Vol 14 No 10, October 2005
1009-1963/2005/14(10)/2077-06

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Pressure dissociation of dense hydrogen*

Chen Qi-Feng(陈其峰)[a)b)†], Cai Ling-Cang(蔡灵仓)[a)],
Chen Dong-Quan(陈栋泉)[b)], and Jing Fu-Qian(经福谦)[a)]

[a)] *Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, Mianyan* 621900, *China*

[b)] *Laboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing* 100088, *China*

(Received 4 March 2005; revised manuscript received 29 June 2005)

The self-consistent fluid variational model (SFVM) has been used to describe the pressure dissociation of dense hydrogen at high temperatures. This paper focuses on a mixture of hydrogen atoms and molecules and is devoted to the study of the phenomenon of pressure dissociation at finite temperatures. The equation of state and dissociation degree have been calculated from the free energy functions in the range of temperature 2000–10,000K and density 0.02–1.0g/cm^3, which can be compared with other approaches and experiments. The pressure dissociation is found to occur in higher density range, while temperature dissociation is a more gradual effect.

Keywords: equation of state, pressure dissociation, self-consistent fluid variational model, dense hydrogen

PACC: 6250, 0570C, 6400

1. Introduction

Knowledge of the equation of state (EOS) for dense hydrogen is of central importance for astrophysics as well as for the general understanding of the behaviour of matter at extreme conditions.[1] Pressure dissociation has been found to become important in dense molecular fluids. The effective one-component model has been used to calculate EOS of fluid He+H_2 mixtures.[2] The effects of dissociation on the EOS have been treated by using dissociation model.[3] Various models were also applied to study the behaviour of hydrogen at ultrahigh pressure. For instance, linear-mixing model of Ross,[4] path-integral Monte Carlo (PIMC),[5] wave-packet molecular dynamics (WPMD)[6] and quantum molecular dynamics (both density functional (DF)[7] and tight-binding (TB)[8] approaches) were performed under conditions that can be reached in shock wave experiments. Furthermore, various simulation methods have proven the importance of this effect by inspecting the variation of the pair distribution function with density.[9] In particular, assuming that effective pair potentials are valid for the interactions in partially dissociated fluid, standard fluid variational theory (FVT) has been applied to such a two-component system with dissociation reaction.[10] In this work, the condition of chemical equilibrium for this reaction ($H_2 \rightleftharpoons 2H$), $\mu_{H_2}=2\mu_H$, was fulfilled self-consistently when minimizing the free energy functional.

Recent developments in shock wave experimental techniques have allowed the 100GPa pressure range in hydrogen to be probed.[11] The principal Hugoniot was determined up to 300GPa in recently reported single shock wave laser-driven experiments.[12] It has been shown that dissociation of hydrogen molecules becomes operative under such ultrahigh pressures. Therefore, in this paper, we first have to take into account pressure dissociation due to the modification of the binding energy of H_2 molecules. The dissociation equilibrium $H_2 \rightleftharpoons 2H$ reflects the very subtle changes in the electronic and structural properties at high pressures via correlation contributions which are consistent with the equation of state. In a next step the ionization equilibrium $H \rightleftharpoons e+p$ should also be treated for even higher densities to give a better description of the plasma state, but this is not the intention of this paper. From the free energy, other thermodynamic function such as the pressure and internal energy are derived. Comparison with other approaches is per-

*Project supported by the Foundation of Laboratory for Shock Wave and Detonation Physics Research (Grant No 51478030203ZW0902) and by the National Natural Science Foundation of China (Grant No 100032040).

E-mail: chen_qifeng@iapcm.ac.cn, or chenqf@nwnu.edu.cn

formed.

2. The self-consistent fluid variational model

2.1. The free energy

At density $\rho \leq 1\mathrm{gcm}^{-3}$, temperature $T \leq 10^4\mathrm{K}$, hydrogen is adequately described as a mixture of H atoms and H_2 molecules. The concentrations of H^- and H^{2+} ions are found to be negligible ($< 10^{-3}$) for obtaining EOS. The molecules and atoms interact via effective two-body potential, which implicitly approximates the real many-body effects. Effective pair potentials of the exponential-6 form have been used to model the interactions between hydrogen molecules and atoms.[13] The three-parameter exponential-6 potential of the form for the mixture of hydrogen atoms and molecules is taken in Eq.(1). The values of parameters ε, r^*, and α are listed in Table 1.

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

Table 1. The exponential-6 potential parameters for the H_2–H_2, H–H and H–H_2 systems are used in present work.[13]

Interaction	$(\varepsilon/k_\mathrm{B})$/K	r^*/nm	α
H_2-H_2	36.4	0.343	11.1
H-H	20.0	0.140	13.0
H-H_2	26.98	0.2415	12.0125

Supposing that the dense fluid hydrogen consists of atoms and molecules which interact via the effective pair potentials described in Eq.(1), we introduce the expression for the free energy of a two-component system with a reaction and give the other thermodynamic quantities. Considering in the following the dense hydrogen fluid at a fixed temperature T, and particle density n, we study the dissociation processes

$$\mathrm{H_2} \rightleftharpoons \mathrm{H} + \mathrm{H}. \quad (2)$$

In order to define the thermodynamics of the system, we introduce the free energy per particle $f^{\mathrm{tot}} = F^{\mathrm{tot}}/N$ and the degree of dissociation $\alpha = N_1/N$, $N = N_1 + N_2$ being the total number of particles. The free energy is given as a sum of the ideal contributions of the pure components f_i^{id} (with i=1, 2, 1=H, 2=H_2) and a term for the correlations among all particles f_{ij}^{c}, and also a term for the quantum correlation.

$$f^{\mathrm{tot}} = \sum_{ij}(f_i^{\mathrm{id}} + f_{ij}^{\mathrm{c}}) + f_{\mathrm{QM}}. \quad (3)$$

The ideal free energies for the atomic and molecular components are given by

$$f_{\mathrm{H}}^{\mathrm{id}}(n,T) = f_{\mathrm{H}}^{\mathrm{trans}}(n,T) + f_{\mathrm{H}}^{\mathrm{spin}}(T), \quad (4)$$

$$f_{\mathrm{H_2}}^{\mathrm{id}}(n,T) = f_{\mathrm{H_2}}^{\mathrm{trans}}(n,.T) + f_{\mathrm{H_2}}^{\mathrm{rot}}(T) + f_{\mathrm{H_2}}^{\mathrm{vib}}(T) - D_0, \quad (5)$$

where D_0=4.478eV is the dissociation energy of isolated hydrogen molecules. T and n are temperature and particle number density, respectively. The translational degrees of freedom for each component can then be integrated, yielding

$$f_i^{\mathrm{trans}}(n,T) = k_\mathrm{B}T\ln(\Lambda_i^3 n), \quad (6)$$

where $\Lambda_i = h/\sqrt{2\pi m_i k_\mathrm{B}T}$ is thermal wavelength. The two spin directions of atom lead to the term

$$f_{\mathrm{H}}^{\mathrm{spin}}(T) = -k_\mathrm{B}T\ln 2. \quad (7)$$

The rotational and vibrational states of the H_2 molecule can be integrated and give[14]

$$f_{\mathrm{H_2}}^{\mathrm{rot}}(T) = k_\mathrm{B}T\left[\ln\left(\frac{T_\mathrm{r}}{T}\right) - \frac{T_\mathrm{r}}{3T} - \frac{1}{90}\left(\frac{T_\mathrm{r}}{2T}\right)^2\right], \quad (8)$$

$$f_{\mathrm{H_2}}^{\mathrm{vib}}(T) = k_\mathrm{B}T\left[\ln(1 - \exp(-T_\mathrm{v}/T) + \frac{T_\mathrm{v}}{2T}\right]. \quad (9)$$

The rotational temperature of the H_2 molecule is T_r=85K, and the vibrational temperature of it is T_v = 6210K. The correlation part is determined variationally using the Gibbs–Bogolyubov inequality. In particular, one obtains in the case of a hard sphere (HS) reference system

$$f^{\mathrm{cor}} = \sum_{ij} f_{ij}^{\mathrm{c}} \approx \min_{d_1,d_2}\{f_{\mathrm{HS}}[T,\alpha,\eta_1,\eta_2] + \alpha f_{11}[\alpha n,\eta_1] + 2\alpha(1-\alpha) \times f_{12}[n,\eta_1,\eta_2] + (1-\alpha)f_{22}[(1-\alpha)n,\eta_2]\}. \quad (10)$$

The expression for the free energy of a binary HS reference system is given by[15]

$$f_{\mathrm{HS}}(n,T,\eta_1,\eta_2) = k_\mathrm{B}T\left[\frac{3}{2}(1 + y_1 - y_2 - y_3) + \frac{3y_2 + 2y_3}{1-\eta} + \frac{3}{2}\frac{1 - y_1 - y_2 - y_3/3}{(1-\eta)^2} + (y_3 - 1)\ln(1-\eta)\right], \quad (11)$$

where

$$y_1 = \sum_i \sum_{j>i} \Delta_{ij} \frac{d_i + d_j}{(d_i d_j)^{1/2}},$$

$$y_2 = \sum_i \sum_{j>i} \Delta_{ij} \sum_k \frac{\eta_k}{\eta} \frac{(d_i \cdot d_j)^{1/2}}{d_k},$$

$$y_3 = \left[\sum_i \left(\frac{\eta_i}{\eta} \right)^{2/3} \left(\frac{n_i}{n} \right)^{1/3} \right]^3,$$

$$\Delta_{ij} = \frac{(\eta_i \eta_j)^{1/2}}{\mu} \frac{(d_i - d_j)^2}{d_i d_j} \frac{(n_i n_j)^{1/2}}{n},$$

$$\eta = \sum_i \eta_i, \quad \eta_i = \frac{\pi n_i}{6} d_i^3.$$

Here $\{n_i\}$ and $\{d_i\}$ are the particle number densities and the diameters of the species, respectively. The correlation contributions f_{ij} are given by integrals over the effective pair potential $\phi_{ij}(r)$ and the respective pair distribution functions $g_{ij}(r)$ which are approximated by those of the hard sphere reference system.

$$f_{ii} = 12\eta \int_1^\infty x^2 \phi_{ii}(dx) g_{ii}(x, \eta) \mathrm{d}x, \qquad (12)$$

$$f_{ij} = 12\eta \int_1^\infty x^2 \phi_{ij}(\bar{d}x) g_{ij}(x, \bar{\eta}) \mathrm{d}x, \qquad (13)$$

where $x = r/d$, and

$$d = [6\eta/(\pi n)]^{1/3},$$

$$\bar{d} = [6\eta_{\mathrm{mix}}/(\pi n)]^{1/3},$$

$$\eta_{\mathrm{mix}} = \{(\eta_1/\alpha)^{1/3} + [\eta_2/(1-\alpha)]^{1/3}\}^3/8,$$

$$\bar{\eta} = (\eta_1^{1/3} + \eta_2^{1/3})^3/8.$$

The pair distribution functions of the hard-sphere reference system use the Percus–Yevick analytical expression[16]

$$g(r, \eta) = \frac{1}{24\pi\eta r \mathrm{i}} \int_{\delta - \mathrm{i}\infty}^{\delta + \mathrm{i}\infty} \frac{tL(t)\mathrm{e}^{rt}\mathrm{d}t}{[L(t) + S(t)\mathrm{e}^t]}, \qquad (14)$$

where

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta),$$

$$L(t) = 12\eta[(1 + \frac{1}{2}\eta)t + (1+2\eta)].$$

The integrals in Eq.(14) can thus be evaluated by means of the residue theorem. f_{QM} is the first-order quantum correction in the Wigner–Kirkwood expansion

$$f_{\mathrm{QM}} = \frac{\beta h^2 n N}{24\pi m^*} \int_d^\infty g(r, \eta) \nabla^2 \phi(r) r^2 \mathrm{d}r. \qquad (15)$$

The minimization of the correlation free energy f^{cor} in Eq.(10) is with respect to the packing fractions η_{i}, which is equivalent to minimizing with respect to the hard sphere diameters d_i, and can be performed by the downhill simplex method in multi-dimension.

2.2. Dissociation equilibrium

Pressure dissociation occurs in dense hydrogen as the temperature and pressure are increased. The fraction α of dissociation molecules is determined by the correlation contributions to the chemical potential according to

$$n_{\mathrm{H_2}} = \frac{n_{\mathrm{H}}^2 \Lambda_{\mathrm{H}}^3}{\sqrt{2}} \sigma^{\mathrm{int}} \exp(D_0 - \mu_{\mathrm{H_2}}^{\mathrm{cor}} + 2\mu_{\mathrm{H}}^{\mathrm{cor}}), \qquad (16)$$

$$\sigma^{\mathrm{int}} = \frac{T}{T_{\mathrm{r}}} [1 - \exp(-T_{\mathrm{v}}/k_{\mathrm{B}}T)]^{-1}, \qquad (17)$$

$$\Lambda_{\mathrm{H}} = \frac{h}{\sqrt{2\pi m_{\mathrm{H}} k_{\mathrm{B}} T}}, \qquad (18)$$

where D_0 is the dissociation of isolated H_2 molecules and Λ_{H} the thermal wavelength of H atoms. σ^{int} denotes the internal partition function of vibrational and rotational states. The correlation parts of chemical potentials can be calculated via the following formula

$$\mu_i^{\mathrm{cor}} = \left(\frac{\partial F^{\mathrm{cor}}}{\partial N_i} \right)_{T, V, N_i \neq N_j}. \qquad (19)$$

The condition of chemical equilibrium $\mu_{\mathrm{H_2}} = 2\mu_{\mathrm{H}}$ for the reaction Eq.(2) has to be fulfilled self-consistently within the free energy minimization as the above description by taking into account the correlation contributions to the chemical potentials according to Eq.(19). Then the pressure (P) and the internal energy (E) of the system may be calculated by

$$P = -\frac{\partial F^{\mathrm{tot}}}{\partial V} = \frac{1}{N} \rho^2 \frac{\partial F^{\mathrm{tot}}}{\partial \rho}, \qquad (20)$$

$$E = \frac{\partial(\beta F^{\mathrm{tot}})}{\partial \beta} = -T^2 \frac{\partial}{\partial T} \left(\frac{F^{\mathrm{tot}}}{T} \right), \qquad (21)$$

respectively, where $F^{\mathrm{tot}} = N f^{\mathrm{tot}}$.

3. Results and discussion

The resulting dissociation degree $\alpha = N_{\mathrm{H}}/(N_{\mathrm{H}} + N_{\mathrm{H_2}})$ is shown in Figure 1 as a function of density for various temperatures. As can be seen, the dissociation increases rapidly with increasing temperature and there is a minimum in each of the dissociation

curves from 6000 to 10000K. The position of the minimum is shifted towards the elevated density with the increase of temperature. The minima of the dissociation degree corresponding to the pressures are 2.23, 6.85, and 19.75GPa at T=6000, 8000, and 10000K, respectively. The minimum of the dissociation degree can be derived from the law of mass action combined with the conservation of the total particle number. At constant temperature and pressure, the dissociation degree is a constant when the dissociation of H_2 molecules comes to an equilibrium. As the density increases from 0.02g/cm^3 to 0.6g/cm^3, the probability of the formation of molecules becomes larger due to the collision recombination of atoms, and the chemical equilibrium is shifted towards the reverse reaction $H_2 \leftarrow 2H$. So the dissociation degree becomes smaller. When the formation of molecules due to the collision recombination of atoms and the collision dissociation of molecules are dynamically balanced with the increase of the density of the system, the dissociation degree comes to a minimum. Further increase in density, the probability of the formation of molecules could become larger due to the collision recombination of hydrogen atoms, but at the same time the probability of the collision dissociation and the repulsive interaction of H atoms would also be increased, the probability of the hydrogen atoms combined to form H_2 molecules would become smaller. At this point, the chemical equilibrium is shifted towards the positive reaction $H_2 \rightarrow 2H$. Therefore the dissociation degree will become larger, and the pressure dissociation will become dominate. The dissociation degree curves in Fig.1 corresponding to the curves of the pressure versus density at the same temperature are shown in Fig.2, along with the data obtained in Monte-Carlo(MC) calculations based on the same potentials for H–H_2 mixture at temperatures between 6000 and 10000K.[17] Note that the general agreement between the MC calculations and the present results is very good below 0.6g/cm^3. The deviations from the MC pressures increase systematically with the density ($\rho > 0.6$g/cm^3). The reason is that the many-particle nature of the interaction might not be well approximated by those effective pair potentials for density above 0.6g/cm^3. Another effect, pressure ionization of hydrogen atoms, should occur under these conditions as well. The polarization correction for the interaction between electrons and neutral particles should be taken into account. Therefore, the short-range parts of the effective pair potentials become more and more important for very high densities.

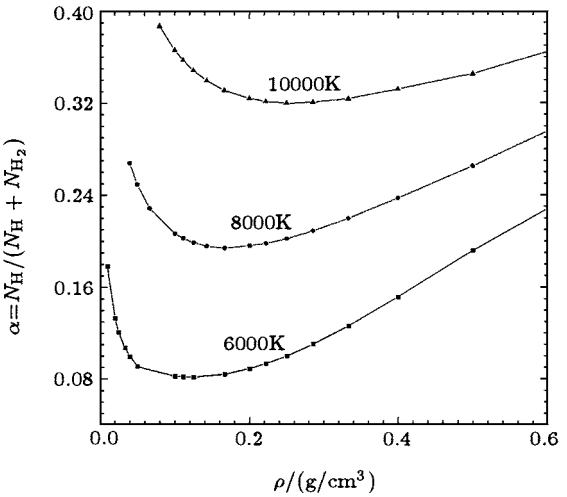


Fig.1. Dissociation degree of fluid hydrogen as a function of the density at different temperatures.

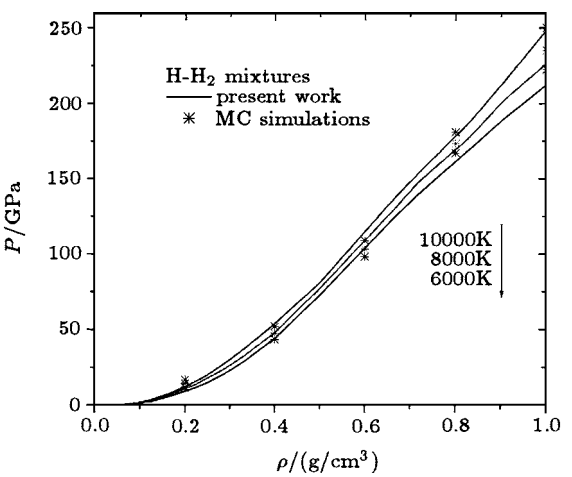


Fig.2. Isotherms for the H-H_2 mixture as a function of density at different temperatures.

Figure 3 shows the concentration of atomic and molecular hydrogen as a function of density at temperature 10000K. For density between ρ=10^{-3} and 0.07 g/cm^3, it shows strong recombination as given by the law of mass action. At higher densities, strong nonideal correlation effects come play, decreasing the dissociation energy and favouring molecular dissociation and ultimately leading to pressure ionization. Temperature dissociation effects are clearly displayed by the low-density part of the isotherm sequence. Note that the hydrogen molecules are the dominant species in the density range of ~0.07–0.5(g/cm^3), the hydrogen atoms are the dominant species beyond this density range. The dissociation degree increases with increasing density.

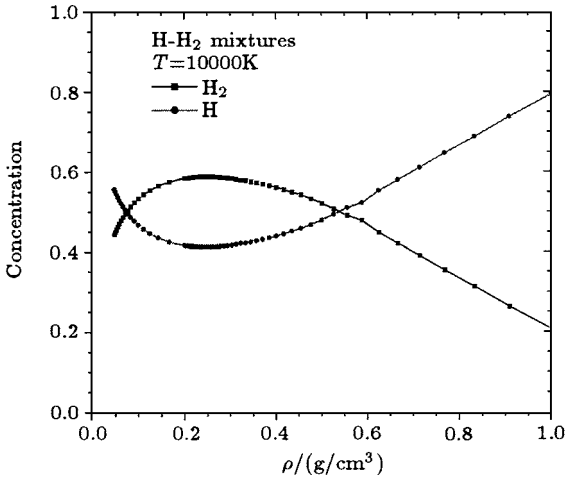


Fig.3. Concentration of atomic and molecular hydrogen as a function of density.

In Fig.4, the pressure is shown as a function of temperature for a constant volume of V =6.0cm^3/mol (r_s=2, where $r_s = d/a_B$ is the mean distance d between the electrons in units of Bohr radius a_B). The present SFVM is compared with path-integral Monte Carlo (PIMC),[18,19] quantum molecular dynamics (QMD)[7] simulations based on a tight-binding electronic structure calculation, tight-binding molecular dynamics (TBMD),[20] wave-packet molecular dynamics (WPMD)[21] simulations, and the linear-mixing (LM) model.[22] The present results lie between those of WPMD and LM in the entire temperature range. The pressure increases very slowly with increasing temperature between 5000 and 14000K, which indicates where the dissociation occurs. The pressure-temperature curves from WPMD and LM show a similar behaviour of the pressure but at values higher and lower than the present absolute values, respectively. The deviations of the present calculations from those of WPMD and LM come from the fact that the dissociation reaction has not been included in the WPMD and LM. The present SFVM and WPMD calculations show an increase of the pressure with increasing temperature up to about 5000K. Further increase in temperature causes the dissociation of the molecules to atoms, leading to a decrease of the thermal pressure. This effect nearly cancels the increase of the kinetic energy with temperature, so we observe a region with $(\partial p/\partial T)_n \approx 0$ between 5000 and 12000K. PIMD seems to overestimate the effectiveness of dissociation below 10000K so that a region with $(\partial p/\partial T)_n < 0$ occurs. The additional considerations of ionization in our model would lead to lower pressure at higher temperatures. Therefore, the present SFVM is applicable to the calculation of EOS in the range of temperature from 2000 to 10000K and density from 0.1 to 0.6g/cm^3.

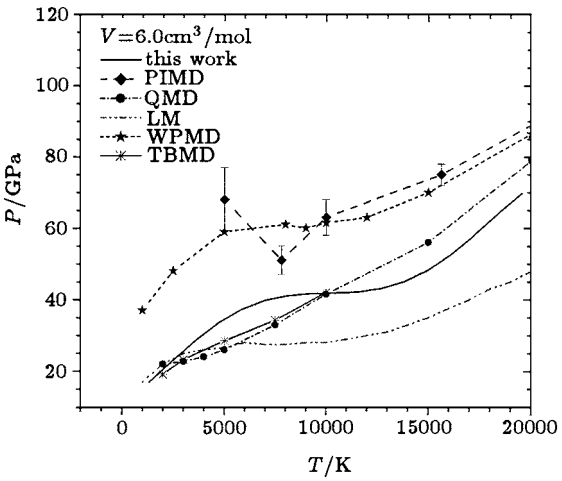


Fig.4. Pressure as a function of the temperature for a constant specific volume of V=6cm^3/mol.

4. Summary

The self-consistent fluid variational model and effective pair potential have been successfully used to describe the phenomenon of molecular dissociation, caused by both temperature and pressure effects in the range of temperature 2000–10000K and density below 0.6g/cm^3. The present SFVM produces pressure and temperature dissociation varying continuously as either the density or temperature increases. SFVM represents a significant effect to describe the interaction properties in a dense mixture of atoms and molecules in chemical equilibrium. It has immediate applications in the study of outer layers of giant planets and the analysis of shock compression experiments on hydrogen, where partial dissociation may occur. Applications of the SFVM to experiments on other diatomic molecules are straightforward. The pressure ionization, the polarization correction for the interaction between electrons and neutral particles, and the many-particle nature of the interaction are not well taken into account in the present calculational model, which leads to the important reason of deviations. In another paper we will take into account the ionization equilibrium H⇌e+p.

References

[1] Sun J X, Wu Q, Cai L C and Jing F Q 2003 *Chin. Phys.* **12** 632

[2] Chen Q F, Sun Z H, Cai L C and Jing F Q 2001 *Chin. Phys.* **10** 1144

[3] Bunker A, Nagel S, Redmer R and Röpke 1997 *Contrib. Plasmas Phys.* **37** 115

[4] Ross M 1996 *Phys. Rev.* B **54** R9589

[5] Ceperley D M, Pierleoni C and Bernu B 1996 *Phys. Rev. Lett.* **76** 1240

[6] Klakow D, Toepffer C and Reinhard P G 1994 *Phys. Lett.* A **192** 55

[7] Collins L, Kwon I, Kress J and Troullier N 1995 *Phys. Rev.* E **54** 6202

[8] Lenosky T J, Kress J D, Collins L A *et al* 1997 *Phys. Rev.* B **55** R11907

[9] Lenosky B, Bickham S R, Kress J D and Collins L A 2000 *Phys. Rev.* B **61** 1

[10] Saumon D, Chabrier G, Wagner D J and Xie X 2000 *High Press. Res.* **16** 331

[11] Knudson M D, Hanson D L, Bailey J E *et al* 2001 *Phys. Rev. Lett.* **87** 225501

[12] Collins G W, Mcelliers P, Da Silva L B *et al* 2001 *Phys. Rev. Lett.* **87** 165504

[13] Ross M, Ree F H and Young D A 1983 *J. Chem. Phys.* **79** 1487

[14] Ebeling W, Steinberg M and Ortner J 2003 *Eur. Phys. J.* D **23** 265

[15] Ebeling W, Förster A, Fortov V E, Gryaznov V K and Polishchuk A Ya 1991 *Thermophysical Properties of Hot Dense Plasmas* (Stuttgart: Teubner) p24

[16] Smith W R and Henderson D 1970 *Mol. Phys.* **19** 411

[17] Ree F H 1983 *J. Chem. Phys.* **78** 409

[18] Militer B and Ceperley D M 2001 *Phys. Rev.* E **63** 066404

[19] Militzer B 2000 Path Integral Monte Carlo Simulations of Hot Dense Hydrogen Ph.D. thesis, University of Illinois at Urbana-Champaign p145

[20] Lenosky T J, Kress J D and Collins L A 1999 *Phys. Rev.* E **60** 1665

[21] Knaup M, Reinhard P G and Toepffer K 1999 *Contrib. Plasmas Phys.* **39** 57

[22] Ross M 1998 *Phys. Rev.* B **58** 669