Plasma-insulator transition of spin-polarized hydrogen

Hong Xu[1] and Jean-Pierre Hansen[2]

[1]*Département de Physique des Matériaux (UMR 5586 du CNRS), Université Claude Bernard-Lyon 1, 69622 Villeurbanne Cedex, France*

[2]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

(Received 1 March 1999)

A mixed classical-quantum density functional theory is used to calculate pair correlations and the free energy of a spin-polarized hydrogen plasma. A transition to an atomic insulator phase is estimated to occur around $r_s = 2.5$ at $T = 10^4$ K, and a pressure $P \approx 0.5$ Mbar. Spin polarization is imposed to prevent the formation of H_2 molecules. [S1063-651X(99)50807-6]

PACS number(s): 05.30.−d, 31.15.Ew, 61.20.−p, 64.70.−p

Although hydrogen is generally considered to be the simplest of elements, its expected metallization under pressure [1] has proven to be a rather elusive transition. It is now accepted that the behavior of solid and fluid molecular hydrogen (H_2) may be very different at high pressures. Despite considerable experimental efforts with static, room temperature compression of solid H_2 in diamond anvils [2] beyond pressures of 2 Mbar, there is still no compelling evidence for a metallic state [3]. The situation is somewhat more favorable for fluid H_2, since shock compression to 1.4 Mbar and a temperature of about 3000 K led to measurements of metallic resistivities [4]. However, theoretical interpretation is hampered by the absence of a clear-cut scenario; in particular, it is not clear whether molecular dissociation precedes ionization or conversely [5]. The presence of several species, H_2, H_2^+, H, H^+, and electrons at a ''plasma phase transition'' [6] complicates a theoretical analysis considerably; to gain a clearer picture of pressure-induced ionization, it may be instructive to consider a model system, which would not involve molecular dissociation.

The model system considered in this Rapid Communication is spin-polarized hydrogen. If all electron spins are assumed to be polarized by a strong external magnetic field **B**, only triplet pair states $^3\Sigma$ can be formed, preventing the binding into H_2 molecules. The low pressure phase will be made up of H atoms and the only possible scenario upon compression will be the ionization of atoms to form an electron-proton plasma, which is expected to be crystalline at low temperatures and fluid at higher temperatures. A rough estimate of the magnetic field needed to spin polarize the electrons is obtained by equating the magnetic coupling energy $-\mu_B B$ (where μ_B is the magnetic moment of an electron) to the difference between the triplet and singlet H-H potential energy functions, calculated at the equilibrium distance of the H_2 molecule [6]; this leads to $B \approx 10^5$ T. This value exceeds the highest magnetic fields achievable in a laboratory by three orders of magnitude, but is well within the range of astrophysical situations. The present calculation neglects possible orbital effects due to a strong applied magnetic field; such effects are expected to be small and their inclusion would lead to a much more involved and less transparent calculation. We prefer to think of our model system as a plasma that has been prepared in a spin-polarized state and

is assumed to remain so even when B is switched off. The subsequent calculation will be restricted to fluid hydrogen.

The thermodynamic properties of the low pressure spin-polarized atomic hydrogen phase may be easily calculated from the known triplet pair potential [7] by standard methods of the theory of classical fluids. We calculated the atom-atom pair distribution function $g(r)$ from the hypernetted-chain approximation (HNC) integral equation [8], and deduced from it the equation of state via the virial and compressibility routes. The resulting excess free energies per atom are plotted in Fig. 4 as a function of the usual density parameter $r_s = a/a_0$, along the isotherm $T = 10^4$ K; here a_0 is the Bohr radius and $a = [3/(4\pi n)]^{1/3}$, where n is the number of H atoms per unit volume. There is a thermodynamic inconsistency, typical of HNC theory, but the small difference between the ''virial'' and ''compressibility'' free energies will have no influence on our conclusions. To allow for a meaningful comparison with the free energy calculated for the high pressure plasma phase, the free energies shown in Fig. 1 contain an electron binding energy contribution of -0.5 a.u. It is implicitly assumed that this binding energy, valid for isolated atoms (i.e., in the limit $r_s \to \infty$) does not change upon compression up to $r_s = 2.5$, due to the overlap and distortion of the individual electron $1s$ orbitals.

A statistical description of the high pressure phase is more challenging. The key parameter characterizing the spin-polarized electron component is its Fermi energy $\epsilon_F = 2.923/r_s^2$ a.u.; the corresponding Fermi temperature $T_F \approx 9.2 \, 10^5/r_s^2$ K. Along the isotherm $T = 10^4$ K considered in the present calculations, the electrons may be considered to be completely degenerate (i.e., in their ground state) up to $r_s \approx 3$. The degeneracy temperature of the protons is 2000 times smaller, so that for $T = 10^4$ K, the latter may be considered as being essentially classical, down to $r_s \approx 0.5$. The proton component is characterized by the Coulomb coupling constant $\Gamma = e^2/(a k_B T) = 31.56/r_s$ along the above isotherm, showing that classical Coulomb correlations are expected to be strong over the density range $1 \leq r_s \leq 3$ considered in this paper. Note that while Γ decreases as r_s increases, the corresponding electron Coulomb coupling constant $\gamma = e^2/(a \epsilon_F) = 0.342 r_s$ increases.

In the ultrahigh density regime $r_s \lesssim 1$, the electron kinetic energy dominates and the proton and electron components
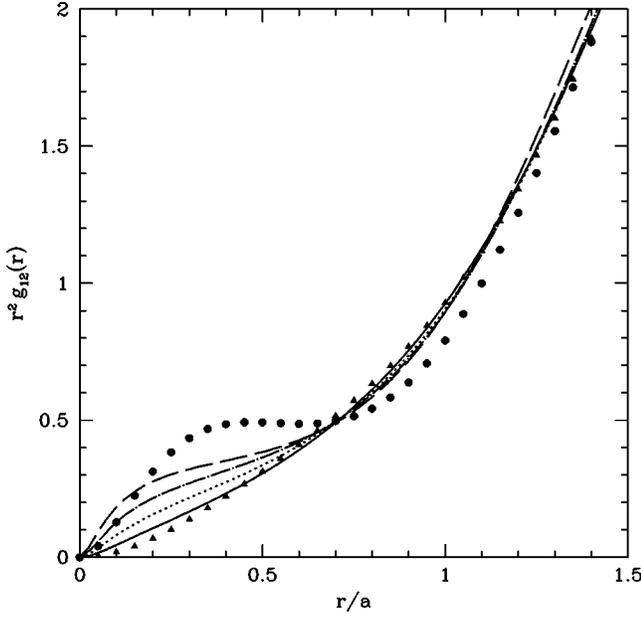
FIG. 1. Radial electron density around a proton, $r^2 g_{12}(r)$ vs r/a for $r_s = 1$ (full curve), 1.5 (dots), 2 (dashed-dotted curve), and 2.5 (dashed curve). The triangles are the linear response results at $r_s = 1$; the circles correspond to $r^2 g_{12}(r)$ in the atomic phase.

decouple in the first approximation (''two-fluid'' model); the weak electron-proton coupling may be treated by linear response theory [9], suitably adapted to the spin-polarized case. Within linear response, the free energy per atom (ion-electron pair) splits into three terms: the ground-state energy of the uniform, spin-polarized electron gas (''jellium''), ϵ_e, the free energy of protons in a uniform neutralizing background (the so-called ''one-component plasma'' or OCP), f_{OCP}, and the first order correction due to the linear screening of the Coulomb interactions by the electron gas Δf:

$$f = \frac{F(\Gamma, r_s)}{N} = \epsilon_e + f_{OCP} + \Delta f, \quad (1)$$

where $\epsilon_e(r_s)$ is taken to be the sum of kinetic $(1.754/r_s^2)$, exchange $(-0.5772/r_s)$, and correlation [10] contributions; f_{OCP} is given by an accurate fit to Monte Carlo simulations of the OCP [9,11]; Δf follows from first-order thermodynamic perturbation theory [9]:

$$\Delta f = \frac{1}{2(2\pi)^3} \int S_{OCP}(k) \hat{w}(k) d\mathbf{k}, \quad (2)$$

where $S_{OCP}(k)$ is the static structure factor of the OCP (which plays the role of reference system). According to linear response theory, $\hat{w}(k)$ is the difference between screened and bare ion-ion pair potentials:

$$\hat{w}(k) = \frac{4\pi e^2}{k^2} \left[\frac{1}{\epsilon(k)} - 1 \right], \quad (3)$$

where $\epsilon(k)$ is the dielectric function of the electron gas which we calculated within the random-phase approximation (RPA) from the Lindhard susceptibility of a gas of spin-polarized, noninteracting electrons, supplemented by a local exchange and correlation correction [10]. All necessary in-

gredients for the calculation of Δf may be found in [9], and the resulting free energy curve is shown in Fig. 1. Although linear response cannot a priori be expected to be quantitatively accurate for $r_s > 1$, it provides a rough estimate of the plasma to atomic phase transition, from the intersection of the free energy curves, which is seen to occur at $r_s \approx 1.9$. The corresponding transition pressure would be 2.3 Mbar.

However, as r_s increases, the ion-electron coupling becomes stronger and the nonlinear response of the electron component to the ''external'' potential field provided by the protons is expected to lower the free energy of the plasma phase. To explore the nonlinear regime we have adapted the HNC-DFT (where DFT stands for density-functional theory) formulation of our earlier work on (unpolarized) metallic H [12] to the spin-polarized case. Within this formulation, proton-proton and proton-electron correlations are treated at the HNC level, which is expected to be a good approximation for the long-range Coulomb interactions, while the energy of the inhomogeneous electron gas follows from the density functional ($E = N\epsilon_e$):

$$E[\rho(\mathbf{r})] = E_K[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_X[\rho(\mathbf{r})] + E_C[\rho(\mathbf{r})], \quad (4)$$

where $\rho(\mathbf{r})$ denotes the local electron density, and E_K, E_H, E_X, and E_C are the kinetic, Hartree, exchange, and correlation contributions. For E_K we adopted the Thomas-Fermi approximation, corrected by a square gradient term:

$$E_K[\rho(\mathbf{r})] = C_K \int [\rho(\mathbf{r})]^{5/3} d\mathbf{r} + \frac{\lambda}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}, \quad (5)$$

where $C_K = 3(6\pi^2)^{2/3}/10$ a.u., while the choice of $1/9 < \lambda < 1$ will be specified below. The mean field Hartree term is of the usual form:

$$E_H[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (6)$$

where $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - n$, while

$$E_X[\rho(\mathbf{r})] = C_X \int [\rho(\mathbf{r})]^{4/3} d\mathbf{r}, \quad (7)$$

with $C_X = -3(6/\pi)^{1/3}/4$ a.u. The correlation contribution $E_C[\rho(\mathbf{r})]$ [within the local-density approximation (LDA)] can be found in [10]. This functional yields an explicit form for the electron-electron direct correlation function $c_{22}(r)$ (henceforth the indices 1 and 2 will refer to protons and electrons respectively) [12]. The remaining direct and total correlation functions $c_{11}(r)$, $c_{12}(r)$, $h_{11}(r)$, and $h_{12}(r)$ are calculated by a numerical resolution of the HNC closure equations and the quantum version of the Ornstein-Zernike (OZ) relations [13], which form a closed set of coupled nonlinear integral equations for the four functions.

Solutions were obtained by a standard iterative procedure along the isotherm $T = 10^4$ K and for density parameters in the range $0.5 \leq r_s \leq 2.5$, corresponding to more than one-hundred-fold compression of the lowest density state ($r_s = 2.5$), which would correspond to 0.17 gr/cm^3. The temperature is roughly equal to that expected inside Saturn, and comparable to temperatures reached in shock compression
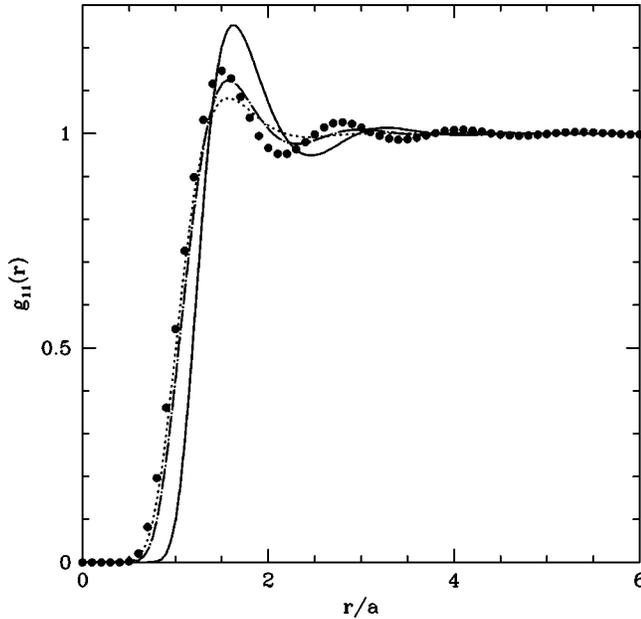
FIG. 2. Proton-proton pair distribution function $g_{11}(r)$ vs r/a for $r_s = 1$ (full curve), 2 (dashed-dotted curve), and 2.5 (circles). The dotted curve is the atom-atom function $g(r)$ at $r_s = 2.5$.

FIG. 3. The proton-proton structure factor $S_{11}(k)$ vs ka for $r_s = 1$ (full curve), 1.5 (dashed-dotted curve), 2 (dots), and 2.5 (circles).

experiments at the NOVA laser facility at Livermore [5]. The iterative solutions were first obtained at the highest densities ($r_s = 0.5$ and 1), where linear response theory provides reasonably accurate initial input. The prefactor λ in the square gradient correction to the electron kinetic energy functional (5) was adjusted to provide the best match between the HNC-DFT result for the local radial density of electrons around a proton, $r^2 g_{12}(r) = r^2 [1 + h_{12}(r)]$, and its linear response prediction, at the highest densities ($r_s = 0.5$ and 1), where linear response should be most accurate; $g_{12}(r)$ turns out to be rather sensitive to λ, and the best agreement is achieved for $\lambda = 0.18$, which is close to the value 1/5 frequently advocated in electronic structure calculations for atoms [10].

Results for the local radial density $r^2 g_{12}(r)$ are shown in Fig. 2 for several values of r_s. As expected, electrons pile up increasingly at small r as r_s increases, and a shoulder is seen to develop around $r/a \approx 0.4$. For comparison, the linear response prediction is shown at $r_s = 1$, while at the lowest density ($r_s = 2.5$), an estimate of $g_{12}(r)$ in the atomic phase is obtained by adding to the electron density in a H atom [namely $r^2 \rho(r) = r^2 \exp(-2r)/\pi$ a.u.], the convolution of the latter with the atom-atom pair distribution function $g(r)$. HNC-DFT results for the proton-proton pair distribution function are shown in Fig. 3 for three densities. As expected, proton-proton correlations are seen at first to weaken as the density decreases, due to enhanced electron screening. However, at the lowest density ($r_s = 2.5$), weakly damped oscillations build up at long distances, which may be indicative of an incipient instability of the proton-electron plasma. The atom-atom $g(r)$ at the same density agrees reasonably well with $g_{11}(r)$ up to the first peak, but it does not exhibit the long-range correlations in the latter. The proton-proton structure factors $S_{11}(k)$ are plotted in Fig. 4 for several values of r_s. A considerable qualitative change is again seen to occur at the lowest density ($r_s = 2.5$), where the main peak is
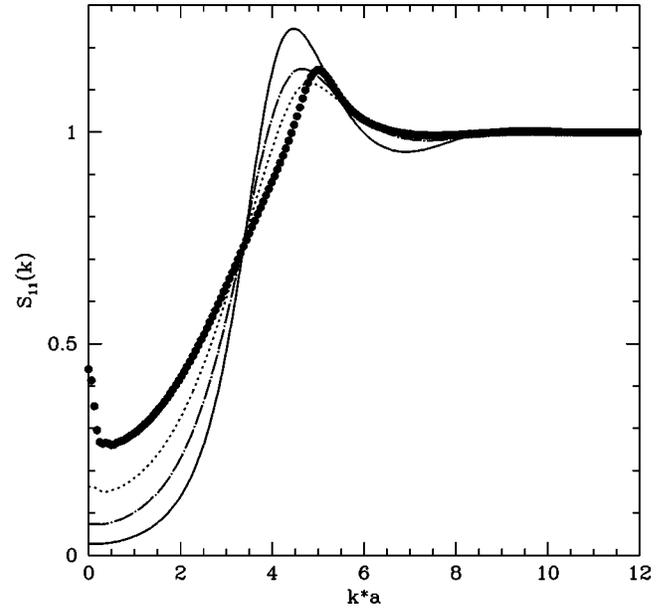
shifted to larger k, while a significant peak builds up at $k = 0$. Such enhanced ''small angle scattering'' is reminiscent of the behavior observed in simple fluids near a spinodal (subcritical) instability. In fact, we were unable to obtain convergence of the HNC-DFT integral equations for $r_s > 2.5$, which hints at an instability of the electron-proton plasma at lower densities. This strongly suggests a transition to the insulating atomic phase, but the simple density func-
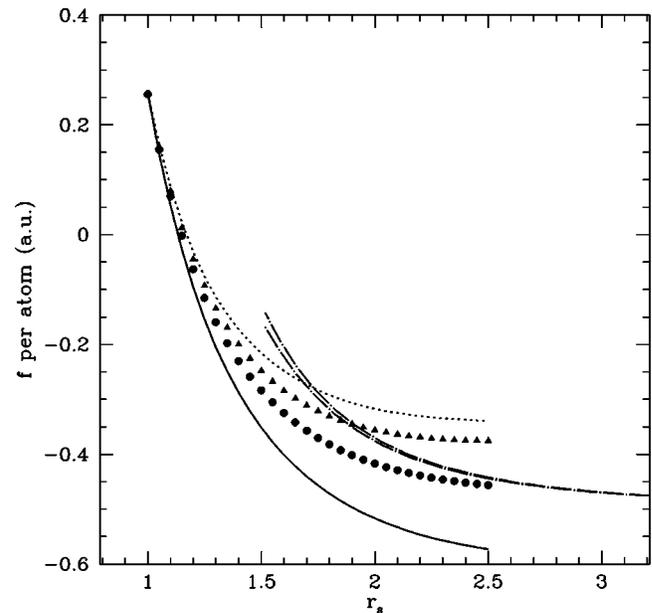
FIG. 4. Free energy per proton-electron pair (or atom) minus the ideal proton contribution vs the density parameter r_s. Full curve, ''virial'' free energy of the plasma phase; dotted curve, ''compressibility'' free energy for the plasma phase; circles, average of the latter two estimates; triangles, linear response result; dashed-dotted curves, ''virial'' (upper) and ''compressibility'' (lower) free energy for the atomic phase.

tional used in this work cannot properly describe the recombination of protons and electrons into bound (atomic) states [14].

In order to confirm this scenario, the free energy of the plasma phase should be compared to that of the atomic phase. This is easily achieved within the high density linear response regime, as shown earlier. However the calculation of the free energy in the nonlinear regime appropriate for lower densities ($r_s > 1$) is less straightforward [12]. In fact, the present HNC-DFT formulation provides only one direct link with thermodynamics, namely via the compressibility relation [8]:

$$\lim_{k \to 0} S_{11}(k) = \lim_{k \to 0} S_{12}(k) = n k_B T \chi_T, \qquad (8)$$

where χ_T denotes the isothermal compressibility of the plasma. From the calculated values of χ_T, the free energy of the plasma follows by thermodynamic integration, starting from a reference state (e.g., $r_s = 1$) for which the linear response estimate is expected to be accurate. The resulting ''compressibility'' free energy curve is plotted in Fig. 4. Somewhat unexpectedly, it lies above the linear response prediction. An alternative route to the free energy is via the virial relation for the pressure; only an approximate virial expression is known within the present HNC-DFT formulation [12], and the resulting ''virial'' free energy curve is also shown in Fig. 4. It falls well below the ''compressibility'' free energy curve, thus illustrating the well known thermodynamic inconsistency of the HNC closure for Coulombic fluids [15]. Any reasonable extrapolation of the two free energy curves would miss the low density limit -0.5 a.u. by as much as 20%. We suggest instead an estimate of the free energy of the plasma phase by taking the average of the ''compressibility'' and ''virial'' values, despite the lack of fundamental *a priori* justification for doing this. A short extrapolation of the resulting curve is likely to intersect or smoothly join on to the free energy of the atomic phase just beyond $r_s = 2.5$. An intersection would correspond to a first-order phase transition, reminiscent of the ''plasma phase transition'' of Saumon and Chabrier [6]. However, due to the uncertainty on the thermodynamics of the plasma phase, a continuous transition cannot be ruled out. The transition pressure P would be of the order of 0.5 Mbar, well below the current experimental and theoretical estimates for the transition of fluid molecular hydrogen to a conducting state [4,6].

In summary, the structure and thermodynamic results derived from an HNC-DFT theory of the spin-polarized proton-electron plasma strongly suggest that this plasma will recombine into an insulating atomic phase at $r_s \approx 2.5$, for a temperature $T = 10^4$ K. We are presently exploring the behavior of the system at lower temperatures.

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

[2] N. H. Chen, E. Sterer, and I. F. Silvera, Phys. Rev. Lett. **76**, 1663 (1996); R. J. Hemley, H. K. Mao, A. F. Goncharov, M. Hanfland, and V. Struzhkin, *ibid.* **76**, 1667 (1996).

[3] B. Edwards and N. W. Ashcroft, Nature (London) **388**, 652 (1997).

[4] S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996); W. J. Nellis, A. A. Louis, and N. W. Ashcroft, Philos. Trans. R. Soc. London, Ser. A **356**, 119 (1998).

[5] G. W. Collins *et al.*, Science **281**, 1178 (1998).

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

[7] See, e.g., C. W. Eaker and C. A. Parr, J. Chem. Phys. **65**, 5155 (1976).

[8] See, e.g., J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, London, 1986).

[9] S. Galam and J. P. Hansen, Phys. Rev. A **14**, 816 (1976).

[10] See, e.g., R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[11] W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. A **21**, 2087 (1980).

[12] H. Xu and J. P. Hansen, Phys. Rev. E **57**, 211 (1998).

[13] J. Chihara, J. Phys.: Condens. Matter **3**, 8715 (1991).

[14] F. Perrot, J. Phys.: Condens. Matter **6**, 431 (1994).

[15] See, e.g., J. P. Hansen, G. M. Torrie, and P. Vieillefosse, Phys. Rev. A **16**, 2153 (1977).