

The viscosity of dense hydrogen: from liquid to plasma behaviour

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 9089

(<http://iopscience.iop.org/0953-8984/14/40/303>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 15:04

Please note that [terms and conditions apply](#).

The viscosity of dense hydrogen: from liquid to plasma behaviour

J Clérouin

Département de Physique Théorique et Appliquée, CEA/DAM Île de France, BP12, 91680 Bruyères Le Châtel Cedex, France

Received 13 May 2002, in final form 17 June 2002

Published 27 September 2002

Online at stacks.iop.org/JPhysCM/14/9089

Abstract

In this paper we shall discuss the viscosity of hydrogen as a prototype of a molecular fluid subjected to dissociation and ionization. In the dissociated phase we shall show that the dependence of the viscosity on temperature exhibits a crossover between an atomic and a screened plasma behaviour, as revealed by recent *ab initio* simulations. If this transition between molecular, atomic and plasma phase is well identified at low density (0.3 g cm^{-3}), at higher density (0.75 g cm^{-3}) the transition is more abrupt and no atomic phase can be identified.

1. Introduction

Equilibrium molecular dynamics (MD) is an efficient tool for computing transport properties such as autodiffusion, electrical or thermal conductivities and shear viscosity through the Green–Kubo relations (non-equilibrium approaches are also possible but more difficult to handle). Because classical MD is based on the *a priori* knowledge of the interactions, this approach must be related to a specific model. One can cite simple liquids, with the simplest ones being the hard-sphere liquid (Alder *et al* 1960) and the Lennard-Jones liquid (Levesque *et al* 1973), atomic liquids and charged systems. This latter case is illustrated by the one-component plasma (OCP) and by Yukawa screened models. In contrast, in *ab initio* molecular dynamics (AIMD) no assumptions are made on the interactions of the system. A continuous change can be produced (with some restrictions) from a simple molecular system to a plasma without any hypothesis on the underlying physics. A *paradigm* of such a complex multiphase system is hydrogen: starting from a well defined molecular system at low temperature, the system dissociates at some given temperature which strongly depends on the density, and eventually hydrogen atoms ionize, producing a plasma. During this process, interactions between molecules, atoms and electrons are changing continuously in a very complex way, which remains a subject of discussions. The fact that recent AIMD simulations of hydrogen

are in good agreement with experimental results¹ and theoretical predictions suggests that most of the physics is captured by these simulations, and encourages us to compute more precisely physical quantities of interest.

Up to now, the computation of transport properties involving collective currents such as the viscosity was possible only with classical MD codes due to the poor statistics of current autocorrelation functions (in contrast with velocity autocorrelation functions, which are easy to obtain) and due to the need to approach as closely as possible the hydrodynamic limit. Due to recent improvements of algorithms and parallel computers, AIMD computation of transport coefficients such as viscosity is now imaginable and has been done for the first time in the case of iron under geophysical conditions (Alfe and Gillan 1998). We shall show here results obtained for 108 atoms of hydrogen propagated over more than 3×10^3 time steps of 0.2 fs in a range of temperature between 1000 and 50 000 K. These numbers are sufficient to produce current time correlation functions with an accuracy of 20% for the viscosity, but have to be compared with recent Yukawa simulations involving 500 particles over 5×10^4 time steps (Salin and Caillol 2002, Saito and Hamaguchi 2002).

In this paper we shall focus on the viscosity of hydrogen through the different physical states encountered when increasing the temperature. We shall show that a simple molecular to atomic dissociation model is not enough to reproduce our AIMD results at high temperature and hence that a crossover with a plasma behaviour occurs at high temperature. This raises the question of finding a correct screening length to describe the plasma phase.

2. The viscosity of a simple fluid

The viscosity of a simple atomic fluid can be written in terms of an autocorrelation function of off-diagonal components of the stress tensor

$$\tilde{\eta} = \frac{V}{k_B T} \int_0^{+\infty} \eta(\tau) d\tau \quad (1)$$

$$= \frac{V}{k_B T} \int_0^{+\infty} \langle \sigma^{\alpha\beta}(\tau) \sigma^{\alpha\beta}(0) \rangle d\tau \quad (2)$$

where $\sigma^{\alpha\beta}$ are the five independent components of the traceless stress tensor, σ^{xy} , σ^{yz} , σ^{zx} , $\frac{1}{2}[\sigma^{xx} - \sigma^{yy}]$ and $\frac{1}{2}[\sigma^{yy} - \sigma^{zz}]$, with

$$\sigma^{\alpha\beta} = \sum_i m_i v_i^\alpha v_i^\beta + \sum_i \sum_{j \neq i} r_{ij}^\alpha F_{ij}^\beta \quad (3)$$

where m_i and v_i^α are the mass and the $\alpha = x, y$ or z component of the velocity of the i th particle and r_{ij}^α and F_{ij}^β the α and β components of the distance and of the force between i and j .

This formulation can be related to the transverse current autocorrelation functions (Hansen and McDonald 1986), but the stress formulation is more straightforward because there is no extrapolation to the hydrodynamic limit to be taken ($\omega \rightarrow 0, k \rightarrow 0$). Moreover, equation (3) shows that the stress components $\sigma^{\alpha\beta}$ are the sums of two components and hence the correlation function $\eta(t)$ has three contributions:

- (i) a kinetic term, which originates from correlations in the velocities;
- (ii) a potential contribution, which originates from interatomic forces, and

¹ Except for the laser experiment, where AIMD results do not confirm the experimental compressibility (Bagnier *et al* 2000), but are in agreement with other AIMD approaches and are restituting previous equations of state.

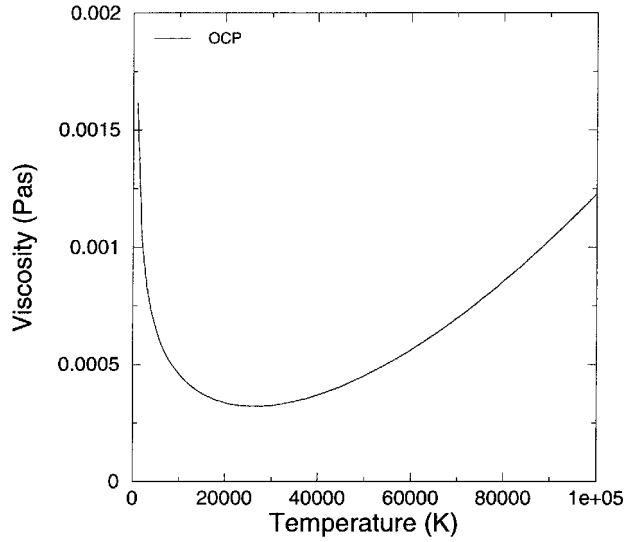


Figure 1. Plot of the viscosity in SI units versus temperature in the Wallenborn–Baus formula, equation (4).

- (iii) a cross term. Depending on which regime we are in, kinetic or potential terms make the most important contribution to the shear viscosity.

An important consequence is that the dependence of the viscosity on temperature is not monotonic. At low temperature potential contributions are dominant and the viscosity decreases with the temperature (liquid behaviour), in agreement with common sense, but at high temperature kinetic terms are dominant and now the viscosity increases with the temperature, which is counter-intuitive (gas behaviour). The consequence of these two opposite behaviours is the existence of a minimum in the viscosity versus temperature.

This minimum has been also evidenced for charged particles by Bernu and Vieillefosse (1978) in the case of the OCP at a temperature corresponding to a coupling parameter $\Gamma = Z^2 e^2 / a(kT) = 10$, where $a = (4/3\pi n)^{-1/3}$ is the mean ion-sphere radius and n is the number density. Using kinetic theory, Wallenborn and Baus (WB) (1978) also showed the existence of a minimum and proposed an analytical formulation of the viscosity

$$\eta^* = \lambda I_1 + \frac{(1 + \lambda I_2)^2}{\lambda I_3} \quad (4)$$

where

$$\begin{aligned} \lambda &= \frac{4\pi}{3} (3\Gamma)^{3/2}, \\ I_1 &= (180\Gamma\pi^{3/2})^{-1}; \\ I_2 &= \frac{0.49 - 2.23\Gamma^{-1/3}}{60\pi^2}, \\ I_3 &= 0.241 \frac{\Gamma^{1/9}}{\pi^{3/2}} \end{aligned} \quad (5)$$

and where η^* is the dimensionless viscosity. The WB viscosity is plotted in figure 1 in SI units (Pa s) versus temperature for a given density of 0.337 g cm^{-3} for hydrogen. This formulation

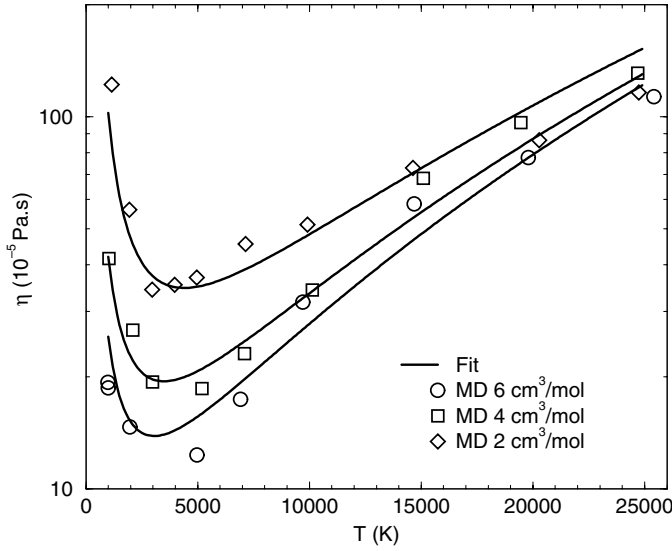


Figure 2. Viscosity in Pa s versus temperature computed for three densities, $6 \text{ cm}^3 \text{ mole}^{-1}$ (empty circles), $4 \text{ cm}^3 \text{ mole}^{-1}$ (empty squares) and $2 \text{ cm}^3 \text{ mole}^{-1}$ (empty diamonds), corresponding to densities of $\rho = 0.337, 0.5$ and 1 g cm^{-3} for hydrogen. The full curve is the fit formula (8).

has been used to compute the viscosity of mixtures (Cl  rouin *et al* 1998) by introducing an effective coupling parameter $\bar{\Gamma}_{eff} = \bar{\Gamma} \bar{Z}^{1/3} \bar{Z}^{5/3}$, where bars means averages over the number composition of the mixture $\bar{Z} = x_1 Z_1 + x_2 Z_2$.

3. Introducing dissociation

We now consider a molecular gas, and we want to investigate the effect of the dissociation on the viscosity of the system. The molecular gas can be described as a system of particles interacting through a exp-6 potential

$$V(r) = \frac{\epsilon}{\alpha - 6} \left\{ 6 \exp \left[\alpha \left(1 - \frac{r}{r^*} \right) \right] - \alpha \left(\frac{r^*}{r} \right)^6 \right\} \quad (6)$$

with parameters $r^* = 3.43 \text{ \AA}$, $\epsilon = 36.4 \text{ K}$ and $\alpha = 11.1$ (Ree 1988). This potential was corrected at short range to allow for very repulsive interactions at high pressure (Ross *et al* 1983). Its viscosity can be computed by classical MD and leads to a classical curve with a minimum. In this regime the viscosity can be also related to the diffusivity with the help of the Stokes–Einstein relation.

In this model (Dufr  che and Cl  rouin 2000), we suppose that some molecules are dissociated into atoms, also interacting with a corrected exp-6 potential with parameters $r^* = 1.4 \text{ \AA}$, $\epsilon = 20 \text{ K}$ and $\alpha = 13.0$. The parameters describing interactions between molecules and atoms are computed using the Lorentz–Berthelot rules (Ree 1988):

$$\begin{aligned} r_{\text{H}_2-\text{H}}^* &= \frac{1}{2} (r_{\text{H}_2-\text{H}_2}^* + r_{\text{H}-\text{H}}^*) \\ \epsilon_{\text{H}_2-\text{H}} &= \sqrt{\epsilon_{\text{H}_2-\text{H}_2} \epsilon_{\text{H}-\text{H}}} \\ \alpha_{\text{H}_2-\text{H}} &= \sqrt{\alpha_{\text{H}_2-\text{H}_2} \alpha_{\text{H}-\text{H}}}. \end{aligned} \quad (7)$$

To determine the proportion of molecules and atoms (dissociation rate) corresponding to a given density and temperature we used the Ross model (Ross 1998), which introduces a simple

Table 1. Dissociation fraction for selected temperatures predicted by the Ross model (Ross 1998) for the three volumes considered in the model.

Volume (cm ³ mol ⁻¹)	<i>T</i> (K)	% diss
6	1 000	0
6	5 000	6
6	10 000	52
6	25 000	93
4	1 000	0
4	5 000	17
4	10 000	69
4	25 000	95
2	1 000	20
2	5 000	84
2	10 000	93
2	25 000	96

density dependence of the dissociation energy. Dissociation fractions are given in table 1 for the three molar volumes considered, and for selected increasing temperatures. It appears that if at large volumes the dissociation is almost zero at 1000 K, it becomes significant (20%) at low volume (2 cm³ mol⁻¹) for the same temperature, illustrating the role of density. At high temperature the dissociation fraction is beyond 50% as soon the temperature reaches 10 000 K and is close to 95% for 25 000 K. At temperatures beyond 20 000 K we can hence consider that the physics is dominated by the atomic interactions.

Using the prescribed proportion of atoms and molecules, the viscosity of the mixture is then computed by classical MD. Typically 864 particles were simulated (molecules or atoms) during a few 10⁴ time steps with an energy conservation better than 10⁻³. The effect of dissociation is to enhance the viscosity compared with the pure case. Simulations have been performed for molar volumes of 6, 4 and 2 cm³ mol⁻¹, corresponding to densities for hydrogen of $\rho = 0.337, 0.5$ and 1 g cm⁻³, and a general scaling law has been found which reproduces the behaviour of the viscosity versus temperature, as shown in figure 2.

$$\eta = T^{5/2} \exp[a + b \ln x + c \ln^2 x] \times 10^{-5} \text{Pa s} \quad (8)$$

where $x = \rho T^{-1/3}$, $a = 38.17$, $b = 3.586$ and $c = 0.0547$.

4. DFT simulations

Extensive AIMD simulations were performed with the VASP code, which is a plane-wave pseudo-potential code developed at the Technical University of Vienna (Kresse and Hafner 1993, Kresse and Furthmüller 1996). Finite electronic temperature is implemented through the Mermin functional, which allows for the study of systems at high temperature. Vanderbilt ultrasoft pseudopotentials (Vanderbilt 1990) were used with an LSDA functional given by the Perdew–Wang 91 parametrization of GGA (including explicitly the spin) (Perdew 1991). Simulations, from which transport coefficients have been computed, were carried out with 108 atoms. It must be noted that, if temperature, pressure and total energies are well converged after 600 time steps of 0.2 fs of purely microcanonical simulations (after 300 time steps of thermalization by velocity rescaling), more time steps are needed to obtain statistically significant transport coefficients, and most of the results were produced with 2000–4000 time steps.

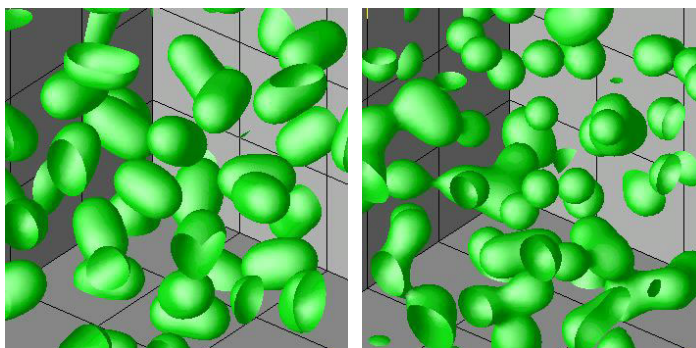


Figure 3. Electronic density at $V = 4 \text{ cm}^3 \text{ mol}^{-1}$ ($r_s = 1.75$) and $T = 500 \text{ K}$ (left) and $T = 15000 \text{ K}$ (right).

(This figure is in colour only in the electronic version)

We have produced simulations at different densities and temperatures covering thermodynamical states from the dense molecular regime to the dense hydrogen plasma. An illustration of the simulated molecular regime is shown in figure 3 (left), where hydrogen molecules are clearly behaving as individual particles. The equation of state in this regime is very close to classical evaluations using the Ross–Ree–Young potential (Ross *et al* 1983) and is coherent with the 0 K experimental curve given by the Vinet equation (Loubeyre *et al* 1996). When increasing the temperature, at a given threshold some molecules are broken and complex dynamical structures appear, such as those shown in figure 3 (right). At higher temperature all molecules are broken and only ionized atoms subsist in a continuous polarizable electronic bath. Although simulations at very high temperature $T > 50000 \text{ K}$ are limited by the increasing number of orbitals required to describe the Fermi distribution at finite temperature and by the conceptual validity of DFT in this regime, AIMD appears as a unique tool able to simulate the continuous transformation of a physical system under changes of thermodynamic variables (temperature and pressure).

It must be noted that in the regimes we are considering, where the electronic temperature T_e is much smaller than the Fermi temperature T_F , the electrons are partially degenerate ($T_e/T_F \ll 1$). The electronic density is supposed to follow adiabatically the ionic motion and enters the computation of the transport coefficients through the screening of ionic interactions. On the other side, in the classical regime ($T_e/T_F \gg 1$), where electrons can be treated as classical particles, the electronic contribution to the transport coefficient would be proportional to the square root of the mass ratio, and hence negligible compared with the ionic contribution.

4.1. Results on transport coefficients

We have computed the diffusion constant from the integration of the velocity autocorrelation function and the viscosity from the stress autocorrelation function equation (1) for different temperatures and for three molar volumes: 6, 4 and $2.7 \text{ cm}^3 \text{ mol}^{-1}$ corresponding to densities for hydrogen of $\rho = 0.337, 0.5$ and 0.75 g cm^{-3} and to $r_s = a/a_B = 2, 1.75$ and 1.5. The case $V = 4 \text{ cm}^3 \text{ mol}^{-1}$ is shown in figure 4. The plot of the autodiffusion versus temperature exhibits clearly the change from the dense molecular fluid to the dissociated system at about $T = 4000 \text{ K}$. In the dissociated regime the OCP prediction of Hansen *et al* (1975)

$$D^* = c\Gamma^{-\alpha} \quad (9)$$

with $c = 2.95$ and $\alpha = 1.35$ strongly underestimates the diffusion constant.

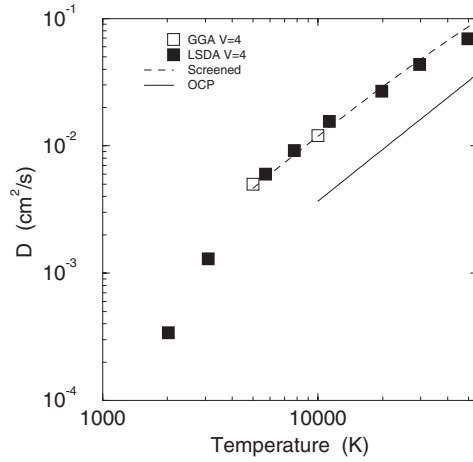


Figure 4. Autodiffusion versus temperature for $V = 4 \text{ cm}^3 \text{ mol}^{-1}$ ($r_s = 1.75$). The full line is Hansen's OCP fit equation (9), and the dashed line is Murillo's screened formula equation (10) with $\lambda = 2 \lambda_{TF}$.

When changing from the molecular to the dissociated system, the usual general trend is observed for the viscosity, with a minimum which corresponds to the change from the liquid to the gas behaviour enhanced by the molecular dissociation. At low temperature, in the dense molecular phase and in the dissociated phase up to 20 000 K the AIMD result is close to the classical dissociation model (dotted curve), equation (8). At higher temperature the values of the viscosity are saturating and lie between the OCP value given by the WB fit equation (4) and the atomic model equation (8).

4.2. Connection with screened plasmas models

The departure of the value of the viscosity from the atomic prediction is clearly related to the ionization and suggests that the system now behaves as a plasma. It is clear from the previous results that the system is far from the limit of the OCP, which corresponds to a completely degenerate electron gas, and is rather relevant to a screened plasma model with particles interacting through the Yukawa potential $V(r) = e^2 \exp -\kappa r/r$.

Two approaches are available for computing transport coefficients for Yukawa systems. First, recently there has been intense activity on simulation of Yukawa systems and MD results are now available (Ohta and Hamaguchi 2000, Salin and Caillol 2002, Saito and Hamaguchi 2002) for the diffusion and the viscosity, which are reported in figures 4 and 5. MD results for a screening parameter $\kappa = 1$ and 2 are bracketing our high-temperature results.

The second way to predict transport coefficients for screened potentials has been suggested by Murillo (2000). Using an argument based upon a equivalent hard-sphere system, Murillo suggested injecting into OCP formulae a renormalized coupling parameter:

$$\Gamma_{OCP} = A(\kappa) + B(\kappa)\Gamma + C(\kappa)\Gamma^2 \quad (10)$$

with κ being the inverse screening length in a units and

$$A(\kappa) = \frac{0.46\kappa^4}{1 + 0.44\kappa^4},$$

$$B(\kappa) = 1.01e^{-0.92\kappa},$$

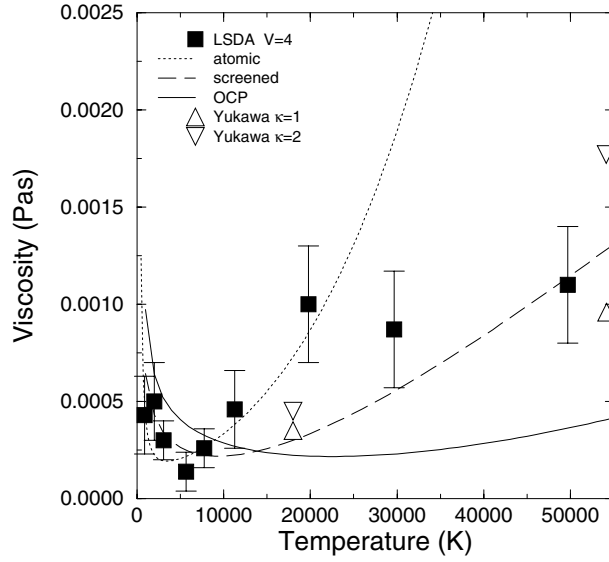


Figure 5. Viscosity versus temperature for $V = 4 \text{ cm}^3 \text{ mol}^{-1}$ ($r_s = 1.75$).

Table 2. TF screening lengths for the densities considered in the simulation.

	$r_s = 2$	$r_s = 1.75$	$r_s = 1.5$
λ_{TF}/a	0.452	0.483	0.522
κa	2.21	2.067	1.91
$2\lambda_{TF}/a$	0.904	0.967	1.05
κa	1.105	1.033	0.960

$$C(\kappa) = -3.7 \times 10^{-5} + 9.0 \times 10^{-4}\kappa - 2.9 \times 10^{-4}\kappa^2.$$

A natural screening length in this regime is the Thomas–Fermi (TF) screening length, which in a units reads

$$\lambda_{TF} = \left(\frac{\pi}{12Z} \right)^{1/3} \frac{1}{\sqrt{r_s}}$$

with $r_s = a/a_B$.

By considering our results (diffusion and viscosity), it appears that $\kappa = 1/\lambda_{TF}$ overestimates the screening of the system when applied to Hansen’s formula, equation (9), for diffusion or the WB formula, equation (4), for viscosity. Such a strong screening yields too large diffusion and viscosity coefficients. We have found empirically that $\lambda = 1/\kappa = 2\lambda_{TF}$ predicts transport coefficients in much better agreement with our high-temperature results and with classical MD data. The TF screening lengths for the densities considered in the simulation are reported in table 2. For all densities considered $2\lambda_{TF}$ gives a screening parameter κ of the order of unity. The fact that the TF screening length must be increased was previously reported by Z  rah *et al* (1992), and the same kind of renormalization has been also proposed by Hansen and Yoshida (1991) to reproduce the pair correlation function of expanded liquid metals. Two arguments can be proposed to justify such a renormalization:

- (i) the use of a finite-temperature screening length would slightly increase the screening length, but this effect is insufficient enough at temperatures considered here, and

- (ii) the description of the system with a screened potential is not justified for strongly non-linear responses, which is particularly the case for hydrogen (no core electrons).

Thus, it appears that the behaviour of the viscosity at high temperature is well represented by a screened plasma model, witnessing the transition from an atomic to a plasma behaviour.

5. Conclusion

The computation of the viscosity by AIMD reveals the different transitions occurring in dense hydrogen. Starting from a dense molecular system with a liquid-like viscosity (decreasing with the temperature), the dissociation reverses this trend and the viscosity is close to a pure atomic model with a gas behaviour (increasing with the temperature). At high temperature ($T > 20\,000$ K), ionization strengthens the interactions and leads to a lower viscosity. In this screened plasma regime, the viscosity can be deduced from the OCP results by a renormalization of the coupling parameter. The choice of the correct screening length is the key to the description of the hydrogen plasma.

References

- Alder B, Gass D M and Wainwright T E 1960 *J. Chem. Phys.* **53** 3813
- Alfe D and Gillan M J 1998 First-principle calculation of transport coefficients *Phys. Rev. Lett.* **81** 5161–4
- Bagnier S, Blottiau P and Cl  rouin J 2000 Local-spin-density-approximation molecular dynamics simulations of dense deuterium *Phys. Rev. E* **63** 015301
- Bernu B and Vieillefosse P 1978 Transport coefficients of the classical one-component plasma *Phys. Rev. A* **18** 2345–55
- Cl  rouin J, Cherfi M H and Z  rah G 1998 The viscosity of dense plasmas mixtures *Europhys. Lett.* **42** 347–2
- Dufr  che J-F and Cl  rouin J 2000 Viscosity coefficient of dense fluid hydrogen *J. Physique IV* **10** 303–6
- Hansen J P, McDonald I R and Pollock E L 1975 Statistical mechanics of dense ionized matter. III. Dynamical properties of the classical one-component plasma *Phys. Rev. A* **11** 1025–39
- Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (New York: Academic)
- Hansen J-P and Yoshida F 1991 *J. Phys.: Condens. Matter* **3** 2583
- Kresse G and Furthm  ller J 1996 *Comput. Mater. Sci.* **6** R558
- Kresse G and Hafner J 1993 *Phys. Rev. B* **47** R558
- Levesque D, Verlet L and K  ukijarvi J 1973 Computer ‘experiments’ on classical fluids. IV. Transport properties and time-correlation functions of the Lennard-Jones liquid near its triple point *Phys. Rev. A* **7** 1690–9
- Loubeyre P, LeToullec R, Hauserman D, Hanfland D, Hemley R J, Mao H K and Finger L W 1996 *Nature* **383** 702
- Murillo M S 2000 Viscosity estimates for strongly coupled Yukawa systems *Phys. Rev. E* **62** 4115–19
- Ohta H and Hamaguchi S 2000 Molecular dynamics evaluation of self-diffusion in Yukawa system *Phys. Plasmas* **7** 4506–14
- Perdew J P 1991 *Electronic Structure of Solids* (Berlin: Akademie)
- Ree F 1988 A high-density, high-temperature mixture model *Simple Molecular Systems at Very High Pressure* vol B 186, ed A Polian, P Loubeyre and N Boccara (Les Houches: Plenum)
- Ross M, Ree F and Young D 1983 The equation of state of molecular hydrogen at very high density *J. Chem. Phys.* **79** 1487–94
- Ross M 1998 Linear mixing model for shock compressed liquid deuterium *Phys. Rev. B* **58** 669–77
- Saigo T and Hamaguchi S 2002 Shear viscosity of the strongly coupled Yukawa system *Phys. Plasmas* **9** 1210
- Salin G and Caillol J-M 2002 Transport coefficients of the Yukawa one-component plasma *Phys. Rev. Lett.* **88** 065002
- Vanderbilt D 1990 Ultrasoft pseudopotentials *Phys. Rev. B* **41** 7892
- Wallenborn J and Baus M 1978 Kinetic theory of the shear viscosity of a strongly coupled classical one-component plasma *Phys. Rev. A* **18** 1737
- Z  rah G, Cl  rouin J and Pollock E L 1992 Thomas–Fermi molecular-dynamics, linear screening, and mean-field theories of plasmas *Phys. Rev. Lett.* **69** 446