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2000 J. Phys.: Condens. Matter 12 A129

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J. Phys.: Condens. Matter **12** (2000) A129–A137. Printed in the UK PII: S0953-8984(00)09284-5

The hydrogen liquids

N W Ashcroft
Cornell Center for Materials Research, and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853-2501, USA

Received 4 November 1999

Abstract. When average one-particle densities are spatially uniform at a microscopic level the state is considered to be a homogeneous liquid. A prescription is required for the basic dynamical elements involved in the averaging itself, and for hydrogen, at low densities and temperatures, these are the familiar hydrogen molecules. But, at compressions now achievable both by static and dynamic means, a more basic description in terms of protons and electrons incorporating residual pairing correlations is necessary. The latter are dependent in large part on the nature of effective state-dependent pair interactions between protons, and in a narrow band of densities near $r_s = 1.33$, these may be especially weak. *The hydrogen liquids* refers to the (quantum) diatomic liquid, the high density monatomic liquid, and the variably correlated transition phases between the two.

1. Introduction; the hydrogen problem

Condensed fluid phases of hydrogen first appeared in the laboratory just over a century ago. Condensation proceeded from a gas of strongly bound two-electron/two-proton (2e + 2p) entities which suffer negligible physical change during the transition to the liquid. These hydrogen *molecules*, and the need to understand the strength of the implied homopolar binding, presented a key initiating problem for the new quantum mechanics of the time. Because of its preponderance in the universe, hydrogen constitutes a fundamental system in nature which provides examples of it over a wide range of thermodynamic conditions. Some 9 out of 10 atoms in the giant planet Jupiter, for example, are hydrogen, and conditions permit fluid phases which are molecular, dissociated (and metallic), and intermediate.

The dense-hydrogen problem can also be constructed from two equally fundamental problems, identical in form, namely

(i) N interacting electrons ($\alpha = \mathrm{e}$) in a uniform compensating background (occupying a volume V),
(ii) N interacting protons ($\alpha = \mathrm{p}$) in a similar background of opposite sign (but otherwise equal density), and
(iii) the coupling between (i) and (ii).

If $\hat{H}_\alpha$ are the corresponding (fermionic) Hamiltonians, neither having specific reference to spin, then all phases of hydrogen are described by

$$\hat{H} = \hat{H}_e + \hat{H}_p - \int_V \mathrm{d}\boldsymbol{r} \int_V \mathrm{d}\boldsymbol{r}'\, v_c(\boldsymbol{r} - \boldsymbol{r}')(\hat{\rho}_p^{(1)}(\boldsymbol{r}) - \bar{\rho})(\hat{\rho}_e^{(1)}(\boldsymbol{r}') - \bar{\rho}) \tag{1}$$

where $v_c(r) = e^2/r$, $\bar{\rho} = N/V$ and where for coordinates $\boldsymbol{r}_{\alpha i}$ the one-particle density operators are defined by

$$\hat{\rho}_\alpha^{(1)}(\boldsymbol{r}) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_{\alpha i}). \tag{2}$$

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The fundamental electron and proton problems in (1) have corresponding Hamiltonians

$$\hat{H}_\alpha = \hat{T}_\alpha + \frac{1}{2}\int_V \mathrm{d}\boldsymbol{r} \int_V \mathrm{d}\boldsymbol{r}'\, v_c(\boldsymbol{r}-\boldsymbol{r}')\{\hat{\rho}_\alpha^{(2)}(\boldsymbol{r},\boldsymbol{r}') - 2\bar{\rho}\hat{\rho}_\alpha^{(1)}(\boldsymbol{r}) + \bar{\rho}^2\} \tag{3}$$

where the two-particle density operators are

$$\hat{\rho}_\alpha^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \hat{\rho}_\alpha^{(1)}(\boldsymbol{r})\hat{\rho}_\alpha^{(1)}(\boldsymbol{r}') - \delta(\boldsymbol{r}-\boldsymbol{r}')\hat{\rho}_\alpha^{(1)}(\boldsymbol{r}) \tag{4}$$

and the $\hat{T}_\alpha$ are total-kinetic-energy operators. To describe deuterium it is only necessary to replace the mass of the proton (m_p) by that of the deuteron (m_d) in the kinetic energy ($\hat{T}_p = \sum_i(-\hbar^2/2m_p)\boldsymbol{\nabla}_{pi}^2$) and to acknowledge a fundamental change in the quantum statistics.

2. The hydrogen liquids

The Hamiltonian described by (1) has considerable symmetry, and although the particular states of $\hat{H}$ also possessing continuous translational and rotational symmetry are of principal concern in what follows, it should be noted that general scaling relations govern the energy states, independent of phase [1]. The form of (1) also leads to quite general predictions of density-dependent instabilities towards pairing in both electron and proton degrees of freedom [2]. By convention the structure of hydrogen (and indeed of most systems) is defined by the physical attributes of the appropriate average of the one-particle density operator for the massive degrees of freedom, here the protons. Thus if the quantum statistical average of the proton one-particle density operator

$$\rho_p^{(1)}(\boldsymbol{r}) = \langle\hat{\rho}_p^{(1)}(\boldsymbol{r})\rangle$$

should be triply periodic in space, then the hydrogen is considered to be in a three-dimensional crystalline phase.

The hydrogen liquids are the phases of (1) satisfying

$$\rho_p^{(1)}(\boldsymbol{r}) = \text{constant} = \bar{\rho} = N/V.$$

This is a condition that does not rule out the possibility of further structuring on a microscopic length scale, the obvious case being proton pairing. This will be revealed through the two-particle density, the corresponding average of (4), namely

$$\rho_p^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \langle\hat{\rho}_p^{(2)}(\boldsymbol{r},\boldsymbol{r}')\rangle = \rho_p^{(1)}(\boldsymbol{r})\rho_p^{(1)}(\boldsymbol{r}')g_p(\boldsymbol{r},\boldsymbol{r}') \tag{5}$$

which for states of continuous symmetry takes the form

$$\rho_p^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \bar{\rho}^2 g_p(|\boldsymbol{r}-\boldsymbol{r}'|). \tag{6}$$

Here $g_p(r)$ is now the standard radial distribution function whose form is well known to reflect pairing correlations in systems where diatomic order is persistent.

Though the Hamiltonian (1) is rather simple, its states, as revealed by the phase diagram, are complex. Figure 1 shows both low-temperature and high-temperature fragments [3] over density ranges which are now accessible by static and dynamic high-pressure methods. At normal pressures and low temperatures, isolated hydrogen condenses from a diatomic gas to first form a uniform liquid ($\rho_p^{(1)}(\boldsymbol{r}) = \bar{\rho}$) where the diatomic molecules remain weakly coupled by interactions including a long-range quadrupolar contribution. Further cooling leads to a crystalline solid (phase I, for $p < 110$ GPa), where $\rho_p^{(1)}(\boldsymbol{r})$ is periodic but where the angular momentum as assigned to the molecule remains a remarkably good quantum number, in spite of the presence of a dense crystalline environment. It requires *very* significant compression to eventually hinder this rotation, the result (phase II, for 110 GPa $\leqslant p \leqslant$ 151 GPa) being a crystal

where proton pairs execute wide-angle libration. With further compression at low temperatures another phase boundary is encountered. The new phase (phase III, for $p \geqslant 151$ GPa) exhibits remarkable infra-red activity [4], not uncharacteristic of an electronic state of (1) where symmetry has been spontaneously broken and where there is a persistent and principally dipolar distortion of electronic charge [5]. The boundary between phases II and III therefore reflects in part the coupling of permanent quadrupoles to the emerging state-dependent dipoles [6]. An increase in temperature can drive the system back to a rotationally unpolarized state (phase I), as it will with phase II. Further increase in temperature will eventually melt the crystalline (but site-rotational) state. Liquid and crystalline states are separated by a melting line which follows a Simon melting law [7] reasonably well for moderate compressions. An important question (especially in view of the relatively high conductivity observed [8] at both elevated temperatures and compressions) is the degree to which the fluid state is one where the integrity of the (2e + 2p) unit is actually preserved when more extreme conditions are reached. This question is crucial to the thermodynamic and correlation functions of the system, and also to an understanding of the transport properties [8]; it is briefly addressed in section 5 whose purpose is to qualitatively assess the role of correlation in the dissociation problem at high densities.

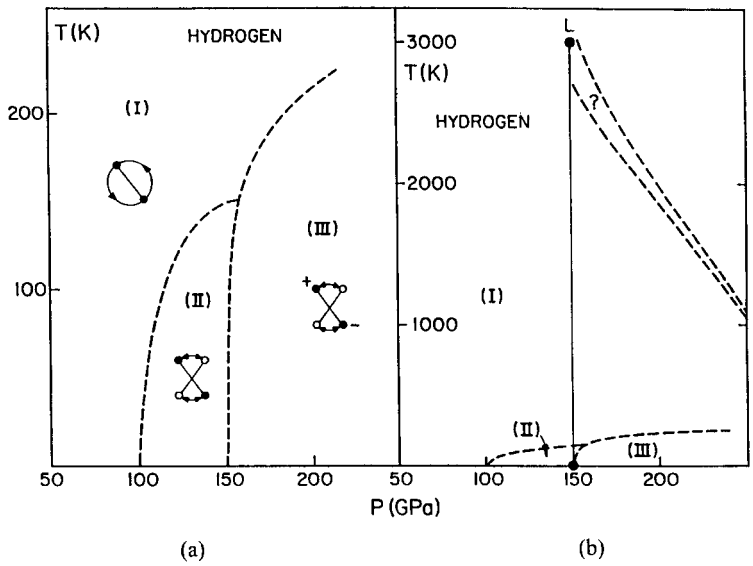

Figure 1. (a) The phase diagram for dense hydrogen at relatively low temperatures. Phase I corresponds to a rotational crystal, phase II to a rotationally hindered (librational) crystal, and phase III to a hindered but highly infra-red-active crystal. At about 410 GPa ($r_s \sim 1.33$) a transition to a monatomic phase is predicted [14]. (b) The phase diagram extended to higher temperatures; the experimental point (L) corresponds to a phase where a conducting state is reported. The dashed region near L indicates a possible boundary separating insulating from conducting behaviour. Between this region and the low-temperature phase boundaries, a melting curve will be crossed; as discussed in the text the state dependence of the pair interaction is considerable, and may well lead to a maximum in the melting curve.

3. The paired hydrogen liquid

For N protons and N electrons in a volume V (alterable by experiment) a starting point for a neutral system is a canonical partition function $Q = \mathrm{Tr}\exp(-\beta\hat{H})$ where the trace is to be

taken over the states of (1). If m_e is the mass of the electron then m_p/m_e (=1836) is sufficiently large that electronic and protonic degrees of freedom can be reasonably separated as a first step and the partition function can then be written:

$$Q = \mathrm{Tr}_p\{\mathrm{Tr}_{e(p)} \exp(-\beta \hat{H})\} = \mathrm{Tr}_p \exp(-\beta H_{eff}(V, T))$$

where the trace over electron states is for momentarily fixed proton configurations. If, further, the electron system is reasonably close to its ground state, then $\hat{H}_{eff}(V, T) = \hat{H}_{eff}(V)$ is an effective Hamiltonian for a description of proton dynamics. It acquires a formal dependence on density if the electron states are themselves sensitive to a volume-dependent boundary condition. In the hydrogen problem a convenient linear measure of atomic volume is provided by r_s where $(4\pi/e)r_s^3 a_0^3 = V/N$. Standard conditions for hydrogen correspond to $r_s \sim 3.13$ and the system then conforms to an assembly of spin-antisymmetric (2e + 2p) units, i.e., electron pairs localized around pairs of protons (the many-electron wave-function is effectively decoupled when, as for $J = 0$ para-hydrogen, the orientational motions of proton pairs are uncorrelated). Under these conditions the configurationally dependent component of $\hat{H}_{eff}$ can be developed in terms of pair, three-body, etc, potentials between the (2e + 2p) units that are clearly the correct elementary objects for the application of quantum statistical physics in both liquid and solid [9] phases.

The critical point of hydrogen corresponds to 33.19 K (of deuterium, to 38.34 K). The proton thermal de Broglie wavelength is $\lambda_p = a_0(4\pi)^{1/2}(m_e/m_p)^{1/2}/(k_B T\ (\mathrm{Ryd}))^{1/2}$ and at 300, 30, and 3000 K, respectively, takes on the values 1.85 a_0, 5.85 a_0, and 0.585 a_0. In the liquid phase at normal pressures, the molecular counterpart λ_m $(=\lambda_p/\sqrt{2})$ has a value comparable to intermolecular spacings. Quantum effects are therefore expected to endure over a considerable range of temperatures; mass-related differences are seen [10, 11] in the static structure factor (which is proportional to the Fourier transform of $g_p(r) - 1$, where g_p is defined in equation (6)). The low-temperature fluid state of hydrogen can itself be subjected to pressure, and for pressures reaching as high as 20 GPa the mean interproton distance shows a noticeable decrease [12]. Liquid hydrogen can also be supercooled at ordinary pressures [13] offering the possibility (not as yet realized) of obtaining Bose–Einstein condensation in a diatomic fluid (Bose–Einstein condensation in monatomic spin-polarized hydrogen being realized).

But the picture of immutable (2e + 2p) molecules changes radically when compressions exceed a factor of 10 and temperatures drive the system towards classical conditions in the translational degrees of freedom.

4. The atomic liquid

Apart from inhomogeneities required, absolutely, by the cusp theorem, the electronic background expected from Hamiltonian (1) becomes increasingly uniform when the average density attains sufficiently high values (or r_s is sufficiently small). For an isolated hydrogen atom, the electron density *at* the proton has an equivalent r_s-value given by $(4\pi/3)r_s^3 a_0^3 = (1/\pi a_0^3)^{-1}$, or $r_s = 0.89$. From this it might well be expected that the requirement on density for transition to a microscopically regular state should be $r_s < 0.89$. (Here a microscopically regular state is one where all near-neighbour interparticle spacings are determined solely by density; they must therefore be just $2\alpha r_s a_0$, where α is close to unity and is fixed by geometry.) However, an instability of depairing character can actually be shown to set in at a lower density [14]. Observe that for infinitely massive protons the lowest energy state of $\hat{H}_p$ by itself is achieved for the BCC structure, and if a pairing state were to nucleate from such a structure, then at fixed density a corner proton and centre proton will reduce their mutual separation by,

say, δ. From the standpoint of the electrostatic terms in of $\hat{H}_p$ this is equivalent to appending fixed dipoles to alternating sites in the original undistorted structure, these leading (for this cubic system) to a *rise* in energy proportional to δ^2. But with the electrons now included (i.e. $\hat{H}_e$), and their coupling to $\hat{H}_p$, there is a corresponding lowering of band-structure energy (most prominently from the {100} Bragg planes which are absent prior to distortion) and this *declines* as δ^2. Both contributions are functions of density, and the distorted (or paired) lattice is calculated to be stable (the electron response energy exceeds the penalty) but only until the density reaches an equivalent $r_s = r_{sc} \approx 1.33$ [14].

This is a variant on the Jahn–Teller and Peierls arguments usually invoked to explain the tendency of symmetric quantum systems to yield to symmetry-lowering distortions. A mechanism for ordering (pairing) can therefore be identified, and it can be assigned an order parameter λ which is proportional to the displacement of one proton in the pair from a convenient lattice site. Then for a sequence of declining pressures (increasing r_s) the Landau theory predicts a Gibbs energy/proton of the form

$$g(\rho, T; \lambda) = \sum_{n=0} a_{2n}(\rho, T)\lambda^{2n}$$

with a transition to a paired state, from monatomic, occurring at $\bar{\rho} = \bar{\rho}_c$ (or $r_s = r_{sc}$).

Subsequent to an electron trace these energies can also be resolved into pair and multi-centre potentials governing the displacements of the protons. The role played by exchange in determining the form of the pair potential $\phi_p^{(2)}(k; r_s)$ is especially pertinent; this is made clear from a comparison of the electron density close to the protons with valence electron densities characteristic of ordinary metals. For larger k, say $k > 1/a_0$, the limiting form for $\phi_p^{(2)}(k; r_s)$ will be $4\pi e^2/k^2$, and is positive definite. When overall densities are not too high, protons are strongly paired, and, as noted, exchange is well known to be important to this. It follows that for these conditions $\phi^{(2)}(k \to 0; r_s)$ should approach the volume average of, say, the Kolos–Wolniewicz potential [15], which is significantly *negative*. The magnitude of the notable exchange energy originates with both the cusp structure of the density *and* its overall scale. The progression, with density, of the depth of the pair potential (and hence the trend of $\phi_p^{(2)}(k = 0, r_s)$) can readily be obtained from analysis of the vibrons in dense hydrogen and deuterium [16]. The depth of the associated well then extrapolates to near-vanishing values at $r_s \sim 1.33$, but its location remains close to 1.4 a_0 (and not to $2\alpha r_s a_0$). From the form of either the dominant exchange terms in the Heitler–London description, or from the local density approximation, the expectation is $\phi_p^{(2)}(k) \sim -b/(a + k^2)^2$ for the behaviour of the departure of $\phi_p^2(k)$ from its $k = 0$ value. At high densities this will diminish in importance (it is the non-uniform component of density, rather than the uniform background on which it is superimposed, which leads to spatial dependence). But for high-density states of *metallic* hydrogen the effective proton–proton interaction will eventually take the screened (and positive) form $4\pi e^2/k^2\varepsilon(k)$, where $\varepsilon(k)$ is the static dielectric constant of the interacting electron gas (incorporating response to just linear order).

At densities where band theory and total-energy calculations declare the onset of a dissociative transition [14] to a metallic state ($r_s \sim 1.33$) the effective potential must continue to reveal at least the remnants of the attractive tendencies of exchange. Thus, $\phi_p^{(2)}(r; r_s)$ as determined *only* by linear response above is expected to exhibit a first minimum at around $2r_s a_0$, and weak Friedel oscillations thereafter. In fact, low-density conditions distinctly favour an exchange-driven minimum in $\phi_p^{(2)}$ at around 1.4 a_0, a separation that declines only a little with density; it follows therefore that a critical dissociation density should occur which corresponds to a situation where the average minimum separation continues to be $\sim 2r_s a_0$ yet there remains a repulsive region (reflecting both the remnants of exchange and the direct interactions) but

one which does not set in until significantly smaller separations.

At high compression it will be necessary to contend with the effects of *inter*molecular exchange which with increasing density will further promote the transition to a microscopically regular state. However, the overall argument just presented is not significantly altered and it suggests that a small band of densities may exist for which hydrogen is *not* highly correlated. For such densities the residual long-range interactions characterized, as noted, by Friedel oscillations, are relatively weak; the context in which *weak* has physical meaning here is that the residual structure in $\phi_p^{(2)}$ is always to be gauged with respect to proton zero-point energy. The two are actually comparable [17], exactly the physical situation that prevails in He, but under normal conditions. For this reason the critical (but possibly quite *narrow* range of densities) just inferred for hydrogen will be one where quantum effects are of quite crucial importance leading either to the possibility of incommensurate structures, or more likely to (a) a ground-state *liquid*, (b) a *liquid* state that may be metallic, exhibiting electron pairing (in hydrogen), and (c) a metallic *liquid* state exhibiting pairing for electrons and superfluidity for deuterons (in deuterium). At the very least, this argument suggests that the melting line for dense hydrogen may possess a maximum in the density range $3.13 > r_s > 1.33$.

The route to a monatomic phase is therefore expected to be complex when viewed in terms of the controlling interproton potentials. Monatomic crystalline structures are predicted [17] to occur at $r_s \lesssim 1.33$ (at $T = 0$), and the transitions to these evidently take place from orthorhombic structures [14]. However, as noted, the existence of the pairing instability is easily demonstrated with the simpler body-centred-cubic case. This example also provides estimates of the separation energy ($\varepsilon(V)$ for protons in a dense environment, and at $r_s = 1.5$ (near ninefold compression) the energy is approximately 1 eV [17], and this will be important below. For the same density range ($r_s \leqslant 1.33$) the fluid phases of hydrogen are also expected to be largely monatomic. The interesting feature of these phases is that because of the significant state dependence of the effective proton–proton interactions, the rise of pairing correlations for higher densities might well exceed those anticipated merely on the basis of the rise in density itself. The assumption that normal monatomic fluid phases should eventually exist for liquid metallic hydrogen was central to early estimates [18] of its electronic transport properties.

5. The intermediate or mixed hydrogen liquid

The effects of temperature are now to be added to this otherwise near-ground-state description indicating a notable depairing induced by increasing density. Though multi-proton complexes are anticipated to form, at least transiently, under such conditions, the case of proton pairs dissociating in an *already* dense environment is of particular physical interest. Once the system is in this conformation, there is the possibility of electronic hopping conduction by a percolation type of mechanism provided the density of dissociated protons (N_p/V, say) is sufficiently high. The purpose of what follows is simply to establish some important measures for the hydrogen liquid under intermediate conditions, and for this it is supposed that the cost of separating a previously bound pair, and embedding the remnants at distant locations is a known quantity, say $\varepsilon = \varepsilon(V)$. The effect of classical state dependence can be included approximately by permitting ε to include an entropic component ($\varepsilon = \varepsilon(V, T)$).

Let N_m be the number of molecules on average under conditions which are taken as largely classical for translational degrees of freedom. If N is the total number of protons in V, and c_p and c_m the concentrations of protons and molecules respectively (and so $N_p + 2N_p = N$ or $c_p + 2c_m = 1$). Then within an approximate treatment of correlation, for example in a

mean-field approach, the partition function for N_p protons and N_m pairs will be

$$Q_N = [ev(1 - b\{c_m + c_p\}/\lambda_p^3 c_p)(\exp \beta a\{c_m + c_p\}/v)]^{N_p} \times [ev(1 - b\{c_m + c_p\}/\lambda_m^3 c_m)(\exp \beta a\{c_m + c_p\}/v) \exp \beta\varepsilon(v)]^{N_m}. \quad (7)$$

Here $v = V/N$ is the mean atomic volume, and (since $v = (4\pi/3)(r_s a_0)^3$) it follows that $v/\lambda_p^3 = (r_s T^{1/2}\ (\mathrm{K})/20.38)^3$. Equation (7) is familiar from the Van der Waals approximation for which a and b have their standard meanings. By the earlier arguments, both are now expected to be significantly state dependent (i.e. $a = a(V)$, $b = b(V)$). Note that to (7) can also be appended the factors $(T/2T_R)^{N_m}$ to represent contributions to the partition function from rotational degrees of freedom in the high-temperature limit, and $(\mathrm{cosech}(\beta\hbar\omega/2))^{N_m}$ to include contributions from a principal vibron. Finally, for a given V there may be common volume-dependent (structure-independent) terms originating from the wide-band character of the electron states.

At low pressures ($r_s \sim 3$) the energy $\varepsilon(V)$ is about 4.8 eV, and it is clear that intramolecular interactions should dominate correlation effects in the determination of c_p. To obtain a first estimate of c_p under these conditions, the free energy following from (7) is minimized with $a = b = 0$, the uncorrelated case. Then c_p is the physical solution of

$$c_p^2 + \delta c_p - \delta = 0$$

where (noting that $\lambda_p/\lambda_m = \sqrt{2}$)

$$\delta = (v/\lambda_p^3 2^{5/2}) \exp(-\beta\varepsilon(V)) \equiv (r_s T^{1/2}\ (\mathrm{K})/36.3)^3 \exp(-\beta\varepsilon(V)). \quad (8)$$

The required solution is $c_p = 2/\{1 + \sqrt{1 + 4/\delta}\}$ and it follows that for low temperatures and large $\varepsilon(V)$

$$N_p \sim \delta^{1/2} \sim N(r_s T^{1/2}\ (\mathrm{K})/36.3)^{3/2} \exp(-\beta\varepsilon(V)/2). \quad (9)$$

There is then little dissociation, as expected.

At high temperatures this argument leads to $c_p \sim 1$, but for both high temperatures *and* high density (where $\varepsilon(V)$ declines) the physics internal to pairs ceases to dominate, and the role of a and b can no longer be neglected. Retaining both in (7), the free energy can again be minimized with respect to c_p and the result is that, in the minimizing condition, $\varepsilon(V)$ needs only to be replaced by

$$\varepsilon(V) + ac_p/v + k_B T\{\ln(1 - bc_p/2v) + (bc_p/2v)/(1 - bc_p/2v)\} \quad (10)$$

and the role of correlation (through a and b) can immediately be assessed from (10). Note at once that (10) confirms in a self-consistent manner the previous conclusion that dissociation is controlled by $\varepsilon(V)$ (c_p can certainly be small when $\varepsilon(V)$ is large). However, it also shows that if densities are such that $\varepsilon(V)$ is a few $k_B T$, then the roles of a and b (and their state dependence) are crucial to the dissociation problem. For recall that in the Van der Waals approximation, b can be a substantial fraction of the atomic volume, v. In a similar way, a is significant on a scale of $k_B T$; in an effective single-particle way it is representing the average interaction between species. The especial importance of $\varepsilon(V)$ is now quite evident; it is a quantity that can be estimated from the ground-state energetics of solid-phase structures, as discussed above. Thus, for $r_s \sim 3.13$, $\varepsilon(V)$ is approximately 4.8 eV, the molecular value, but this drops to about 1 eV when $r_s \sim 1.6$ [17]. For $T \sim 300$ K, $4k_B T \sim 1$ eV, implying that there are significant changes in the uncorrelated estimates for c_p ($c_p \sim 0.45$, for $a = b = 0$).

This conclusion can also be substantiated by focusing only on the role of excluded-volume effects ($b = 0$, $a \neq 0$). Here the problem can be addressed somewhat more accurately by examining the change in proton chemical potential associated with short-range correlation of

a hard-sphere character. If $\sigma = \sigma(V)$ is, in atomic units, a physical hard-sphere diameter representing the short-range region of $\phi_p^{(2)}(r; V)$, then the packing fraction is $\eta = (\sigma/2r_s)^3$. For uncorrelated protons the first factor of the partition function (7) gives

$$\mu_p = k_B T \ln\{v/\lambda_p^3\} \tag{11}$$

but if the number dependence of the Carnahan–Starling free energy [19] is used instead to fix the chemical potential, then

$$\mu_p = k_B T \ln\{\mathrm{e}^{-\gamma} v/\lambda_p^3\}$$

where

$$\gamma = \gamma(r_s) = \eta(8 - 9\eta + 3\eta^2)/(1 - \eta)^3.$$

This confirms that even for modest values of packing fractions ($n \sim 0.1$), corrections to the uncorrelated estimates for dissociation will be considerable. Note that a form quite similar to (9) can be written down for pairs (including the consequences of $\varepsilon(V)$), and the equilibrium concentration c_p (and the effective $\varepsilon(V)$ as in (10)) is then also determined by the two separate factors of (7) from the required equilibrium condition $\mu_m = 2\mu_p$. Aside from residual quantum aspects, these elementary classical estimates therefore reveal that for the mixed hydrogen liquid a far more detailed knowledge is required of the state dependence of the effective interactions if *standard* routes for the thermodynamic functions are pursued. It should be noted, however, that the partition function for (1) can be established, *ab initio*, as a coherent state path integral [2] which requires no resolution into effective potentials, an alternative pathway which can also be examined in the high-temperature limit.

The recent dynamic compression experiments on dense hydrogen report densities $r_s \sim 1.5$ and temperatures of 3000 K (gas gun [8]) for hydrogen, and $r_s \sim 1.73$ and very much higher temperatures (via laser shocks [20]) for deuterium. (It may be observed that at $r_s = 1.5$ an ideal gas already generates a pressure of 100 GPa at 23 000 K.) At $r_s = 1.5$ (and $T = 0$), the energy difference between paired and unpaired structures is ~0.3 eV per pair; at $r_s = 1.73$ it is about 1.1 eV/pair. In both experiments significant dissociation is therefore predicted by (9) and its extension to the correlated case via (10). For the gas-gun case [8] the fraction c_p still may well exceed the percolation threshold for conduction. These considerations show that of the liquid states of hydrogen, those lying intermediate between the fully paired and fully dissociated phases present the most significant theoretical challenge, especially if conditions are such that in addition to persistence of strong correlation between protons, the electron system is also becoming partially degenerate. In this respect the continuing impetus from both gas-gun [8] and laser-shock [20] experiments can be seen as quite crucial to the physics of the hydrogen liquids.

Acknowledgments

This work was supported by the US National Science Foundation.

References

[1] Moulopoulos K and Ashcroft N W 1990 *Phys. Rev.* B **41** 6500
[2] Moulopoulos K and Ashcroft N W 1999 *Phys. Rev.* B **59** 12 309
[3] Ashcroft N W 1998 *Strongly Coupled Coulomb Systems* ed Kalman *et al* (New York: Plenum) p 81
[4] Hanfland M, Hemley R J and Mao H K 1993 *Phys. Rev. Lett.* **70** 3760
[5] Edwards B and Ashcroft N W 1997 *Nature* **388** 652
[6] Edwards B 1997 *Thesis* Cornell University, Ithaca, NY

[7] See, for example, Babb S E 1963 *Rev. Mod. Phys.* **35** 400
[8] Weir S T, Mitchell A C and Nellis N J 1996 *Phys. Rev. Lett.* **76** 1860
[9] van Kranendonk J 1983 *Solid Hydrogen* (New York: Plenum)
[10] Zoppi M, Celli M and Soper A K 1998 *Phys. Rev.* B **58** 11 905
[11] Zoppi M, Soper A K, Magli R, Barrochi F, Bafile V and Ashcroft N W 1996 *Phys. Rev.* E **54** 2773
[12] Ulivi L, Zoppi M, Gioé L and Pratesi G 1998 *Phys. Rev.* B **58** 2383
[13] Maris H J, Seidel G M and Williams F I B 1987 *Phys. Rev.* B **36** 6799
[14] Johnson K and Ashcroft N W 2000 *Nature* at press
[15] Kolos W and Wolniewicz L 1965 *J. Chem. Phys.* **43** 2429
[16] Ashcroft N W 1990 *Phys. Rev.* B **41** 10 963
[17] Ashcroft N W 2000 to be published
[18] Stevenson D and Ashcroft N W 1974 *Phys. Rev.* A **9** 782
[19] Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635
[20] Collins G W, DaSilva L B, Celliers P, Gold D M, Foord M E, Wallace R J, Ng A, Weber S V, Budil K S and Cauble R 1998 *Science* **281** 1178