{1}{N} \int_V d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \rho_p^{(1)}(\mathbf{r}) \int_V d\mathbf{r}' e^{-i\mathbf{k} \cdot \mathbf{r}'} \rho_p^{(1)}(\mathbf{r}') \{g^{(2)}(\mathbf{r}, \mathbf{r}') - 1\} \quad (7)$$

which reduces for a translationally and rotationally invariant fluid ( $\rho_p^{(1)}(\mathbf{r}) = \bar{\rho}$ ) to the expected

$$S_p(k) - 1 = \int_V d\mathbf{r} \bar{\rho} e^{i\mathbf{k} \cdot \mathbf{r}} (g_p(r) - 1).$$

For crystalline phases the averages required in, for example, equation (6), are to be taken over states appropriate to a dynamical lattice, usually anharmonic phonons. A significant

accounting for anharmonicity can be achieved by working within the self-consistent harmonic approximation [4] for which in systems sustaining only acoustic phonons the frequencies are given by

$$m_p \omega^2(\mathbf{q}, j) e_\alpha(\mathbf{q}, j) = \left( \sum_{\mathbf{R} \neq 0} (\cos \mathbf{q} \cdot \mathbf{R} - 1) \sum_\beta \int \frac{d\mathbf{k}}{(2\pi)^3} \phi_p^{(2)}(k) k_\alpha k_\beta \right. \\ \left. \times \exp \left[ -\frac{1}{2} \sum_{\mu, \nu} k_\mu k_\nu \lambda_{\mu\nu}(\mathbf{R}) \right] \exp(i\mathbf{k} \cdot \mathbf{R}) \right) e_\beta(\mathbf{q}, j) \quad (8)$$

and where for branch  $j$ ,  $\mathbf{e}(\mathbf{q}, j)$  is a polarization vector. For low temperatures the quantity  $\lambda_{\alpha\beta}$  in (8) is defined by

$$\lambda_{\alpha\beta}(\mathbf{R}) = 2[\langle u_\alpha(\mathbf{R}) u_\beta(\mathbf{R}) \rangle - \langle u_\alpha(\mathbf{R}) u_\beta(0) \rangle] \\ = \frac{\hbar}{m_p \bar{\rho}} \sum_j \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} (1 - \cos \mathbf{q} \cdot \mathbf{R}) e_\alpha(\mathbf{q}, j) e_\beta(\mathbf{q}, j) \omega^{-1}(\mathbf{q}, j). \quad (9)$$

Here  $\mathbf{u}(\mathbf{R})$  is the displacement of a proton away from Bravais lattice site  $\mathbf{R}$ . By  $\phi_p^{(2)}(k)$  is meant the linearly screened proton–proton interaction, namely  $\phi_p^{(2)}(k) = 4\pi e^2/k^2 \epsilon(k)$ , where  $\epsilon(k)$  is the wave-number-dependent dielectric function of the interacting electron gas. This embodies the linear response statement

$$\phi_p^{(2)}(k) = v(k) + v(k)^2 \chi^{(1)}(k) \quad (10)$$

with  $\chi^{(1)}(k)$  the linear response function of the interacting electron gas introduced above. The average appearing in (9) is now to be carried out over harmonic states. With these definitions the static structure factor  $S_p(\mathbf{k})$  becomes (for  $\mathbf{k} \neq 0$ )

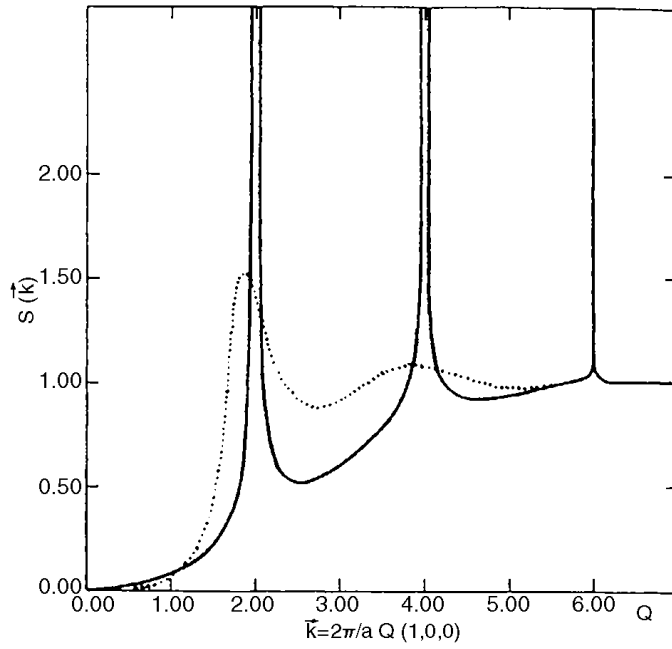
$$S_p(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \exp \left( -\frac{1}{2} \sum_{\alpha\beta} k_\alpha k_\beta \lambda_{\alpha\beta}(\mathbf{R}) \right). \quad (11)$$

Within the linear screening approximation implicit in (8), equations (8) and (9) can be solved self-consistently, and the results then used in (11). For a density of  $r_s = 1.36$  and for a fcc lattice, the result is shown in figure 1 [5]; the static structure factor for a ground-state fluid phase [6] is also shown for comparison, and it is immediately clear that the weight between the Bragg peaks is very substantial, even for  $k$  values around  $2k_F$ , and since, as noted,  $S_p(\mathbf{k})$  enters into the energetics (and also facilitates direct inclusion of electron–phonon coupling) it will follow that already at the present level of linear response a ground-state fluid could be competitive with a crystalline arrangement.

The reason for this rests with the obvious transfer of weight from the structure-dependent Bragg peaks to the continuum between them, thereby weakening the overall sensitivity to crystalline arrangement. In this context it is particularly instructive to examine the Lindemann ratio of metallic hydrogen in a simple structure, (say fcc) at  $r_s \sim 1.36$ . From the self-consistent phonons and polarizations this is also straightforward to determine this using  $L = \langle \mathbf{u} \cdot \mathbf{u} \rangle^{1/2} / R_{nn}$  ( $R_{nn}$  being a near-neighbour separation at  $r_s = 1.36$ ) with the result that [5]

$$L = 0.17.$$

This may be compared with typical classical values  $\sim 0.1$  at melting, and quantal values of 0.23 for Fermion hard spheres and  $\sim 0.28$  for the weakly coupled heliums. Knowledge of the static structure factor is also important for the determination of electronic transport in normal states (see below). Given  $S_p(\mathbf{k})$  all multi-phonon processes would be included in a description



**Figure 1.** (Full line): the static structure factor for protons in metallic hydrogen in a face centred cubic crystal of lattice constant  $a$  at  $T = 0$  ( $r_s = 1.36$ ). The wave-vector  $\mathbf{k}$  is chosen to be along [100] and in the units given here  $2k_F$  has a value of 1.56. The required frequencies and polarizations necessary to determine the static structure factor have been determined in a self-consistent manner. (Dotted line): static structure factor for an isochoric fluid phase (from [6]).

of electron scattering by protons [7]. It is therefore also a measure of the importance of electron–phonon coupling.

But inclusion of second-order response and beyond has a major impact on the supposed existence of a stable dynamic crystalline state: to begin with, the sensitivity to structure of assumed monatomic lattices is diminished even further by transference of additional weight from Bragg peaks to the intervening continuum of the corresponding static structure factors. This can be seen by noting that the weight originates with the Debye–Waller factor  $\exp(-2W(\mathbf{k}))$  where at low temperatures

$$2W(\mathbf{k}) = \langle (\mathbf{k} \cdot \mathbf{u})^2 \rangle = (1/\bar{\rho}) \sum_j \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \{ \hbar^2 (\mathbf{q} \cdot \boldsymbol{\epsilon}(\mathbf{k}))^2 / 2m_p \} / \hbar\omega(\mathbf{q}, j). \quad (12)$$

The effect is therefore enhanced at higher orders through the appearance of further Debye–Waller factors (three in the next order, then six, and so on). It follows that the extent to which proton dynamics reduces structural sensitivity becomes increasingly marked at each successive order.

Further, for densities beyond a critical value (where depairing of protons is anticipated) the linear screening picture for dense hydrogen is still quite far from reality, as can be seen from elementary arguments. First, the local ground-state electron density  $\rho_o$  actually *at* the proton in a free hydrogen atom is  $\rho_o = 1/\pi a_o^3$ . Accordingly as a fraction of this the average density  $\bar{\rho}$  in a condensed phase of hydrogen is

$$\bar{\rho}/\rho_o = 3/4r_s^3$$

and at eight-fold compression over normal densities this amounts to only 0.2. The cusp theorem of Kato [8] therefore ensures that for the compressions of hydrogen of interest here the average slope of the charge density at the proton can be mildly increased but overall very little changed from standard free-atom values. For scattering states similar arguments [9] suggest that the curvature of the charge density at the proton is also little altered. The combined consequence of these constraints is that if this non-uniform electronic charge density is to be developed by response to proton fields of an initially uniform electron gas (with density  $\bar{\rho}$ ) then it is mandatory to go beyond common linear procedures. Thus, if (11) is developed to one higher order, it becomes

$$\phi_p^{(2)}(k) = v(k) + v(k)^2 \chi^{(1)}(k) - \int \frac{d\mathbf{q}}{4\pi^3} v(q)v(|\mathbf{k} - \mathbf{q}|) \chi^{(2)}(-\mathbf{k}, \mathbf{q}) \quad (13)$$

where  $\chi^{(2)}$  is now the quadratic response function for the uniform interacting electron gas.

The last term in (13) leads to qualitative changes over the results obtained from linear response, as was noted by Kaim *et al* [10]. Incorporation of quadratic response immediately leads to a significant tendency towards proton pairing, but it is a tendency which progressively declines in binding capacity (though largely preserving a characteristic separation) as density increases. The linear response pair potential exhibits the expected Friedel oscillations with a first minimum occurring around  $r = 2.55r_s$  but with a diminishing depth which vanishes at  $r_s \sim 1.34$  [6]. This very same feature, a vanishing of the primary minimum  $\phi^{(2)}(r; r_s)$ , is preserved when the electronic response problem is carried out using (13) except that as noted inclusion of quadratic response shifts the location of the minimum quite close to the free molecule value of  $\sim 1.4a_o$  [11]. Beyond this minimum, the residual structure in the potential is quite weak, typically  $10^{-3}$  Ry, or values notably lower than the proton zero-point energies discussed above. The nonlinear response nevertheless enhances the Friedel structure in the pair-interaction and even changes somewhat the character of the pairing since nonlinear effects can bring in the influence of more distant protons. Though the conclusion rests on the assumption of a metallic starting state, it should be remembered that for the paired but insulating phases it requires only a moderate extension in proton-proton separation to induce a transition from insulator to metal where the analysis then fully applies. Within an energy of  $\sim 10^{-2}$  Ry it appears that there is preservation of a characteristic pairing separation around  $1.3-1.5 a_o$ , and a steeply rising interaction at shorter separations.

It has been argued above that both according to slope and curvature, the electronic density has a cusp at the proton and that the associated length scale remains close to  $a_o$ . In a fully many-body context, the local density approximation to the expected exchange contribution from this charge density (taken to have a local form  $\exp(-2r/a_o)/\pi a_o^3$ ) gives, in Ry per electron,

$$-(6/a_o^3)(3/\pi^2)^{1/3} \int_0^{r_o a_o} r^2 dr \exp(-8r/3a_o)$$

where  $r_o a_o$  is typical of an inter-proton spacing. The main point is not the fact that characteristic values are already reasonable for the hydrogen problem in terms of the contribution to pairing; it is that the integrand in the above peaks at  $(3/4)a_o$ , clearly demonstrating the importance of the region a little less than one Bohr from the proton. This suggests that in local energetic terms the propensity of pairing is likely to be maximized near  $1.5 a_o$ . Because of the largely invariant cusp and curvature properties it is therefore straightforward to understand the persistence of a quite repulsive region in the proton-proton interaction developing below this separation, with but a weak oscillatory remnant, small on the scale of zero-point energies, beyond this. Accordingly the physical characteristics resemble those of a moderately hard-sphere quantum system; apart from a large structure independent overall energy, the situation is not significantly

different from the one faced by London [12] in accounting for the persistence of fluid states in  ${}^4\text{He}$  down to the lowest temperatures. For dense hydrogen the corresponding packing fraction would be  $(\sigma/2r_s a_o)^3 \sim 0.15$ , where  $\sigma \sim 1.4a_o$ . The energy of a quantum hard-sphere system (either boson or Fermi) will be gauged by quantity  $\hbar^2/m_p\sigma^2$ , i.e.  $\sim 1/m_p$ .

Hard-sphere Fermions have been the subject of simulation studies [13] and also of analysis by density functional methods [14]; the density at coexistence of the fluid state satisfies

$$\bar{\rho}\sigma^3 = 0.31$$

or in terms of  $r_s$

$$r_s = 0.92(\sigma/a_o).$$

Since  $(\sigma/a_o) \sim 1.4$  (expressing, as emphasized, the exchange driven invariance of the near hard-core dimension) the importance of the density range around  $r_s \sim 1.3$  is now clear. But the system is also charged and has a very substantial bulk modulus. Long wavelength phonons therefore lead to distant correlations and (as also noted by London [12]) to a zero-point energy  $\sim 1/m_p^{1/2}$ . That the zero-point energy will remain significant in a fluid state is easily seen from the fact that as a charged system the compressional (phonon) correlations and the zero-point energy associated with just the longitudinal acoustic mode will be (from the Bohm–Staver relation)  $((9\pi)^{2/3}\sqrt{3}/8)(m_e/m_p)^{1/2}/r_s^2$  or  $0.0469/r_s^2$  Ry per proton.

These are very substantial energies and were remarked upon earlier. The consequence is that if the zero-point energy is then considerably in excess of the residual structure in the pair interaction then a depairing of protons is indicated at a critical density, beyond which the system should enter a fluid state. Further insight into the likely appearance of a pressure induced fluid phase follows from the observation that already at the level of *linear* response the effective proton–proton interactions can be mapped onto Yukawa functions [15]. Monte Carlo simulations for Fermion systems conforming to such interactions have been carried out by Ceperley *et al* [16] and these indicate that at  $r_s \sim 1.6$  a fluid ground state will be competitive with crystalline arrangements. But the primary manifestation of nonlinear response is to considerably *decrease* the repulsive range of the interaction, in comparison to cell size increasing therefore the span of density over which the fluid state will be found. This argument leads to a further conclusion; nonlinear effects must themselves eventually diminish at sufficiently high density and from the Monte Carlo investigations on Fermion Yukawa systems, it is clear that a pressure induced fluid state will once again recrystallize, only to give way to a fluid again at densities sufficiently high so that screening itself becomes physically unimportant.

Ground-state energy calculations for *static* lattice models of hydrogen have long predicted an eventual transition from paired to monatomic structures [3], critical densities being in the vicinity of  $r_s = 1.35$ . Detailed calculations of zero-point energies for energetically competitive structures disturbed by harmonic phonons have been carried out by Takezawa *et al* [17]. When simply added to the energies of static structures, transition pressures are found to be significantly altered, in fact downward. An interesting question, suggested by the use of the full  $S_p(\mathbf{k})$  (i.e. going beyond one-phonon terms) is the degree to which incorporation of the strong electron–phonon coupling will now be important. A partial answer to this may be found in a generalization of the self-consistent phonon route (described above for a monatomic structure) to paired structures. When applied to the *Cmca* structure it is found that inclusion of dynamics in a manner which approximately includes phonons, can lead to energy shifts of around 2 mR [18]. But in general the preceding arguments suggest that with inclusion of dynamics the ensuing monatomic states are likely to be fluids. However, static and dynamic attractions can exist between electrons in fluid metallic states of dense metallic hydrogen



or deuterium. If they are of sufficient magnitude, ordered electronic states may then ensue [19] at appropriate temperatures, as is next discussed.

### 3. Fluid states at low temperatures

A liquid phase of metallic hydrogen will be a dual Fermion system, with equal (or nesting) Fermi wave vectors for its proton and electron sub-systems taken as non-interacting. In the presence of correlation, low lying excited states of the combined system can be treated by Fermi liquid theory. The most notable consequence is that a linear term in the specific heat is expected with a very substantial magnitude (traced immediately to the scale of the proton mass entering the density of low lying proton states) and strikingly different from the low-temperature phonon contribution associated with the specific heat expected from a crystalline phase [20]. Long wavelength collective excitations (e.g. longitudinal phonons) will contribute to the specific heat at  $O(T^3)$ . The difference between crystal and liquid is perhaps even more evident in transport properties, for example the static resistivity. The electron system in fluid metallic hydrogen can exchange energy with the proton system, the latter characterized by an exceedingly high density of states. Solution of the Landau–Silin–Boltzmann equation leads to the expected  $T^2$  dependence but again of a scale which greatly exceeds crystalline values anticipated from the scattering of phonons (of moderate wave vectors) in corresponding crystalline states.

The thermodynamic properties of non-interacting bosons above any ordering temperature should not be significantly different from those of classical particles. However, liquid metallic deuterium will continue to have an electronic component contributing a linear term in the specific heat, at moderate temperatures. For normal states the statistical differences between liquid metallic hydrogen and deuterium should therefore be striking, as gauged by the low-temperature thermodynamic functions. The same will be true for transport properties.

The statistical differences between *ordered* states of liquid metallic hydrogen and deuterium will again be notable. Hamiltonians (3) and (4) are expected to lead to states possessing off-diagonal long-range order with factorization of the single-particle density matrix expected for electrons, protons and deuterons as the case may be. Prominent among the states of order, for hydrogen, is electronic superconductivity with charge fluctuations in the proton system contributing in part to the pairing mechanism. Because of the strength of the electron–proton interaction (no pseudopotential reduction occurs in this system) a strong-coupling pathway is indicated and from direct solutions of the Eliashberg equation high-temperature superconductivity ( $T_c \sim 10^2$  K) is predicted. Providing a corresponding gap has opened for the electron system, no dissipation of energy in the coupled electron–proton system is permitted and this is important in considering subsequent ordering of the proton system at much lower temperatures ( $\sim 10^{-3}T_{pf}$ , where  $T_{pf}$  is the Fermi temperature of the free proton system). By the variational principle actual kinetic energies for interacting protons must exceed this. As noted above, the effective proton–proton interaction retains a quite repulsive inner core with a Friedel structure outside of it. Spin fluctuations may play a role in determining a pairing mechanism but the main point is that the presence of these short-range characteristics suggests that the pattern in  $^3\text{He}$  may be followed and that  $p$ -wave or higher pairing may ensue. If this occurs any superfluid state that develops (in the presence of prior superconducting order in the electron system) will be anisotropic. However the Meissner–Ochsenfeld effect in the companion electron system could easily preclude standard magnetic field probing of this.

Liquid metallic deuterium can also support electronic superconductivity, again by pairing originating primarily with charge fluctuations, and with ordering temperatures expected to be lower than in liquid metallic hydrogen by virtue of the doubling of nuclear mass. If again a gap is developed in the electron system, dissipation-free motion of this Boson system is possible in principle at a lower temperature. Since the Boson spin here corresponds to  $s = 1$ , the elementary estimate for the Bose–Einstein consideration for free Bosons (accounting for spin degeneracy) gives

$$T_c \text{ (K)} = 52.44/r_s^2$$

or  $T_c = 28.8 \text{ K}$  at  $r_s = 1.35$ . Inclusion of interactions leads to excitations both of a collective, phonon-like character, and also of a particle-like (excitation out of the condensate) character. These give, respectively, contributions to the heat capacity with temperature dependence  $T^3$  and  $T^{3/2}$  with corresponding dependences for transport properties [20].

Above any superconducting transition temperature (and above any Bose condensation temperature) liquid metallic hydrogen and deuterium should begin to adopt properties similar to those of conventional liquid metals, at least in the structural characteristics important to electron scattering. There is a difference, however, that may be important to experiment. As noted originally by Mannari [21], the cross-section for electron scattering is linked to the time-dependent density–density correlation function, here  $S_p(k, \omega)$ . In Born approximation, the resistivity will then be given by

$$\rho = \rho_a (16\pi^4/3)^{2/3} r_s \int_0^1 dy y^3 v_s^2(y) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_p(y, \omega) \frac{\beta\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \quad (14)$$

where for scattering vector  $\mathbf{q}$ ,  $y = q/2k_F$ . Here  $\rho_a$  is the atomic unit of resistivity ( $\rho_a = a_0\hbar^2/e^2 \equiv 21.7 \mu\Omega \text{ cm}$ ) and  $v_s(q)$  is the linearly screened electron–proton (Coulomb) interaction scaled to its long-wavelength limit ( $2\epsilon_F/3$ ). For conventional liquid metals, the temperature usually satisfies  $\beta\hbar\omega \ll 1$  for fluctuational energies characteristic of the fluid state. Under these conditions

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S_p(y, \omega) \frac{\beta\hbar\omega}{(e^{\beta\hbar\omega} - 1)} \approx S_p(y) \quad (15)$$

the static structure factor, leading to estimates of resistivities in the range of  $10 \mu\Omega \text{ cm}$ . In the present case, however, full knowledge of  $S_p(y, \omega)$  will be needed to establish the scale and temperature dependence of electron transport and especially its progression to the Fermi liquid limits discussed above. At conditions close to  $r_s \sim 1.5$  the pair interaction depth is changing quite rapidly with density, progressing from a scale sufficient to bind protons, to one where unpaired but energetic protons have provided the basis for the low temperature fluid state. Accordingly the behaviour of  $S_p(y, \omega)$  will also reflect these dynamical features, particularly pairing correlations. The measurement by Weir *et al* [22] of the conductivity of hydrogen at  $p \sim 150 \text{ GPa}$  and  $T \sim 3000 \text{ K}$  is a case in point, for the temperature here translates into  $0.02 \text{ Ry}$  which is representative of pair potential depths at these densities. Thus the high-temperature result (15) may not be fully reached and resonant energy transfer between electrons and protons exhibiting strong pairing fluctuations may still be playing an important role.

#### 4. Scaling approaches

There is an evident need to treat the hydrogen problem, for all phases, in a manner which deals with the electrons and protons on an entirely equivalent footing, and this has been recognized

for some time [23]. Towards this end (3) can be rewritten in a way that leads to a scaling form for the ground-state energy (and also for free energies). Let  $\bar{h}^2/\bar{m}e^2$  be the modified Bohr radius, with  $\bar{m} = m_e/(1 + \epsilon)$ , where  $\epsilon = m_e/m_p$ . In terms of this now define  $r_o$  through the statement  $r_o = r_s a_o/a = r_s/(1 + \epsilon)$ . Next, scale all coordinates and momenta according to  $\bar{\mathbf{r}}_e = \mathbf{r}_e/r_s$ ,  $\bar{\mathbf{r}}_p = \mathbf{r}_p/r_s$ ,  $\bar{\mathbf{p}}_e = (r_s/\hbar)\mathbf{p}_e$  and  $\bar{\mathbf{p}}_p = (r_o/\hbar)\mathbf{p}_p$ . Then with  $e^2/2a$  as a scaled Rydberg, (3) is expanded to read

$$\begin{aligned}\hat{H} &= \left(\frac{e^2}{2a}\right) \frac{1}{r_o} \left( \frac{1}{r_o(1+\epsilon)} \sum_i \bar{\mathbf{p}}_{i,e}^2 + \frac{\epsilon}{r_o(1+\epsilon)} \sum_i \bar{\mathbf{p}}_{i,p}^2 \right. \\ &= \left. + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\bar{\mathbf{r}}_{i,e} - \bar{\mathbf{r}}_{j,e}|} - \sum_{i,j} \frac{1}{|\bar{\mathbf{r}}_{i,e} - \bar{\mathbf{r}}_{j,p}|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\bar{\mathbf{r}}_{i,p} - \bar{\mathbf{r}}_{j,p}|} \right) \\ &= \hat{T}_e + \hat{T}_p + \hat{U} = \hat{T} + \hat{U}.\end{aligned}\quad (16)$$

The Hellmann–Feynman theorem can now be applied, both with respect to  $r_s$ , but also with respect to the constituent masses. If  $\psi$  is, for example, the normalized ground-state wavefunction of  $\hat{H}$ , then for example, the pressure is

$$\begin{aligned}p &= -\left(\frac{\partial E}{\partial V}\right)_N = -\left\{\frac{\partial \langle \hat{H} \rangle}{\partial V}\right\}_N = -\frac{r_o}{3V} \left\{\left\langle \frac{\partial \hat{H}}{\partial r_o} \right\rangle\right\}_N = -\frac{r_o}{3V} \left\{\langle \psi | \frac{\partial \hat{H}}{\partial r_o} | \psi \rangle\right\}_N \\ &= -\frac{r_o}{3V} \left\{-2\frac{\langle \hat{T} \rangle}{r_o} - \frac{\langle \hat{U} \rangle}{r_o}\right\}\end{aligned}$$

yielding

$$3pV = 2\langle \hat{T} \rangle + \langle \hat{U} \rangle$$

which is, of course, the virial theorem. Similar derivatives carried out with respect to the masses, regarded as parameters, yield

$$r_o \frac{\partial E}{\partial r_o} - m_e \frac{\partial E}{\partial m_e} - m_p \frac{\partial E}{\partial m_p} = -E = -E(r_o, m_e, m_p) \quad (17)$$

which is an exact statement, independent of phase [24]. The result transcends the ground state, and will be valid for all states, and hence all combinations of states, in particular those states entering into a classical combination. The general solution to (17) has a scaling form, namely

$$E/N = f(m_e r_s, m_p r_o)/r_o$$

and for a one-component system (for example, as described by the Hamiltonian of equation (2)) the corresponding result is

$$E/N = g(m r_o)/r_o.$$

Since  $E(r_s)/N$  is known with considerable accuracy for the interacting electron gas, it must follow that provided a translationally invariant state is preserved for the proton system the corresponding energy/proton can be obtained by scaling [24]. The kinetic energy/proton can also be obtained and actually attains values of  $\sim 0.02/r_s^{3/2}$  Ry [24] confirming yet again the considerable proton energy scale invoked in the general arguments above.

What is clearly required is an extension of these scaling laws to finite temperatures. As has been noted above, the static structure factor enters into the internal ground-state energy. The same is true for the Helmholtz energy. For  $a, b = e, p$  the scaling can be generalized [24]

$$S_{ab}(\bar{\mathbf{k}}) = f(m_e r_o, m_p r_o, T r_o)$$

where  $\bar{\mathbf{k}} = \mathbf{k}r_s a_o$ . Extensions of this temperature scaling to the entire Helmholtz energy are under consideration but in the interim it is clear that this problem could benefit considerably from further *ab initio*, path integral simulations [25]. In particular the general arguments advanced above clearly indicate the possibility of transitions at fixed temperature from crystalline arrangements to liquids of higher density. Thus assessments focussing on the melting curve, and especially the continuity of its slope will be especially valuable. For lacking the latter, the clear implication would then be the existence of crystalline structures as yet unsuspected, but possibly linked to the progressive enhancement of Friedel structure now seen as potentially associated with nonlinear response [11]. Finally, the existence of a melting point maximum succeeded by a relatively precipitous decline in the melting curve with pressure may also have consequences on the form of hydrogen's shock Hugoniot.

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