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Equation of state of a hydrogen plasma by density functional molecular dynamics

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The orbital-free molecular dynamics model is used in a finite temperature extension of Kirshnits (Zh. Eksp. Teor. Fiz. **32**, 115 (1957) [Sov. Phys. JETP **5**, 64 (1957)]) to compute the equation of state of a hydrogen plasma. The pressures, corrected to account for the nontransferability of the pseudopotential, are in a good agreement with existing theories.

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Due to its abundance in astrophysical conditions and its key role as a fuel for fusion devices, hydrogen is of great theoretical and technological interest. Its properties have therefore been investigated by many experimental, theoretical, and numerical techniques, in a wide range of physical situations. In particular, the equation of state (eos) of hydrogen at high pressure and temperature has stimulated recent investigations.

Ichimaru, Iyetomi, and Tanaka (IIT) have devised a useful equation of state of hydrogen at high pressure and finite temperature. At low electron-ion coupling, a linear approximation was employed [1], while modifications were subsequently included to take nonlinear electron polarization into account [2]. Although this scheme relies on some approximation regarding the correlation functions, it embodies most limiting regimes, and is believed to be accurate in intermediate regions.

The advent of *ab initio* molecular dynamics techniques has allowed for the calculation of the dynamical evolution of the system by combining a classical molecular dynamics simulation for the ions with a full quantum resolution for the electrons. By doing this, the dissociation region [3] and the strong coupling regime [4] have been investigated. To overcome some difficulties of the genuine Car-Parrinello method with excited states, Alavi *et al.* [5] have proposed a new *ab initio* method suitable for metallic and electronically hot systems and more recently, Pierleoni *et al.* [6] have used an adaptation to fermions of the path integral Monte Carlo method (PIMC) to determine the equation of state of hydrogen at various densities and temperatures.

In view of those results, we found it useful to complement these efforts by another approach that is primarily based on the density functional molecular dynamics (DFMD) technique [7,8], and is subsequently extended to finite temperature and more accurate kinetic energy functionals [9]. This orbital-free method, a combination of classical molecular dynamics and density functional theory, gives the ionic trajectories together with the deformation of electronic density at low computer cost. It implicitly assumes the adiabatic approximation (but nonadiabatic effects are presumably small in the considered regime) and requires specification of the functional of the density.

The equation of state $P=f(T,\rho)$ at high density ($\rho \geqslant 10^{23}$ cm^{-3}) and high temperature ($T \geqslant 1$ eV), will cross several regions, each of them described by a particular physics. For a system of N ions in a volume V and at temperature T we characterize the interactions by the coupling parameter $\Gamma = e^2/a_i k_B T$ where $\frac{4}{3}\pi a_i^3 = V/N$ and the electronic density by $r_s = a_e/a_B$, a_B being the Bohr radius (note that for hydrogen, $a_e = a_i$). For $T > 13.6$ eV and $r_s < 2$, we expect a fully ionized hydrogen plasma. At high temperature the coupling parameter is very low and the electron degeneracy measured by $\theta = T/T_F = (2r_s/\Gamma)(4/9\pi)^{2/3}$ is also very low ($\theta \gg 1$, $\Gamma \ll 1$). This is the nearly classical region for which the eos can be accurately predicted by the Debye-Hückel theory. The opposite low temperature region is characterized by a high degree of electronic degeneracy and a strong coupling ($\theta \ll 1$, $\Gamma \gg 1$). In the high density limit ($r_s \ll 1$), the one component plasma is a good approximation and can be used to predict the eos. In the intermediate region, the electrons are partially degenerate ($\theta \simeq 1$, $\Gamma \simeq 1$) and the electronic polarizability must be described self-consistently.

In a finite temperature description, the free energy, which serves as an effective potential for the ions is given by

$$F[\rho,R_i] = U_{ee}[\rho] + U_{II}[R_i] + U_{eI}[\rho,R_i] + F_{\mathrm{xc}}[\rho] + F_e[\rho], \tag{1}$$

where U_{II}, U_{eI}, U_{ee} are the usual ion-ion, electron-ion, and electron-electron electrostatic contributions, F_e is the electronic kinetic free energy, and F_{xc} is the exchange-correlation term in the local density approximation. First, since we want to study the electron gas at arbitrary degeneracy, we need a finite temperature functional for the kinetic energy expressed as $F_e[\rho] = \int \mathscr{F}[\rho] dr$. A good compromise between accuracy and simplicity is given by the finite temperature Thomas-Fermi-Kirshnits gradient expansion (TFK) [10] as derived by Perrot [11]

$$\mathscr{F}[\rho] = \mathscr{F}_0[\rho] + h(\rho)|\nabla\rho|^2/\rho, \tag{2}$$

where $\mathscr{F}_0$ is the well-known Thomas-Fermi free energy at finite temperature and $h(\rho)$ is a function characterizing the polarizability of the electron gas. This function is evaluated by the identification of this polarizability with the finite temperature linear response of the electron gas at large wavelengths and interpolated by an analytic formula [11]. At zero temperature, the usual Kirshnits coefficient $h = \frac{1}{72}$ is recovered. This kinetic energy functional yields an electron response function $\chi_e(k)$ accurate up to terms in k^2 in recipro-

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cal space at $k\to 0$ (the usual von Weisäcker gradient correction would give the correct $k\to\infty$ behavior at zero temperature). The exchange-correlation energy can also be extended to finite temperature, and we will also use the interpolation given in [11].

The minimization of Eq. (1) with respect to the density and the dynamical evolution of the whole electron-ion system is done by a Car-Parrinello–like (CP) scheme in which the density is the sole dynamical variable. By taking the derivatives with respect to the density and ionic coordinates of the Lagrangian,

$$\mathscr{L}=\tfrac{1}{2}\mu\int\dot{\rho}^2(\mathbf{r})d\mathbf{r}+\tfrac{1}{2}\sum_{i=1}^{N}M_i\dot{\mathbf{R}}_i^2-F[\rho(\mathbf{r}),\mathbf{R}_i]-\mu\left(\int\rho(\mathbf{r})d\mathbf{r}-N\right), \tag{3}$$

we obtain the dynamical evolution of the whole system. This orbital-free scheme has two fortunate consequences. First, while in the usual CP scheme the orthonormality constraint is very time consuming, here there is just an overall neutrality constraint which can be very easily handled by setting the zero component of the Fourier transform of the density. Second, when simulating a conducting media such as metal or a plasma, it is not necessary to introduce some thermostat to the electrons to keep the electronic and ionic degrees of freedom decoupled. The density-density response function is used to modify the fictitious electronic masses μ for each Fourier component and to eliminate high frequency harmonics, as explained in [9]. This modification is essential to allow for a manageable time step, particularly when using a gradient expansion for the electronic kinetic energies.

The term U_{ei} describes the electron-ion interaction. In a hydrogen plasma where the external potential created by the proton is the bare Coulomb potential $4\pi/k^2$, the pressure P is given by the virial theorem in its usual form [12],

$$3PV=2K+U, \tag{4}$$

where U stands for all potential terms $U=U_{ee}+U_{ei}+U_{II}$ and K for all kinetic contributions (electrons and ions) given by the derivative of corresponding free energies with respect to the temperature. The Coulomb potential has been used for calculations of the pressure with static ions and we have checked that our results agree with previous calculations [13]. For static calculations, it is always possible to cope with the Coulomb divergence in the vicinity of nucleus by shifting away the grid points from static ions, whereas moving ions can come very close to the grid points giving rise to numerical inaccuracies. Therefore a pseudopotential (psp) has been introduced to regularize the short range interaction. We have used here the local $1s$ part of the Bachelet-Hamann-Schlüter pseudopotential [14] which is equivalent to a sum of Gaussian charges. The short range regularization of the Coulomb interaction modifies the virial theorem which now reads [15] as

$$3PV=2K+U_{ee}+U_{II}+3U_{ei}+\sum_{k}\rho_k S(-k)k\,\frac{\partial V_{\mathrm{ps}}(k)}{\partial k}, \tag{5}$$

where $V_{\mathrm{ps}}(k)$ is the Fourier transform of the pseudopotential and $S(k)$ is the usual static structure factor.

TABLE I. Pressure (in Mb) of a 54-ion system and $r_s=1$ computed in a dynamical simulation $P^{\mathrm{psp}}_{\mathrm{dyn}}$ for different values of the cutoff and corrected by the difference between the pressure of the same system (0 K) on a bcc lattice $P^{\mathrm{psp}}_{\mathrm{lat}}$ with the pressure obtained with a pure Coulomb potential ($P=31.27$ Mb).

r_c (a.u.)	$P^{\mathrm{psp}}_{\mathrm{dyn}}$ (Mb)	$P^{\mathrm{psp}}_{\mathrm{lat}}$ (Mb)	$P^{\mathrm{Coul}}_{\mathrm{lat}}$ (Mb)	$P^{\mathrm{corr}}_{\mathrm{dyn}}$ (Mb)
0.2	37.7	34.3	31.27	34.6
0.4	40.0	36.6	31.27	34.6
0.8	47.7	44.1	31.27	34.8

A smooth potential (with a large cutoff r_c) makes dynamical simulations easier but introduces a systematic bias in the pressure due to a transfer of electronic charge from the center to the boundary of the atoms. This is a drawback of the nontransferability of the pseudopotential, whose transferability is ensured only in the context of the Kohn-Sham equations. To show that this effect is independent of ionic motion, we have used a model pseudopotential, that consists of a homogeneous smearing of the radius r_c of the ionic core. For such a pseudopotential, we have computed for a system of 54 ions the dynamical pressure $P^{\mathrm{psp}}_{\mathrm{dyn}}$ at $r_s=1$ and $\Gamma=35$ and the static pressure with the ions on a bcc lattice $P^{\mathrm{psp}}_{\mathrm{lat}}$ for different cutoffs (for 1, 2, and 4 atomic units, see Table I). The effect of increasing r_c is to increase the pressure, as expected. For the same static configuration we have also computed the pressure using the bare Coulomb potential $P^{\mathrm{Coul}}_{\mathrm{lat}}$ (which does not depend on r_c). The difference ΔP between the static Coulomb pressure and the static pseudopotential pressure is used to correct the dynamical pressure $P^{\mathrm{psp}}_{\mathrm{dyn}}$

$$P^{\mathrm{corr}}_{\mathrm{dyn}}=P^{\mathrm{psp}}_{\mathrm{dyn}}-P^{\mathrm{psp}}_{\mathrm{lat}}+P^{\mathrm{Coul}}_{\mathrm{lat}} \tag{6}$$

TABLE II. Static correction ΔP, and corrected pressure P_c [see Eq. (6)] in Ry/a_B^3 vs temperature for $r_s=1$ and $r_s=2$. Also given is the ratio $r_1=(P/P_{\mathrm{id}}-1)$, where P_{id} is the ideal pressure of the ions and the quantum electron system as given in Refs. [1,2].

r_s	T (a.u.)	$\theta=T/T_F$	Γ	ΔP	P_c	r_1
1	0.024	0.013	41.66	0.0327	0.16984	−0.5327
1	0.1	0.054	10	0.0423	0.21266	−0.4732
1	0.319	0.173	3.135	0.0425	0.35629	−0.3464
1	0.5	0.272	2	0.0441	0.48965	−0.2831
1	0.769	0.418	1.3	0.0446	0.6882	−0.2410
1	1	0.543	1	0.0432	0.87437	−0.2111
1	2	1.086	0.5	0.0458	1.80451	−0.1070
1	10	5.431	0.1	0.0326	9.47824	−0.0126
2	0.05	0.108	10	0.00232	0.00241	−0.8338
2	0.1	0.217	5	0.00235	0.00614	−0.6750
2	0.1923	0.418	2.6	0.00229	0.01363	−0.5191
2	0.2695	0.585	1.855	0.00223	0.02167	−0.4112
2	0.5	1.086	1	0.00229	0.04655	−0.2629
2	1	2.172	0.5	0.00189	0.10874	−0.1074

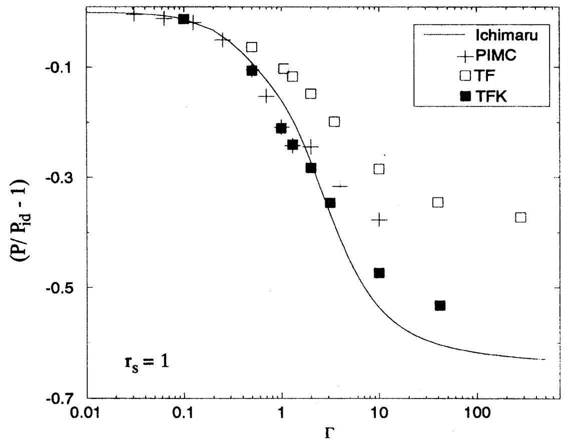

FIG. 1. Excess pressure with respect to the ideal quantum system vs the coupling parameter Γ for $r_s=1$. The solid line is the Ichimaru fit, crosses are PIMC simulations, open squares are DFMD simulations with finite temperature, and filled squares are Thomas-Fermi DFMD simulations with Kirshnits gradient expansion at finite temperature.

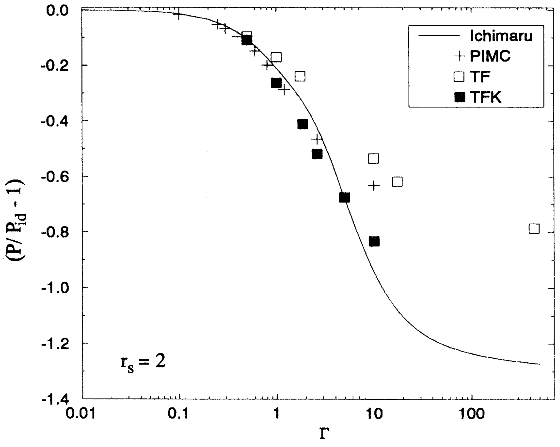

FIG. 2. Same as Fig. 1, with $r_s=2$.

in order to obtain a corrected pressure almost independent of the cutoff as shown in Table I. Although this works well for hydrogen a cleaner procedure is certainly called for if one wants to study high Z elements.

We studied a system of 128 protons at two densities corresponding to two values of the Wigner-Seitz radius $r_s=a/a_0$, viz. $r_s=1$ and $r_s=2$ and for a wide range of coupling parameters Γ. Moreover, since the finite temperature version of the kinetic energy functional is required as soon as $\theta \simeq 1$, we used a Nose-Hoover thermostat on the ionic degrees of freedom, to match accurately the input temperature of the electronic and the simulation temperature of the ionic subsystems.

At $r_s=1$, one expects an atomic plasma in the whole temperature range, well described by the Debye-Hückel theory at low coupling (here $\theta \gtrsim 3$), and by a semiclassical model at intermediate coupling. The comparison of our results (summarized in Table II) with the aforementioned theories is displayed in Fig. 1, and a good agreement is observed between the various models. More precisely, while in excellent agreement with PIMC simulations for $\Gamma<2$, our data start to deviate at strong coupling, remaining in the vicinity of the IIT equation of state. For comparison, we have also plotted finite temperature Thomas-Fermi (TF) calculations, which yield much higher pressures.

For $r_s=2$, exactly the same trend is observed Fig. 2, that is a pressure very close to the prediction of Ichimaru, but still lower than the PIMC simulations at high coupling. At this density, molecular formation is expected for a coupling parameter $\Gamma \simeq 2$. The TF pressure falls closer to the other predictions at low coupling, but remains systematically higher.

The very good agreement between IIT and our simulation shows that, in both cases, the compromises involved in the approximate description of the electron proton plasma, that is an approximate functional of the density on the one hand, and an approximate description of the correlation function, yield the same results especially at strong coupling. The difference with PIMC data for large values of Γ is more difficult to understand, and should certainly prompt more work in this regime.

According to Ref. [6] the change of slope at $\Gamma=2$ and at $r_s=2$, should be linked to molecular bonding. To test whether some tendency to bonding is included in the TFK kinetic functional, we considered the "ionic" contribution to the pressure, denoted P_{ion}. It was obtained by subtracting from the total pressure, the pressure computed with a static lattice of ions ("electronic pressure"). The value of P_{ion} in excess of the ideal gas value is reported Fig. 3 for the two values of r_s. For comparison, the same quantity is displayed when the kinetic energy functional is reduced to the Thomas-Fermi expression, which does not reproduce bonding. At $r_s=1$, both TF and TFK show the same trend, that is, ion-ion correlations are dominated by repulsive electrostatic forces which are already well described by the Thomas-Fermi theory. At $r_s=2$ in the TF model the ions behave as a perfect gas of quasi-isolate atoms. Still, the TFK model shows strong ion correlation.

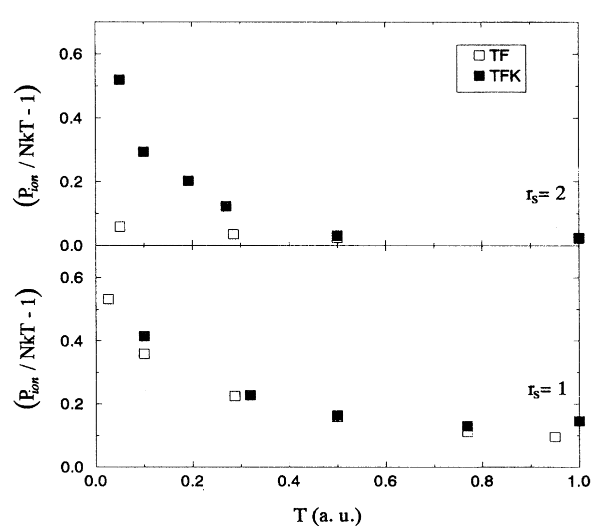

FIG. 3. Ionic contribution to the pressure vs temperature (in atomic units) for $r_s=1$ (lower curve) and $r_s=2$ (upper curve).

In conclusion, while there seems to be almost perfect agreement between the aforementioned calculation in a wide range of coupling, at higher coupling there remains some uncertainties in the equation of state of hydrogen. At very low degeneracy, a full *ab initio* MD simulation would throw a useful light on these data. Those encouraging results on the hydrogen equation of state demonstrate the reliability of this orbital free scheme, and more systematic comparison on static and dynamical properties of hydrogen will be published subsequently.

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