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Density functional theory applied to metallic hydrogen: pair correlations and phase transitions

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Abstract

A density functional theory (DFT) for a two-component system of classical ions and degenerate electrons is presented. The theory is based on an ‘*orbital-free*’ free energy of the ion–electron plasma, which includes a square-gradient correction to the Thomas–Fermi kinetic energy of the degenerate electrons. Pair correlations in the metallic phase of hydrogen are calculated and compared to ‘*ab initio*’ DFT-MD simulation data. The freezing transition of a pressure-ionized hydrogen plasma and the plasma–insulator transition of spin-polarized fluid hydrogen are considered.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The present paper is a short review of a series of articles devoted to a simple two-component density functional theory (DFT) of hydrogen plasma [1–4]. The study of the structure and the thermodynamics of systems composed of ions and electrons such as metallic liquids or plasma is a challenging task, mainly because of the many-body problem involving the electrons (see e.g. [5]). For many physical situations (metallic liquids, or dense plasmas), the ions can be considered as a classical component. Adopting this hypothesis, the simplest description of a ion–electron system is the one-component plasma (OCP) model [6], which treats the electrons as forming a homogeneous background neutralizing the total charges. The OCP serves as a reference system for more elaborate studies of liquid metals and dense plasmas. The simplest of these, that using the linear response theory (LRT) [7], gives reasonable results in the regime of very high density, where the electronic density responds linearly to external perturbations (i.e. the ionic configurations), with the response function given by that of the homogeneous electron gas. Within this framework, the ion–electron system is seen as an effective one-component system, where the effective ion–ion interaction is computed by taking into account the screening of the bare ion–ion potential provided by the linearly responding conduction electrons. Steps towards two-component treatments of ion–electron system began when some authors [8–10] applied the DFT to those systems. In the DFT formalism, one can formally

treat both components on an equal footing, with the inhomogeneous electron gas obeying the Hohenberg–Kohn–Mermin theorem [11, 12]. But, while Mermin’s theorem states that the energy (or free energy) of the system is an unique functional of the inhomogeneous local densities, its actual form is unknown for the electron gases. In [8] and [9], the Kohn–Sham representation has been used. This implies heavy numerical computations [13], involved in the resolution of the Kohn–Sham orbitals. On the other hand, in [10], the kinetic energy functional of an inhomogeneous electron gas was taken to be the Thomas–Fermi functional, which stems from a local density approximation (LDA) of the kinetic energy [16]. This of course was too crude an approximation. Recently, we have proposed a density functional formulation [2] in which a square-gradient correction was added to the Thomas–Fermi kinetic energy of the degenerate electrons. On choosing judiciously the prefactor of the square-gradient correction, our theory gave the ion–ion and ion–electron pair correlations in hydrogen plasma in good agreement with the results of *ab initio* molecular dynamics simulations [14].

Besides the structure, we are also interested in the thermodynamics of the ion–electron system. The computation of the free energy difference between a system in which both the ion and the electron components are inhomogeneous and a homogeneous reference system can be done within our DFT formalism, as can be seen in our first application of the present DFT [1], i.e. the freezing transition of the pressure-ionized hydrogen plasma. When the system is disordered on average (the fluid phase), things are complicated by the quantum nature of the electrons. The only exact route at our disposal is a double-density integration of the isothermal compressibility, linked to the ion–ion or ion–electron structure factors at very large wavelength. However, this route is subject to numerical imprecision [2, 3]. In [2], we suggested using an ‘ion-sphere’-type approximation to obtain the average kinetic and potential energies of the system in order to use the virial theorem to compute the equation of state and the free energy of the metallic fluid. Unfortunately, when applied to spin-polarized fluid hydrogen plasma [3], the virial and compressibility routes lead to quite large thermodynamic inconsistency. In a more recent study [4], we applied the coupling-constant integration procedure to the ion–electron fluid in order to evaluate its free energy. This more accurate calculation led to quite reasonable results (cf [4]).

The paper is organized as follows. In section 2 we recall the formalism of the present DFT and present some key equations of the theory. Section 3 shows results for pair correlations in metallic hydrogen. Section 4 revisits the freezing transition of dense hydrogen plasma. Section 5 is devoted to the case of the plasma–insulator (PI) transition of the spin-polarized fluid hydrogen. And section 6 gives some conclusions.

2. An ‘orbital-free’ density functional theory of ion–electron systems

We consider a system of dense plasma. The formalism can be readily extended to metallic liquids. Our system is viewed as a two-component fluid, i.e. ions, carrying a charge Ze and electrons, carrying a charge $-e$, with Coulomb interaction between the particles. The present DFT formalism has been described in detail in our previous work (see [1, 2]). We sketch here only the main lines of it. Under the effect of external potentials $\{\phi_\alpha(\mathbf{r}), \alpha = i, e\}$, the local densities of the two components $\{\rho_\alpha(\mathbf{r})\}$ become non-uniform. And the Hohenberg–Kohn–Mermin theorem [11, 12] leads to the Euler–Lagrange equations:

$$\frac{\delta F}{\delta \rho_\alpha(\mathbf{r})} + \phi_\alpha(\mathbf{r}) = \mu_\alpha; \quad \alpha = i, e \quad (1)$$

where F is the free energy functional, which, as usual, can be split into the ideal-gas part (F_{id}) and excess part (F_{ex}), with $F_{id} = F_{id}^{(i)}[\rho_i] + F_{id}^{(e)}[\rho_e]$ and $F_{ex} = F_{ex}^{(ii)} + F_{ex}^{(ie)} + F_{ex}^{(ee)}$.

We notice that for $T \ll T_F$, we have $F_{id}^{(e)} = E_K^{(e)}[\rho_e]$ (kinetic energy functional), and $F_{ex}^{(ee)} = E_H(e)[\rho_e] + E_{XC}^{(e)}[\rho_e]$ (Hartree and exchange correlation functionals). The second functional derivatives of F are the inverse elements of the susceptibility matrix:

$$\frac{\delta^2 \beta F}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\gamma(\mathbf{r}')} = \chi_{\alpha\gamma}^{-1}(\mathbf{r}, \mathbf{r}') \quad (2)$$

which in turn splits into an ideal-gas part and an excess part:

$$\chi_{\alpha\gamma}^{-1}(\mathbf{r}, \mathbf{r}') = \chi_\alpha^{(0)-1}(|\mathbf{r} - \mathbf{r}'|) \delta_{\alpha\gamma} - k_B T c_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|). \quad (3)$$

The first term is diagonal. The second term, due to the excess free energy, defines the direct correlation functions (DCFs). The fluctuation-dissipation theorem for the ion–electron mixture states (see, e.g., [2])

$$\chi_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = \rho_\alpha(\mathbf{r}) \rho_\gamma(\mathbf{r}') h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') + \rho_\alpha \delta_{\alpha\gamma} \delta(\mathbf{r}, \mathbf{r}') \quad (\alpha\gamma = ii \text{ and } ie) \quad (4)$$

where $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = g_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') - 1$ is the two-point (or pair) correlation function, while $g_{\alpha\gamma}$ denotes the pair distribution function (pdf) for particles of species α and γ ($\alpha\gamma = ii$ and ie).

These relations, combined with equation (3) and the fact that for the classical component (the ions) we have $\chi_i^{(0)-1}(\mathbf{r}, \mathbf{r}') = \frac{1}{\rho_i(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}')$, lead to three Ornstein–Zernike relations linking the χ -matrix to the c -matrix [2, 9, 13]:

$$h_{ii}(\mathbf{r}, \mathbf{r}') = c_{ii}(\mathbf{r}, \mathbf{r}') + h_{ii} * (\rho_i c_{ii})(\mathbf{r}, \mathbf{r}') + h_{ie} * (\rho_e c_{ie})(\mathbf{r}, \mathbf{r}') \quad (5a)$$

$$h_{ie} * (\rho_e \chi_e^{(0)-1})(\mathbf{r}, \mathbf{r}') = c_{ie}(\mathbf{r}, \mathbf{r}') + h_{ii} * (\rho_i c_{ie})(\mathbf{r}, \mathbf{r}') + h_{ie} * (\rho_e c_{ee})(\mathbf{r}, \mathbf{r}') \quad (5b)$$

$$(\chi_{ee} - \chi_e^{(0)}) * (\chi_e^{(0)-1})(\mathbf{r}, \mathbf{r}') = (\rho_i h_{ie}) * (\rho_e c_{ie})(\mathbf{r}, \mathbf{r}') + \chi_{ee} * (c_{ee})(\mathbf{r}, \mathbf{r}') \quad (5c)$$

where $*$ denotes a convolution product. For the quantum component (the electrons), $\chi_e^{(0)}$ for homogeneous non-interacting fermions is the well known Lindhard function [15], which, in atomic units (au), reads

$$\hat{\chi}_e^{(0)}(k) = -\frac{k_F}{\pi^2} \left[\frac{1}{2} + \frac{1-q^2}{4q} \ln \left| \frac{1+q}{1-q} \right| \right] \quad (6)$$

where $q = k/2k_F$, and $k_F = (9\pi/4)^{1/3}/r_s$ is the Fermi momentum. Within the framework of our ‘orbital-free’ density functional $F[\rho_i, \rho_e]$, $\chi_e^{(0)}$ will depend on the approximation used for kinetic energy functional of the inhomogeneous electron gas. In the Thomas–Fermi approximation, $E_K = C_K \int [\rho_e(\mathbf{r})]^{5/3} d\mathbf{r}$ ($C_K = 3(3\pi^2)^{2/3}/10$), we have

$$\hat{\chi}_e^{(0-TF)}(k) = -\frac{k_F}{\pi^2} \quad (7)$$

whereas the Thomas–Fermi plus square-gradient correction (‘Weizsäcker’) approximation (TF-W(λ)), with

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

gives

$$\hat{\chi}_e^{(0-TFW)}(k) = -\frac{k_F}{\pi^2} \left(\frac{1}{1+3\lambda q^2} \right) \quad (9)$$

where $1/9 < \lambda < 1$ (cf [16]). Another more elaborate functional (Perrot’s functional) [17] gives $\chi_e^{(0)}$ under the original Lindhard form.

In most applications, we need to know χ (or, equivalently, g_{ii} , g_{ie} and χ_{ee}), and c for a homogeneous fluid. For this, we have three Ornstein–Zernike equations at our disposal. In Fourier space, we write (cf equations (5a)–(5c) and [2])

$$\hat{h}_{ii}(k) = \hat{c}_{ii}(k) + n_i \hat{h}_{ii}(k) \hat{c}_{ii}(k) + n_e \hat{h}_{ie}(k) \hat{c}_{ie}(k) \quad (10a)$$

$$\frac{n_e \hat{h}_{ie}(k)}{\hat{\chi}_e^{(0)}(k)} = \hat{c}_{ie}(k) + n_i \hat{h}_{ii}(k) \hat{c}_{ie}(k) + n_e \hat{h}_{ie}(k) \hat{c}_{ee}(k) \quad (10b)$$

$$\frac{\hat{\chi}_{ee}(k) - \hat{\chi}_e^{(0)}(k)}{\hat{\chi}_e^{(0)}(k)} = \hat{c}_{ee}(k) \hat{\chi}_{ee}(k) + n_i n_e \hat{h}_{ie}(k) \hat{c}_{ie}(k) \quad (10c)$$

where n_α is the average density of species α . The procedure of Percus [18], fixing one ion at the origin, providing the external potential ϕ_α , leads to two Euler–Lagrange equations, for g_{ii} and g_{ie} . In the simplest case, the first one is a hypernetted chain (HNC) integral equation, the second one an integro-differential equation (cf [2]). To close the system, another equation is needed. This is given by assuming a form for E_{ex}^{ee} , giving c_{ee} directly. For example, within the LDA for the exchange energy and neglecting the correlation energy of the electrons, we have

$$k_B T c_{ee}(\mathbf{r} - \mathbf{r}') = -\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{4}{9} C_X \frac{\delta(\mathbf{r} - \mathbf{r}')}{[\rho_e(\mathbf{r})]^{2/3}} \quad (11)$$

where $C_X = 3(3/\pi)^{1/3}/4$. The well known random phase approximation corresponds to neglecting the exchange term in (11).

Once λ is fixed (see the next section), the equations described above define entirely the pair and DCFs needed to characterize the structure of our two-component ion–electron system.

3. Pair correlations in metallic hydrogen

We consider hydrogen under high pressure and temperature, i.e. $0 < r_s < 1.5$ and $T > 3000$ K. We recall that r_s is defined by $n_e = 3/(4\pi r_s^3 a_B^3)$ with a_B the Bohr radius. Under these conditions, the system forms a plasma phase, and our formalism in section 2 applies. Before solving for the pair and direct correlations, we fixed λ as explained in [2]. For a dense plasma at $r_s = 0.5$, we make the depth of the first minimum of $g_{pe}(r; \lambda)$ equal to that obtained by standard linear response, g_{pe}^{LRT} , taking the Lindhard function for $\chi_e^{(0)}$ and the OCP as the reference system (subscript ‘ p ’ stands for proton). Figure 1 shows the comparison of these g_{pe} against DFT-MD simulation results of [11]. We can see from figure 1 that the optimal choice $\lambda = 0.41$ gives very good agreement with both MD and LRT results for $r > 0.5a_B$, but it violates the cusp condition at the origin. The choice of $\lambda = 1$ is globally not at all satisfactory, although it fulfils the cusp condition. We point out that the behaviour of the MD results near the origin is an artefact of the finite cut-off in the plane-wave expansion of the energy of the inhomogeneous electron gas. We also found that optimal λ is quite independent of T , showing the robustness of the method. Figure 2 shows the influence of λ on $g_{pp}(r)$, for a moderate density, $r_s = 1$; we see that again $\lambda = 0.41$ gives the proton–proton distribution in good agreement with MD results, whereas taking $\lambda = 1$ leads to overestimated structure in g_{pp} . This can be understood from figure 1, as a consequence of a too weak electron density polarization around the protons. In figure 3, we compare our $g_{pp}(r)$ with the QHNC results [9] and the simpler DFT of Ofer *et al* [10]. While the agreement with Ofer *et al* is good, the QHNC finding is slightly shifted to larger r , perhaps because χ_e was used in the latter. We can also examine the proton–electron DCF c_{pe} . In a mean-field approximation, we assume $c_{pe} = -\beta v_{pe}$. We can see from figure 4 that c_{pe} obtained from our DFT-HNC theory is only mean-field-like above a certain distance $r_c > a_B$, which depends on the density, with r_c larger

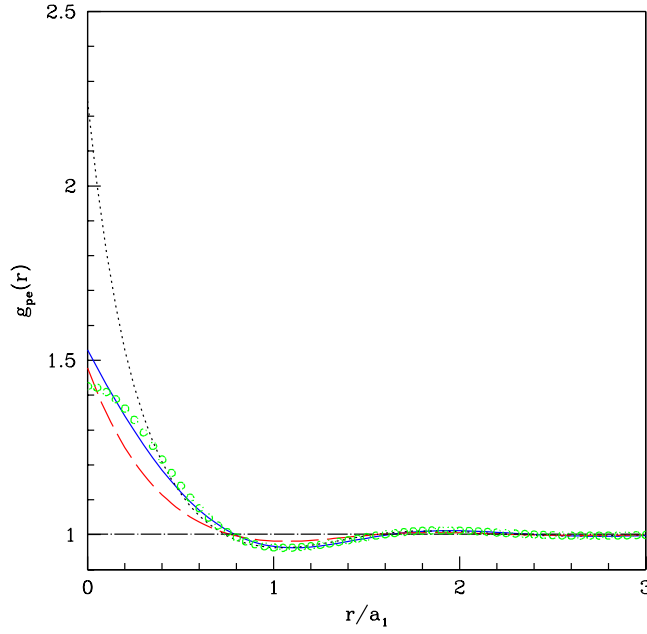


Figure 1. The proton–electron pair distribution function $g_{pe}(r)$ of hydrogen plasma at $r_s = 0.5$ and $T = 10\,000$ K. Displayed are results from the present HNC-TFW theory with $\lambda = 0.41$ (dotted curve), $\lambda = 1$ (dashed curve); compared to the linear response prediction (solid curve) and the DFT *ab initio* simulation results [14] (circles). a_1 is the ion-sphere radius defined by $n_p(4\pi a_1^3/3) = 1$.

when n_e decreases (r_s increasing), indicating that a mean-field approximation is more suitable at high densities ($r_s < 0.5$). In figure 5, c_{pe} in the Fourier space is plotted. Again, we see that $\hat{c}_{pe}(k)$ is Coulomb-like for small k -values. But its asymptotic behaviour, although tending to zero, deviates from the mean-field curve.

4. The freezing transition

In this section we show an earlier application of the present DFT, which is the freezing transition of a dense hydrogen plasma. In order to simplify the theoretical framework, the freezing theory of Ramakrishnan and Yussouff [19] is adopted. For very dense systems ($r_s < 0.5$), the crystal lattice can be assumed to be the bcc lattice (as for the OCP). We split the free energy difference between the solid and fluid phases into ideal-gas and excess parts, with

$$\frac{\beta \Delta F_{id}}{N_p} = \int d\mathbf{r} \rho_p(\mathbf{r}) \ln[\rho_p(\mathbf{r})/n_p] - \frac{1}{2} \sum'_{\{\mathbf{G}\}} \{\chi_e^0\}^{-1} \xi_e^2(\mathbf{G}) \quad (12)$$

and

$$\frac{\beta \Delta F_{ex}}{N_p} = -\frac{1}{2} \sum_{\alpha=p,e} \sum_{\beta=p,e} \sum'_{\{\mathbf{G}\}} c_{\alpha\beta} \xi_\alpha(\mathbf{G}) \xi_\beta(\mathbf{G}) \quad (13)$$

where $\{\mathbf{G}\}$ are the reciprocal-lattice vectors; $\sum'_{\{\mathbf{G}\}}$ indicates that we exclude the $\mathbf{G} = 0$ vector; $\xi_\alpha(\mathbf{G})$ are the order parameters for species α in the solid phase. Here, the electronic density is treated at linear response level. And we leave out—as is done for OCP [20]—the contribution

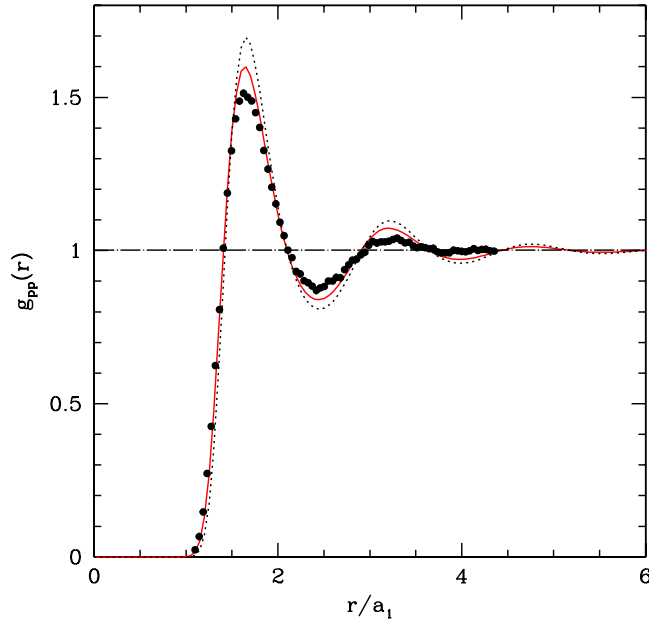


Figure 2. The proton–proton pair distribution function $g_{pp}(r)$ of hydrogen plasma at $r_s = 1$ and $T = 3000$ K. Displayed are results from the present HNC-TFW theory with $\lambda = 0.41$ (solid curve), $\lambda = 1$ (dotted curve); compared to the DFT *ab initio* simulation results [14] (dots).

from the second star in the reciprocal-lattice space. For simplicity, we express $\rho_p(r)$ as a sum of Gaussians centred at the lattice sites; i.e.,

$$\xi_G^{(p)} = e^{-G^2/4\zeta} \quad (14)$$

is adopted. When the variational principle is applied to the electrons, one obtains

$$\xi_e(G) = -\xi_p(G)\hat{c}_{pe}(G)/[\{\chi_e^{(0)}\}^{-1}(G) + \hat{c}_{ee}(G)] \quad (15)$$

linking the order parameters of the electrons linearly to those of the protons. And minimizing ΔF with respect to ζ will fix the latter as a function of the proton coupling parameter Γ ($\Gamma \equiv Z^2 e^2 / (k_B T) a_1$, with a_1 the ion-sphere radius), and the density parameter r_s . As c_{ee} is given by the LDA form of equation (11), c_{pp} and c_{pe} must be supplied. In principle, they can be obtained as in section 3, but the procedure, coupled with the freezing problem, appears to be numerically difficult, since large proton coupling constants Γ must be involved in the present study. In [1], a simple form for c_{pe} was adopted:

$$c_{pe}(r) = -\beta v_{pe}(r) \operatorname{erf}(r/r_0) \quad (16)$$

with an *ad hoc* choice of $r_0 > a_B$; whereas c_{pp} came from numerical resolution of the integral equation

$$g_{pp}(r) = \exp(-\beta v_{pp}(r) + g_{pp}(r) - 1 - c_{pp}(r) + B(r)) \quad (17)$$

with the bridge function $B(r)$ given by the Rogers and Young closure for the OCP [21], so that the OCP freezing can be correctly recovered, and \hat{h}_{pp} , \hat{c}_{pp} and \hat{h}_{pe} are linked by the first OZ relation (10a), in which $\hat{h}_{pe}(k)$ is given by the second OZ relation, as a function of $\chi_e^{(0)}$ and \hat{c}_{ee} . To make the theory self-contained, $\chi_e^{(0)}$ is taken to be the Lindhard response function. For given $r_s < 0.5$, we determined the melting temperature by searching for Γ_m such that $\Delta F(\Gamma_m) = 0$. The main results of this study are in figures 1, 2 of [1]. The conclusions are:

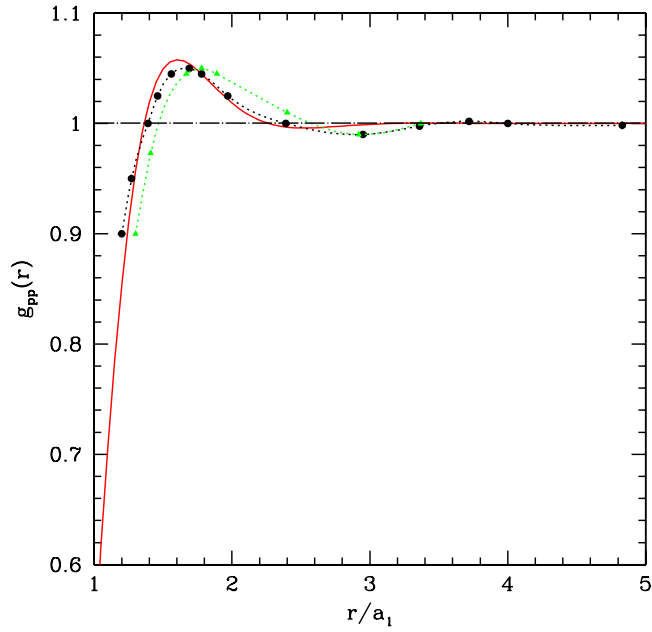


Figure 3. The proton–proton pair distribution function $g_{pp}(r)$ of hydrogen plasma at $r_s = 1$ and the proton coupling constant $\Gamma = 10$ ($T = 3.16 \times 10^4$ K). Displayed are results from the present HNC-TFW theory with $\lambda = 0.41$ (solid curve), compared to the QHNC results of Chihara [9] (dotted curve marked by triangles) and the HNC-TF work by Ofer *et al* [10] (dotted curve marked by filled circles).

- (1) as r_s increases, Γ_m increases quite rapidly (i.e. the freezing temperature decreases strongly);
- (2) at freezing, the Lindmann parameter remains relatively constant.

These results, while qualitatively correct, could be improved quantitatively. One can consider, e.g., a more evolved freezing theory, along the lines indicated by [22], but this is onerous to implement. The formalism is not suited for freezing of hydrogen plasma with $r_s > 0.5$, since molecules are not built in and quantum effects on protons should be included when Γ_m increases further. The formalism, however, can be used for other systems, as in [23], where the freezing of Al is tentatively studied.

5. The plasma–insulator transition of a spin-polarized fluid

In the present section we are interested in the metallic–insulator transition of hydrogen induced by the pressure [3, 4]. For the solid phase, although such a transition had been predicted by Wigner some time ago [24], it has been very hard to get experimental evidence of it [25]. On the other hand, for the fluid phase, such evidence has been found recently [26]. As the experimental system is rather complex, with H_2 , H_2^+ , H, H^+ and electrons present, a full description is beyond the scope of the present DFT. Rather, we study the PI transition of a spin-polarized fluid hydrogen, in order to focus on the aspect of pressure-induced ionization, without tackling the aspect of pressure-induced molecular dissociation. The study is conducted by comparing the free energies of the two phases, described by two different Hamiltonians, as in [27], because our two-component fluid picture is suited for the plasma phase, but not for atomic recombination.

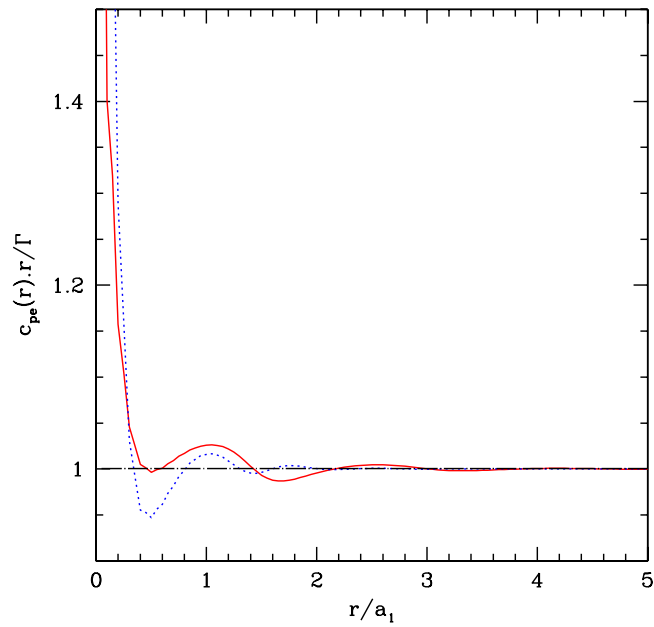


Figure 4. The proton–electron direct distribution function $c_{pe}(r)$ of hydrogen plasma obtained from the present HNC-TFW theory with $\lambda = 0.41$. Displayed is the function $c_{pe}(r)r/\Gamma$. The solid curve corresponds to the state point $r_s = 0.5$ and $T = 6320$ K, and the dotted curve to $r_s = 1$ and $T = 3000$ K. The mean-field asymptote (dash-dotted line) is also shown.

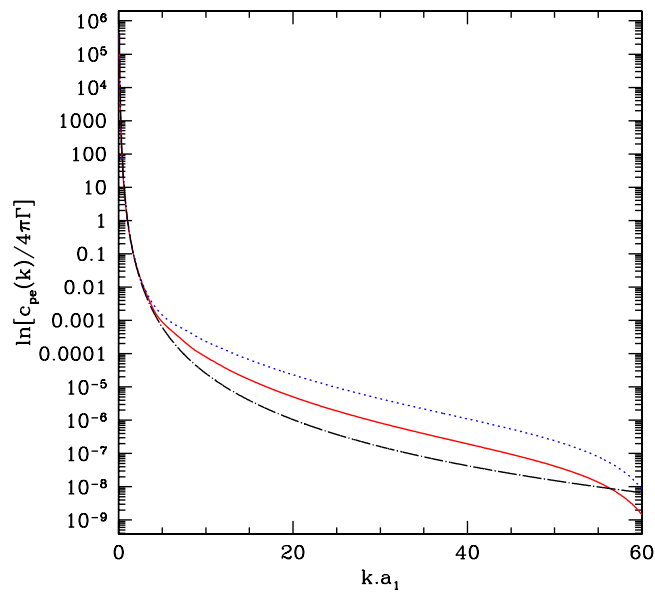


Figure 5. As figure 4, but in Fourier space. Displayed is the function $\ln[\hat{c}_{pe}(k)/4\pi\Gamma]$ versus ka_1 . The solid curve corresponds to the state point $r_s = 0.5$ and $T = 6320$ K, and the dotted curve to $r_s = 0.5$ and $T = 3000$ K. The mean-field approximation is also shown (dash-dotted curve). Notice the log scale on the y-axis.

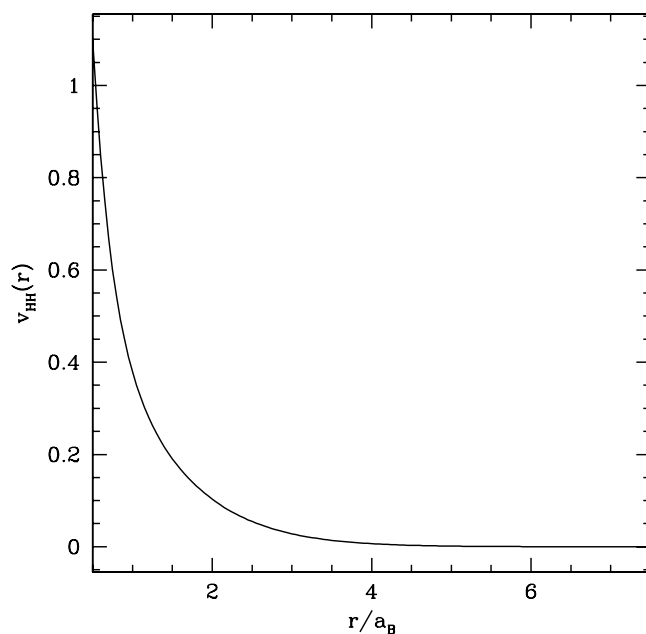


Figure 6. The triplet pair potential in the atomic $H\uparrow$ phase given by [28], in atomic units.

The low-pressure insulating phase is composed of $H\uparrow$ atoms in the fluid phase. The effective pair interaction is known [28]. We see from figure 6 that it is rather short ranged. A standard integral equation theory of liquids leads to structural and thermodynamic properties of the system [5]. For the sake of consistency with the plasma phase, we have adopted the HNC closure for the atomic fluid. This leads to an analytical formula for the free energy [29]. The high-pressure phase is the plasma phase, described by the ion–electron Hamiltonian. As we showed in [3], the effect of increasing r_s can be seen in the proton–proton and proton–electron pair distribution functions $g_{pp}(r)$ and $g_{pe}(r)$, and in the proton–proton structure factor $S_{pp}(k)$. In particular, for $T = 10\,000$ K and rather low density, $r_s = 2.5$, there is a sharp increase of $S_{pp}(k)$ for $k = 0$, hinting at a fluid near a spinodal instability. In order to confirm this, in [3] we calculated the free energy of the plasma phase by two routes: the compressibility route and an approximate virial route [2]. Unfortunately, an important thermodynamic inconsistency, typical of a HNC closure, was observed, in the region of interesting r_s (2–2.5). However, taking the average value of the two free energy curves, we were indeed able to estimate that the PI transition was located at $r_s \approx 2.5$ for $T = 10\,000$ K. Serious convergence difficulties prevented us from pushing calculations beyond $r_s = 2.5$. In a more recent piece of work [4], a third route for calculating the free energy has been proposed. It consists of the well known coupling-constant integration method [5]. The resulting free energy lies very close to the one given in [3], validating the procedure used in [3] (cf figure 9 of [4]). We believe the third route to be the most reliable way of computing the free energy of the present plasma phase, and it can of course be applied to other ion–electron systems.

6. Conclusions

From the above examples, we see that the present ‘orbital-free’ DFT/HNC theory provides a simple framework for the structure and thermodynamics of ion–electron plasmas. The

theory avoids the Kohn–Sham orbitals by the use of a Thomas–Fermi–Weizsäcker kinetic energy functional of the degenerate electron gas. For metallic hydrogen, pair correlations that we obtained compare quite well with available *ab initio* simulation results [14]. Two phase transitions have been investigated within the present DFT, i.e. the freezing of hydrogen plasma and the PI transition of spin-polarized fluid hydrogen. Although there is no direct comparison of our results with simulation ones, we showed clearly qualitatively correct tendencies.

There are some limitations of the theory: first, a criterion for finding λ as a function of r_s is lacking; second, as the effective ion–ion interaction [2] ϕ_{ii} becomes more short ranged, the HNC closure may not be the best suited one. A thermodynamic consistency criterion is needed. This is at the moment difficult to find, since an exact virial equation of state does not exist. Although the approximate one in [2] could be used, its practical implementation can be onerous. Despite these drawbacks, the present theory remains quite simple and gives reasonable results for hydrogen plasma. It can be applied to other ion–electron systems for which $T \ll T_F$, e.g. metallic liquids, or their mixtures, for which *ab initio* studies have been carried out but are costly [30], or systems of astrophysical interest, e.g. H–He mixtures, for which the demixing transition has been investigated by means of *ab initio* simulations [31].

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