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Thermodynamic and Transport Properties of Hydrogen and Deuterium Fluids Within Atom–Atom Approximation[1]

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Computer simulation results for highly compressed molecular hydrogen and deuterium fluids at pressures up to 100 GPa are presented. Nonempirical atom–atom approximation for nonrigid molecules was used for description of intra- and intermolecular interactions. Quantum corrections are included within the Feynman variational approach. Pressure, energy, isothermal compressibility, thermal expansion, heat capacities, and speed of sound, as well as transport properties of hydrogen and deuterium fluids at elevated temperatures and high densities, are computed using appropriate computer simulation procedures. Predictions of self-diffusion, shear viscosity, and thermal conductivity of shock-compressed deuterium and hydrogen fluids are presented.

KEY WORDS: atom–atom potentials; computer simulation; deuterium; heat capacity; high density; molecular hydrogen; self-diffusion; thermal conductivity; viscosity.

1. INTRODUCTION

The structure and thermodynamic and transport properties of hydrogen isotopes in the condensed phase have been studied intensively for many years. A rich body of experimental material in the cryogenic [1] as well as in high-temperature [2, 15] regions has been accumulated. At high pressures the most important experimental results have been obtained in the solid phase by the diamond-anvil method [3].

Fluid hydrogen isotopes at intermediate temperatures remain much less investigated. The existing published data have yielded the equation of

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state for the solid state [5] and for the fluid phase of normal hydrogen at temperatures up to 500 K and pressures up to 2 GPa [4]. Between the high-temperature and high-pressure dynamic shock-compression data and the low-temperature limit, no experimental studies have been performed. The transport properties of hydrogen or deuterium fluids in this region of high density and elevated temperatures are almost unknown.

Since it is quite difficult to do an experiment here, it is of particular importance to undertake a theoretical prediction of the properties of highly compressed fluid hydrogen. However, there is an extremely restricted choice of nonempirical methods for predicting the properties of such dense systems. Methods based on the direct quantum-mechanical computer simulation, e.g., the path-integral Monte Carlo (PIMC) method [6], are very demanding of computational resources and have not yet attained the necessary accuracy.

There are certain difficulties in applying to hydrogen the well-developed methods of the theory of liquids, which make use of the model of rigid, impermeable molecules. The absence of closed atomic electronic shells makes hydrogen extremely compressible and stable at the same time in the condensed phase. The softness of the intermolecular repulsion in hydrogen becomes very important at high densities. It is just what makes hydrogen different from many other substances, and therefore, the well-known and useful molecular models such as hard spheres and dumbbells could not be applied to hydrogen without essential modification.

The difficulties facing the theoretical prediction of the properties of highly compressed hydrogen are also due to the appreciable quantum effects [5]. Nonrigidity effects, which play an important role in highly compressed fluid hydrogen at high temperatures [7, 9], remain substantial at intermediate temperatures as well, especially near the line of crystallization, where the density of the fluid is high. In this region, one cannot also neglect quantum effects, particularly for the light isotopes of hydrogen. The goal of the present study is to investigate the possibility of using the approximation based on atom–atom potentials (AAP) [9] to predict the behavior of thermophysical properties of dense hydrogen at intermediate temperatures and high densities.

2. *AB INITIO* ATOM–ATOM POTENTIALS

In the AAP approximation [7, 9], the energy of interaction of hydrogen molecules is expressed in terms of the interaction energy of individual pairs of atoms. Two hydrogen atoms interact differently depending on their total spin. In the singlet ground state the atoms form an H_2 molecule—a bound $^1\Sigma$ state with a well depth of about 4.75 eV and a bond length of 0.74 Å.

In the triplet exited state $^3\Sigma$, the curve of the interaction energy does not have a minimum (except for a small dispersion well at a distance greater than 3 Å).

In the AAP approximation, the intermolecular interaction energy can be expressed relatively simply in terms of the interaction energy of the atoms within the molecule. This approximation is based on the Bohm–Ahlrichs theorem, which was proved by those authors in Ref. 8 in the Hartree–Fock approximation, in which the molecular orbitals are represented by a linear combination of atomic orbitals (LCAO MO). According to the theorem, the energy of the nonvalent interaction of two atoms (i.e., the interaction energy of two atoms belonging to different molecules with closed electronic shells) is equal to the weighted average (i.e., with allowance for the degeneracy with respect to projections of the spin and orbital angular momenta) of the interaction energy of two free atoms calculated in this same approximation.

According to the theorem, the nonvalent interaction potential $\phi(r)$ of hydrogen atoms can be calculated as a linear combination of the singlet and triplet potentials, with weights proportional to the multiplicities of these states:

$$\phi(r) = \tfrac{1}{4} U(^1\Sigma \mid r) + \tfrac{3}{4} U(^3\Sigma \mid r) \tag{1}$$

Here $U(^1\Sigma \mid r)$ is the interaction energy of two atoms in the $^1\Sigma$ ground state (with antiparallel spins); $U(^3\Sigma \mid r)$ is the interaction energy of atoms in the $^3\Sigma$ exited state (with parallel spins).

Within the AAP approximation the total energy of two H_2 molecules found in their ground electronic states consists of intra- and intermolecular contributions:

$$U_2 = U(^1\Sigma \mid R_{12}) + U(^1\Sigma \mid R_{34}) + \phi(r_{13}) + \phi(r_{14}) + \phi(r_{23}) + \phi(r_{24}) \tag{2}$$

The indices 1 and 2 refer to the atoms bound together in the first molecule, while 3 and 4 refer to the atoms bound in the second molecule. Here and below $R_{ij} = R_{12}, R_{34}, \ldots$ are the intramolecular interatomic distances (the instantaneous lengths of the chemical bonds in the molecules), while $r_{ij} = r_{13}, r_{14}, \ldots$ denote the instantaneous distances between atoms of different molecules (intermolecular distances).

For N atoms ($N/2$ molecules) the generalization of Eq. (2) is expressed as

$$U_N = \sum_{\text{intra}} U(^1\Sigma \mid R_{ij}) + \sum_{\text{inter}} \phi(r_{ij}) \tag{3}$$

The first sum in Eq. (3) is over the intramolecular interactions of all $N/2$ molecules, and the second sum is over all the $N(N-1)/2$ pairs of atoms belonging to different molecules. Equation (3) is applicable to any spatial distribution of atomic centers if an additional rule for the selection of bonded atomic pairs (chemical bonds localization) is adopted. We applied the following algorithm [9]. The first pair at a given specific configuration of N atoms is taken to be that which has the shortest interatomic separation. Excluding these two atoms, the next pair is taken to be that having the shortest interatomic distance among the remaining $N-2$ atoms, etc., until all the atoms have been exhausted.

We applied the following analytical approximation for the ground $^1\Sigma$ state [9]:

$$U(^1\Sigma \mid R) = D_e[\exp(-2x) - 2\exp(-x) - ax^3(1-bx)\exp(-cx)] \tag{4}$$

where $x = 1.4403(r/r_e - 1)$, $r_e = 0.74126$ Å, $D_e/k = 55{,}088$ K, $a = 0.1156$, $b = 1.0215$, and $c = 1.72$. Equation (4) gives an excellent approximation of the $^1\Sigma_g^+$-curve within a wide range of distances (0.3 to 5 Å). The nonvalent interaction potential $\phi(r)$ was represented in the approximation proposed by Saumon and Chabrier [13]:

$$\phi(r) = \varepsilon[\gamma\exp\{-2s_1(r-r^*)\} - (1+\gamma)\exp\{-s_2(r-r^*)\}] \tag{5}$$

The parameters appearing in Eq. (5), $r^* = 3.2909$ Å, $\varepsilon = 1.74 \times 10^{-3}$ eV, $\gamma = 0.4615$, $s_1 = 1.6367$ Å^{-1}, and $s_2 = 1.2041$ Å^{-1}, were obtained in Ref. 13 on the basis of the well-known variational calculations of Kolos and Wolniewitz [10] for the H_2 molecule. Equation (5) also gives a very accurate description of the potential from Eq. (1) over a wide interval of distances (from 0.5 to 3.5 Å), including the region of strong repulsion at short distances and the region of weak dispersional attraction at large distances.

Thus, the AAP approximation, Eqs. (1)–(3), with the potentials in Eqs. (4) and (5) permits a quite simple determination of the potential surface of the ground state of a system consisting of an arbitrary number of hydrogen molecules. We note that this approximation does not contain any adjustable parameters found from the experimental data, but uses only the pair potentials $U(^1\Sigma \mid R)$ and $U(^3\Sigma \mid R)$ obtained from *ab initio* calculations [10].

A comparison of the predictions of the AAP approximation with the results of direct quantum-mechanical calculations of the H_2–H_2 interaction energy and with the results of experiments on the scattering of molecular beams has shown [7] that this approximation gives an entirely satisfactory description of the short-range repulsion of the molecules but that the molecular attraction at large distances is overestimated somewhat [12]. At large intermolecular distances, the AAP approximation does not recover also the asymptotic behavior of the orientational part of the intermolecular potential, in particular, that of its quadrupole–quadrupole component. This shortcoming, which is important at relatively low densities, can also be important in the description of some phase transitions in solid hydrogen [5]. At the same time, at high pressures in the isotropic phase, where the main role is played by the short-range repulsive forces, this aspect of the AAP approximation plays a secondary role.

3. QUANTUM CORRECTIONS

For predicting the thermodynamic behavior of dense deuterium and, especially, hydrogen at lower temperatures on the basis of the AAP approximation, we modified this approach to incorporate quantum-mechanical effects, which play a governing role in the behavior of these light molecules at low temperatures. We adopted [12] the approach proposed by Feynman, which is based on his variational procedure for the free energy [11].

In this approach the free energy of a quantum-mechanical particle in an external field can be calculated approximately by a classical method if its potential energy $V(r)$ is replaced by a certain effective potential given by

$$\tilde{U}(r, T) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} V(r + \lambda t) \exp(-t^2)\, dt \tag{6}$$

The parameter

$$\lambda = h/\sqrt{24\pi m k T} \tag{7}$$

plays the role of the quantum-mechanical wavelength associated with the given particle; k is Boltzmann's constant.

In the simplest cases, the quantum corrections to the potential within the approximation in Eq. (6) are easily calculated explicitly. As was shown in Ref. 12, considering quantum effects in the framework of the Feynman approach reduces simply to some increase in the effective interatomic repulsion. A rough estimate of the possible influence of these effects on the repulsion of the atoms was made by taking into account that the parameter b is close to 2 (a.u.)$^{-1}$ for many atoms [7]. For example, for deuterium at $T = 500$ K the increase in the repulsion is only about 2.5%, but for hydrogen at $T = 200$ K it is already about 20%.

As for the intramolecular vibrations, their quantum character is manifested at much higher temperatures, so that a quantum correction becomes comparable to the heat capacity itself at temperatures below 1000 K. In view of this (while remaining formally within the framework of the Feynman approach), we replaced the first-order quantum correction to intramolecular energy with the exact expression for a harmonic oscillator [12]. At high temperatures, it goes over to the original Feynman approach, and at low temperatures, it gives the exact expression for the harmonic-oscillator contribution to the free energy and the other thermodynamic properties.

Thus one can assume that in the investigated temperature interval, taking quantum effects into account in the intermolecular interaction can be done at the level of a correction to the intermolecular potential, and the Feynman variational approach [11] can be completely applicable to highly compressed hydrogen isotopes at temperatures higher than ambient.

4. MONTE CARLO SIMULATION

To predict the equilibrium properties of fluid hydrogen on the basis of the AAP approximation with the quantum corrections introduced above, we chose the method of Monte Carlo simulation. The calculation was done in an NVT ensemble, with N hydrogen atoms placed in a rectangular cell with periodic boundary conditions. The size of the cell was determined by the specified density $n = N/V$, and the initial configuration corresponded to a random distribution of molecules with bond lengths close to the equilibrium bond length R_e. Each step in the experiment included a random choice of an individual atom, for which an attempt was made to move it to a new position within a specified distance δ. Discrimination of the steps was carried out by the standard Metropolis method [14]. The value of δ was chosen such that about 40% of the steps were successful. It took about 1000 successful steps per atom to establish the equilibrium distribution. Probable errors were estimated by standard statistical methods for a significance level of 0.05.

The isothermal compressibility, the thermal pressure, and the isochoric heat capacity C_V were computed along with the pressure and the total energy [12]. The calculations were performed for $N = 256$ or $N = 500$ atoms in the cell (128 and 250 H_2 or D_2 molecules in the cell, respectively). The interatomic interaction potential was "cut off" at a distance $r_{max} = 5$ Å; this did not introduce any new errors of practical consequence.

5. MOLECULAR (ATOMIC) DYNAMICS PROCEDURE

To predict transport properties of dense fluid hydrogen, we examined a classical system of N atoms forming nonrigid homonuclear diatomic molecules. The method applied is similar to the well-known molecular dynamics method [16], except for the structure element chosen. We consider the separate atoms in molecules within classical mechanics as elements of structure and perform such *atomic dynamics* (AD) simulations at a constant number of atoms N, volume V, and energy E (NVE simulation) with periodic boundary conditions. Newton equations of atomic motion have been integrated using the simplest three-point algorithm described by Norman et al. [16]. Low masses of hydrogen isotopes along with high frequencies of intramolecular vibrations and strong intermolecular forces require relatively short time steps in numerical integration of equations of motion.

The time step Δt ranged from 10^{-4} ps (10^{-16} s) at relatively high temperatures and densities up to 10^{-3} ps (10^{-15} s) at lower temperatures and/or densities. Larger values of Δt speed up the equilibration (relaxation) period in AD simulation but require special efforts for maintaining the desired temperature. We applied correction factors to all velocities during the relaxation period, preceding the main AD run to keep the temperature close to the given value, and also checked the correspondence among atomic velocities, center-of-mass velocities, and the Maxwell's distribution.

We used "near-equilibrium" atomic distributions generated in our Monte Carlo simulations as starting atomic configurations, and after a Maxwell equilibrium distribution was reached, we computed the self-diffusion D, viscosity η, and thermal conductivity κ and corresponding velocity, shear stress, and heat-flux autocorrelation functions (ACF). We also calculated interatomic and intramolecular distribution functions. All results presented below are averaged values over 1000 runs of 0.2 ps each. Every set of runs took from 100 up to 200 h on a PC.

6. RESULTS AND DISCUSSION

6.1. Thermodynamic Functions

The results of MC computer simulation and the data obtained in Ref. 4 are in quite good agreement overall (see Table I). The only disagreement is that the calculated pressure of the fluid hydrogen is somewhat (about 0.2 GPa) lower than experiment, even when the quantum corrections are taken into account [12]. This is apparently due to the aforementioned characteristic overestimate of the attraction of the molecules at large distances in the AAP approximation [9].

As expected, quantum effects particularly influence the isochoric heat capacity over the entire investigated temperature interval. The corrections to the thermal expansion coefficients and sound velocity are less important, but even for them, the agreement with experiment is improved when these corrections are taken into account. As the temperature increases, this

Table I. Predicted (MC) and Experimental [4] Pressures P, Isochoric (C_V) and Isobaric (C_P) Heat Capacities, Thermal Expansion α_T, Isothermal Compressibility β_T, and Speed of Sound a of Fluid Hydrogen on the $P=2$ GPa Isobar at $T=200$ K ($V=11.17\ \mathrm{cm^3 \cdot mol^{-1}}$, $\lambda=0.20$ Å), $T=300$ K ($V=11.63\ \mathrm{cm^3 \cdot mol^{-1}}$, $\lambda=0.16$ Å), and $T=500$ K ($V=12.53\ \mathrm{cm^3 \cdot mol^{-1}}$, $\lambda=0.13$ Å)

	T (K)						
	200		300		500		
	MC	[4]	MC	[4]	MC	[4]	Δ^a
P (GPa)	1.81	2.00	1.75	2.00	1.72	2.00	0.01
C_V/R	2.84	2.98	3.22	3.24	3.12	3.14	0.03
C_P/R	3.26	3.62	3.62	3.64	3.56	3.68	0.05
α_T (10^{-3} K^{-1})	0.48	0.42	0.37	0.39	0.32	0.36	0.03
β_T (GPa^{-1})	0.15	0.15	0.15	0.16	0.18	0.18	0.02
a (km $\cdot$ s^{-1})	6.59	6.40	6.59	6.38	6.34	6.37	0.05

[a] Estimated statistical error of MC simulation; $N=256$.

agreement becomes better and better, although even for $T=200$ K the predictions remain satisfactory. It is seen that the quantum corrections in the given temperature interval give approximately the same contribution to the pressure (of the order of 10%) as the typical value of the intramolecular contribution [9] due to the nonrigidity of the hydrogen molecule. Considering the quantum corrections is necessary in calculating not only the heat capacity but also the thermal expansion, and it substantially improves the agreement with experiment, especially at low temperatures. For an approach that does not contain even one adjustable parameter, the agreement can be considered completely satisfactory.

6.2. Transport Properties

In Table II, we present the predicted pressures and transport properties of fluid hydrogen at high densities and different temperatures. The simulation results are also compared to shock-compression data [2, 15].

Self-diffusion coefficients D have been estimated in three ways: (a) from the long-time slope of the mean-square atomic displacement, (b) as integrals of the time-dependent atomic velocity ACF, and (c) as integrals of the time-dependent molecular center-of-mass velocity ACF. All approaches give the same result within estimated error limits. The computation of shear viscosity and thermal conductivity is computationally much more time consuming (it requires many more runs in AD simulation). Unfortunately, we

Table II. Predicted Pressures and Transport Coefficients of Hydrogen and Deuterium Fluids

					Predicted			
Isotope	N_a	T (K)	V ($cm^3 \cdot mol^{-1}$)	P (GPa)	P_{MC} (GPa)	D_{AD} ($10^{-8} m^2 \cdot s^{-1}$)	η_{AD} ($10^{-4} Pa \cdot s$)	κ_{AD} ($W \cdot m^{-1} \cdot K^{-1}$)
H_2	256	300	11.63	2.0 [4]	1.72[a]	2.89 ± 0.04	0.48 ± 0.20	1.09 ± 0.37
H_2	256	500	12.53	2.0 [4]	1.75[a]	6.22 ± 0.06	0.56 ± 0.09	1.14 ± 0.18
D_2	500	2275	3.44	100 [2]	107.4	4.08 ± 0.04	5.30 ± 1.07	5.32 ± 1.20
D_2	256	2820	7.98	12.0 [15]	12.9	13.54 ± 0.09	1.26 ± 0.21	1.71 ± 0.24
D_2	500	3910	4.51	52.5 [15]	59.8	11.3 ± 0.1	2.9 ± 0.7	3.4 ± 0.8
D_2	256	4660	7.02	22.6 [15]	22.2	20.1 ± 0.14	1.5 ± 0.3	2.9 ± 0.35

[a] Includes quantum corrections [16].

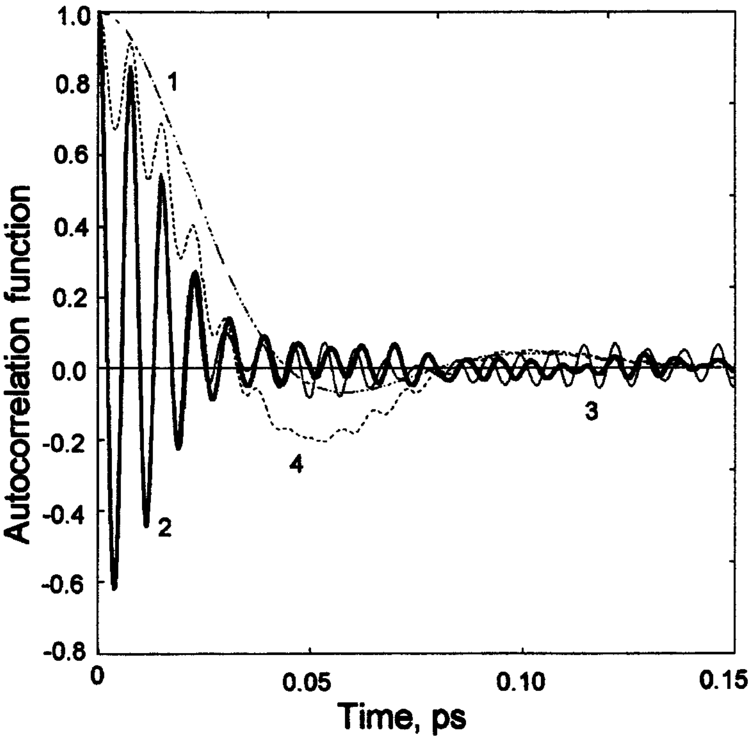

Fig. 1. Molecular (1) and atomic (2–4) normalized autocorrelation functions of the compressed fluid hydrogen at a relatively low temperature, $T = 300$ K ($P = 2$ GPa). The fine oscillation structure of the heat flux (thick line; 2), the atomic shear stress (thin solid line; 3), and the velocity ACF (dotted line; 4) have the same time period as the intramolecular vibration mode.

are not aware of any measured or predicted values of transport coefficients at shock-compression conditions with which to compare our predictions. The estimated statistical error of the predicted shear viscosity and thermal conductivity is still significant, but the more precise prediction is beyond the power of AD simulation on available PCs and requires a high-performance computer.

6.3. Velocity Autocorrelation Functions

In Figs. 1 and 2 we present the time-dependent atomic ACFs along with the molecular center-of-mass (dotted line) velocity ACF at low and high temperatures. There is a pronounced fine oscillation structure of the atomic velocity ACF, while the time dependence of the molecular center-of-mass velocity ACF is smooth and quite usual for simple liquids at high

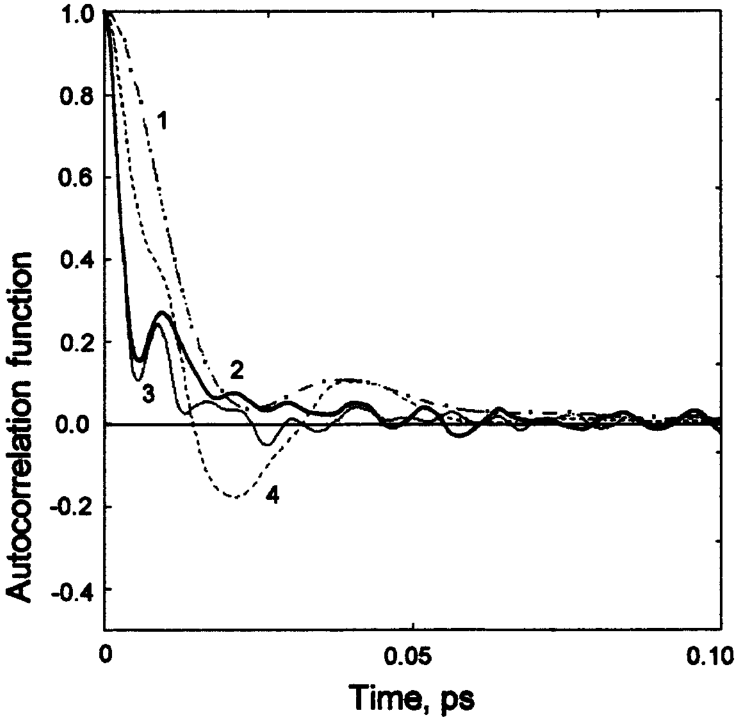

Fig. 2. ACFs in hydrogen fluid at a high temperature, $T = 3910$ K, and $P = 50$ GPa fall away much faster, and their oscillation structure is less pronounced than at low temperatures. The labels are the same as in Fig. 1.

densities. The period of those oscillations is close to the period of intramolecular vibration [17]. It is clear that highly compressed molecular fluid, composed from nonrigid molecules, will behave like a system of strongly coupled oscillators. The ACF oscillations are much more pronounced at higher densities and lower temperatures. The higher the temperature is, the more damped the ACF oscillations are.

7. CONCLUSIONS

The predictions of the AAP approximation are in reasonable agreement with existing experimental data both at moderate and at high temperatures, in spite of the fact that the AAP potentials do not explicitly contain contributions from the short-range multiparticle and long-range electrostatic intermolecular forces and that the electronic excitation of the molecules is not fully taken into account [7, 9].

Quantum corrections introduced to the AAP approximation [12] provide the possibility to calculate the thermodynamic properties and structure parameters of fluid hydrogen at high pressures, beyond the limits of the experimentally investigated region.

The temperature and density dependence of self-diffusion in fluid hydrogen predicted within the AAP approximation was examined in Ref. 17. Self-diffusion coefficients demonstrate a very slow decrease with compression, in contrast with predictions of the hard-sphere model. The temperature dependence of D is gas-like (power law) rather than inverse-exponential, typical for the activation mechanism of diffusion. Our simulations have also shown that the time-dependent atomic autocorrelation functions in diatomic fluids had a fine oscillation structure, more pronounced at lower temperatures and higher compressions.

Both the Enskog and the Frenkel approaches fail to describe the simulated density and temperature dependence of self-diffusion coefficients in dense fluid hydrogen (see Ref. 17 for details). It is not surprising because the hydrogen interatomic repulsion, as mentioned above, is very soft. The $\log(nD) - 1/T$ dependence is far from linear, in contrast to Frenkel's activation theory. At the same time the slope of $\log(nD) - \log(T)$ dependence is nearly constant [17] and changes with density from values close to 0.5 (corresponding to the known ideal-gas law) up to 1.5 and more. Unfortunately, the uncertainty of our shear viscosity and thermal conductivity predictions makes them inconclusive with respect to the suitability of existing theories for highly compressed hydrogen fluid.

Of course, a simple model such as AAP approximation cannot pretend to complete a description of dense hydrogen. At least two important effects have been omitted in the present calculations. First, using atom–atom models means that the effects of electronic polarizability and long-range forces are not correctly treated. Second, we have ignored electronic excitations, leading in the end to the metallization of hydrogen at higher densities and to the dissociation at higher temperatures.

Although the AAP approximation does suffer from the list of shortcomings mentioned above, as a nonempirical approach this approximation has its indisputable advantages and its own sphere of application. This approach requires a minimum of initial information for predicting the properties, makes it possible to describe the effects of molecular nonrigidity, and can be useful for predicting not only the thermodynamic behavior of molecular fluids at high pressures but also the diffusion, viscosity, and other transport properties of compressed fluids.

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