Ab Initio Determination of Thermal Conductivity of Dense Hydrogen Plasmas

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Ab initio molecular dynamics is used to compute the thermal conductivity of hydrogen at 80 $\mathrm{g\,cm^{-3}}$ and temperature up to 800 eV. Pressures and ionic structure are compared with orbital-free calculations. Thermal conductivity is evaluated using the Kubo-Greenwood formula and is compared with models currently used in hydrodynamical simulations of inertial confinement fusion.

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Among the numerous parameters that condition the success of future inertial confinement fusion (ICF) experiments, electronic thermal conduction plays a central role. First, it is a key ingredient to control all kinds of hydrodynamical instabilities occurring during the implosion process at the ablation front [1], at the fuel-ablator interface [2] or at the hot spot-fuel interface [3–5]. Second, precise knowledge of the electronic heat conduction is also needed for a correct description of the development of the central hot spot against the dense cold fuel and the propagation of the thermonuclear burn wave [6]. In the indirect drive scheme, thermal conduction also controls the efficiency of the x-ray conversion in the hohlraum walls. Despite this importance, the electronic heat conductivity is poorly known in some thermodynamical regimes, in particular, in hot and dense matter. The first calculations were made for weakly coupled plasmas [7] (high temperatures and low densities), then for strongly degenerated plasmas [8] (low temperatures, high densities). The most popular conductivity models [9,10] in hydrodynamic codes interpolate between these two regimes as well as the solid-liquid state. They widely disagree at high density so that an independent determination is needed. Contrary to the aforementioned models, quantum molecular dynamics simulations (QMD) has been proved to be a powerful tool to finely study matter in the warm dense regime [11] but was, up to now, limited in terms of temperatures and densities. In this Letter, we report the first QMD calculations at both high temperatures and densities, namely, hydrogen along the 80 $\mathrm{g\,cm^{-3}}$ isochore and temperatures up to 800 eV. The *ab initio* approach allows us to compute at the same time both the equation of state and the thermal conductivity. This later is computed consistently from the nuclei trajectories and the electronic wave functions thanks to a plane-wave implementation of density functional theory (DFT) coupled with the Kubo-Greenwood formalism.

Let us recall here that, in QMD calculations, the one-body electronic states are populated through a Fermi-Dirac distribution, so that high temperatures commonly involve a large number of orbitals, which is currently numerically intractable. Nevertheless, when considering hydrogen in a very dense regime, 80 $\mathrm{g\,cm^{-3}}$, degeneracy effects lead to the reduction of thermal excitations since the ratio between temperature and Fermi energy stays of the order of unity or less, even at 300 eV (see Table I). Reaching high densities is numerically difficult in QMD because of the use of pseudopotentials that separate core from valence electrons, the first being frozen with the nucleus. This frozen-core approximation, which is valid at moderate density, fails at high densities due to pressure delocalization of the core electrons and the overlap of the pseudization spheres. To overcome this limitation and reach a regime where hydrogen is extremely dense, a pseudopotential is built with a reduced cutoff radius. This would inevitably lead to a large plane-wave basis. But, at the same time, electronic eigenstates—due to delocalization—are nearly plane waves in this regime. Therefore, for most of the studied temperatures, the size of the basis set is finally substantially reduced allowing for reasonable computational time. Such a very dense and hot system is a new field of applications for *ab initio* simulations, particularly for the computation of thermal conductivity [12].

Simulations for hydrogen were performed at several temperatures lying from $k_BT = 2$ eV to $k_BT = 800$ eV along the 80 $\mathrm{g\,cm^{-3}}$ isochore. The plasma state is commonly characterized by two nondimensional parameters. The first one is the ion-ion coupling parameter Γ_{ii}, which is the ratio between the mean electrostatic potential energy and the mean kinetic energy of the ions: $\Gamma_{ii} = Z^{\star 2}/(k_BTa)$. T is the ionic temperature and a the mean ionic sphere radius written as $a = (3/4\pi n_i)^{1/3}$ with n_i the ionic number density. The average ionization degree $Z^\star$ is equal to unity in this thermodynamical regime. The second parameter, which is the ratio of the temperature to the Fermi temperature $T_F = (3\pi^2 n_e)^{2/3}/3$, characterizes the

TABLE I. Ion-ion coupling parameter and electronic degeneracy parameter for hydrogen at 80 $\mathrm{g\,cm^{-3}}$.

k_BT(eV)	2	5	20	43	86	172	300	800
Γ_{ii}	35	14	3.51	1.64	0.82	0.42	0.25	0.1
$\theta = T/T_F$	0.004	0.01	0.04	0.10	0.18	0.35	0.61	1.64

electronic degeneracy. Table I summarizes the values of these two parameters for the studied temperatures.

As shown in Table I, matter goes from strongly coupled ($\Gamma_{ii} > 1$) and highly degenerate ($\theta \ll 1$) at 2 eV to a moderate coupling and a partial degeneracy at 800 eV. Two methods are engaged in generating both the ionic trajectories and the equation of state in thermodynamical equilibrium. On one hand, QMD simulations are performed with the *ab initio* plane-wave code ABINIT [13–15] in the framework of finite temperature DFT. The Perdew-Zunger parametrization of the local density approximation (LDA) [16] is used for the exchange and correlation potential. We did not take into account an explicit temperature dependency of the exchange-correlation functional since its impact has been shown to be negligible [17]. The simulations of hydrogen at 80 $\mathrm{g\,cm^{-3}}$ ($a = 0.32$ a.u.) and high temperatures require a pseudopotential with a small cutoff radius to prevent the pseudization spheres from overlapping. A Coulombic pseudopotential with a cutoff radius $r_{\mathrm{cut}} = 0.005$ a.u. is a good approximation. The plane wave cutoff energy is set to 100 a.u.. Because of pressure delocalization, the electronic eigenstates are nearly plane waves so that the basis set is greatly reduced (1734 plane waves are used). Moreover, since the degeneracy parameter stays small in the entire temperature range, the Fermi-Dirac distribution is close to an Heaviside distribution which leads to a small number of bands even for highly accurate simulations (electronic states with an occupation down to 10^{-6} are considered). Such QMD simulations were run for temperatures below 300 eV—electronic and ionic temperatures being equal. Ionic structures are generated using the Γ point for the representation of the Brillouin zone and 256 particles in a cubic simulation cell with periodic boundary conditions. After thermalization, each temperature point was simulated for 8000 time steps [18] in the isokinetic ensemble.

On the other hand, orbital-free molecular dynamics (OFMD) simulations [12,17,19,20] were run for the same thermodynamical conditions. In the orbital-free scheme, the Mermin functional, which involves orbitals in the kinetic-entropic term only, is replaced by a direct approximation of the electronic free energy in terms of the local density. The orbital-free functional is obtained by a semiclassical development of the Mermin functional [21] which leads to the well-known finite temperature Thomas-Fermi expression for the kinetic-entropic part. It is important to point out that this method is numerically extremely efficient and allows calculations at 800 eV while QMD calculations become prohibitive. As for the previous QMD simulations, 256 particles were propagated in a cubic simulation cell with periodic boundary conditions. Numerical convergence, in terms of plane-wave basis set [22], was insured for all the simulations.

The equation of state (eos), restricted here to the relation between pressure and temperature, is obtained from both quantum and semiclassical molecular dynamics simulations, and, is shown in Fig. 1 compared to the eos deduced from the Kerley table [23]. The excellent agreement between the results of OFMD (which is the reference at high temperatures) and QMD shows the ability of quantum simulations to deal, not only with cold and dense system as in [12], but also with high temperature in the extremely dense regime.

Figure 2 shows the two radial pair distribution functions (pdf) for 5 eV and 172 eV. The curves highlight the behavior of, respectively, a strongly ($\Gamma_{ii} = 14$) and moderately coupled ($\Gamma_{ii} = 0.42$) system; see Table I. The agreement with the pdf from the one component plasma (OCP) model, computed at corresponding coupling parameter, is excellent. Nevertheless, pdf's are not very sensitive to the detailed electronic structure and, consequently, the agreement of the ionic structures does not imply that the electrons are fully degenerate. Table I shows, besides, that the electronic bath is only partially degenerate in contradiction with the underlying assumptions of the OCP model. It was even proved [20] that such an agreement can be achieved for partially ionized systems by a suitable choice of the effective ionization or, equivalently, of the coupling constant. The pdf's computed with the OFMD model are not shown in Fig. 2 since they are almost indistinguishable from both QMD and OCP results.

Apart from ionic structure and eos, thermal conductivity is obtained using QMD in the following way. For selected statistically independent atomic configurations, a self-consistent ground state calculation is performed to get the detailed electronic structure. A $4 \times 4 \times 4$ Monkhorst-Pack ***k**-points* mesh is used since transport coefficients are much more sensitive to the precise electronic quantum states than molecular dynamics—i.e., forces—is. The thermal conductivity is evaluated with the Kubo-Greenwood formulation [24,25] in the version of Chester-Thellung [26]. The electronic thermal conductivity K reads

$$K = \frac{1}{T}\left(\mathcal{L}_{22} - \frac{\mathcal{L}_{12}^2}{\mathcal{L}_{11}}\right), \tag{1}$$

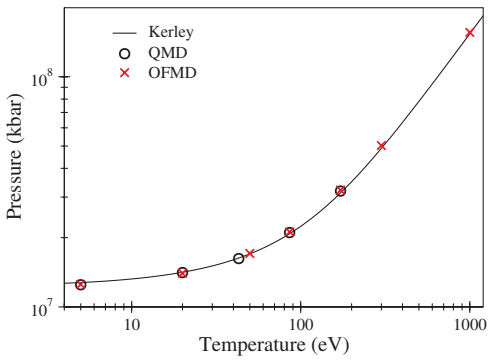

FIG. 1 (color online). Pressure vs temperature for hydrogen from QMD (circles) compared to the orbital-free (squares) and the Kerley (solid line) results.

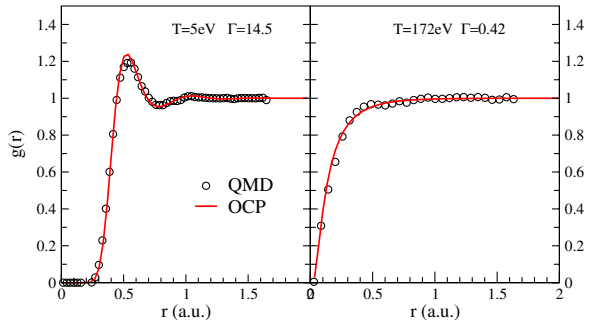

FIG. 2 (color online). Calculated pair distribution functions for hydrogen at 5 and 172 eV compared to the OCP ones.

where $\mathcal{L}_{ij}$ are the Onsager kinetic coefficients given by

$$\mathcal{L}_{ij} = -\frac{(-1)^{i+j}}{\Omega}\int d\epsilon \frac{\partial f(\epsilon)}{\partial \epsilon}(\epsilon - \mu)^{(i+j-2)}\hat{\sigma}(\epsilon), \quad (2)$$

$f(\epsilon)$ being the Fermi-Dirac distribution function and μ the chemical potential. The scattering cross section $\hat{\sigma}(\epsilon)$ is calculated by means of the following Kubo-Greenwood formula

$$\hat{\sigma}(\epsilon) = \frac{1}{\Omega}\sum_{k,k'}|\langle \psi^k|\hat{\boldsymbol{v}}|\psi^{k'}\rangle|^2 \delta(\epsilon_k - \epsilon_{k'} - \epsilon).$$

In the previous equation, Ω is the volume of the simulation cell, ϵ_k are the electronic eigenvalues and $\langle \psi^k|\hat{\boldsymbol{v}}|\psi^{k'}\rangle$ are the matrix elements of the velocity operator. Equation (1) is applied to the energy dependent form of the kinetic coefficient; the thermal conductivity is obtained by extrapolating to zero energy transfer, i.e., towards elastic scattering. This formulation was implemented in the ABINIT code for Troullier-Martins potential and leads to good results for liquid aluminum [27]. The Troullier-Martins potential is in general nonlocal and the momentum operator is used to represent the velocity operator. Since the Coulombic potential used in this paper is fully local, we can use directly the velocity operator. The chemical potential is obtained by fitting the set of occupation numbers corresponding to the set of eigenvalues with the usual functional form for the Fermi-Dirac distribution at finite temperature. The δ distribution must be broadened by a Gaussian function. The Gaussian broadening is tested to obtain smooth curves.

To get statistically converged results, the thermal conductivity is averaged over six independent snapshots picked up during the course of one simulation at given thermodynamical conditions. For the lowest temperatures, $k_B T < 300$ eV, ionic positions are directly taken from QMD simulations whereas, beyond this value, they are extracted from OFMD simulations. Even if the two approaches lead to the same ionic structure, OFMD is much less time consuming than QMD, particularly at high temperatures. We stress that at 800 eV we used 8000 bands for the calculation of thermal conductivity whereas only 300 are sufficient at 5 eV. This former calculation is extremely time consuming and reaches the computational limits of the QMD approach.

Figure 3 shows the calculated thermal conductivity as a function of temperature—error bars being smaller than the size of the symbols. QMD results are compared to both the Hubbard [8,9] and the Lee-More [10] models. The function $G_{\Gamma_{ii}}$ of the Hubbard model, which accounts for the ionic structure, has been recalculated with a finer grid to get smoother results by using a tabulated form for the static structure factor $S(k)$ made by Rogers *et al.* [28]. The Lee-More model uses different formulas for the electron collision time in solid, liquid and plasma. Let us point out that we have taken into account, in the plasma conductivity formula, the well-known correction for the electron-electron collisions, which is particularly important for hydrogen. For very high temperatures, beyond T_F, QMD and Lee-More model should merge into the Spitzer thermal conductivity [7] which is proportional to $T^{5/2}$. To check this we have performed a particularly long and time consuming simulation at 800 eV to ensure a good convergency of the conductivity and found a result in agreement with Spitzer. Higher temperature simulations would be too heavy and useless in a fully kinetic regime.

It appears that our results are in fairly good agreement with the Hubbard model although the temperature dependence of the QMD conductivity is of the form $\alpha T^{0.85}$ and not proportional to T. Let us recall that the Hubbard model is based on the following hypotheses. First, it assumes a complete Fermi degeneracy and uses the Born approximation, electronic states are treated as independent plane waves. Second, the ionic structure is supposed to be either Debye or OCP-like. From Table I and Fig. 3, it is clear that all our computed points (except at 800 eV) are lying at temperatures below the Fermi temperature but QMD cal-

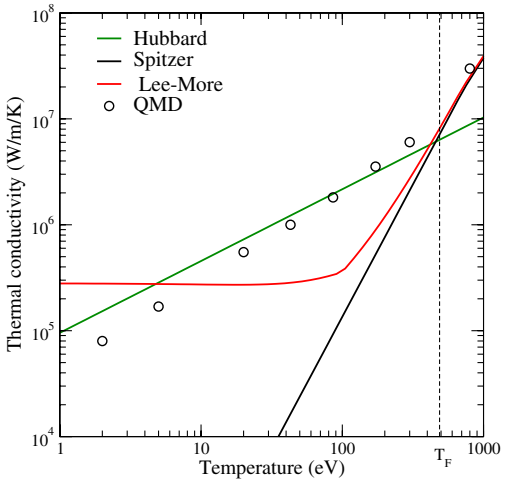

FIG. 3 (color online). Thermal conductivity for hydrogen (circles) as a function of temperature compared with Spitzer, Hubbard, and Lee-More thermal conductivity models. The Fermi temperature for hydrogen at 80 g/cm^3 is shown by the dashed vertical line.

culations treat exactly partial degeneracy without perturbative expansion, going beyond the simple approximations of the Hubbard model. Besides, the OCP-like ionic structure also confirms the partially degenerate behavior of the electronic component, as shown in Fig. 2. The slight difference at low temperature with the Hubbard model can be traced back to the emerging ionic structure, as revealed by the pdf in Fig. 2, which is not correctly accounted in $G_{\Gamma_{ii}}$ function. We can also see that the agreement with the Lee-More model is not satisfactory in the degenerate range.

In summary, we have shown that *ab initio* simulations provide an efficient way to study electronic thermal conductivity of hydrogen under extreme conditions as reached in ICF experiments. We used a Coulombic potential with a very small cutoff radius to be able to describe pressure up to 10^7 kbar. Despite the large plane-wave cutoff needed, the calculations are tractable and we were able to study thermal conductivity from the coupled to the kinetic regime. We have exposed a complete and efficient chain of calculations to compute microscopic properties of dense matter where $T/T_F \leq 1$ [29]. The orbital-free treatment of the electrons for the molecular dynamics yields the ionic structure—as well as diffusion coefficient or viscosity [20]. Then a quantum treatment is performed to get the detailed electronic structure leading to the electronic transport coefficients, among which the thermal conductivity. These tools allowed us to validate thermal conductivity models currently used in ICF hydrodynamical simulations. Because these methods are parameter free, they open a new field of applications for *ab initio* calculations, in particular, the transport coefficients of mixture.

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