

## Hopping conductivity in dense hydrogen fluid

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A transition from semiconducting behavior to conductivities typical for simple metals was observed in dense hydrogen fluid at 1.4 Mbar and 3000 K in multiple shock-compression experiments [S. T. Weir, A. C. Mitchell, and W. J. Nellis, *Phys. Rev. Lett.* **76**, 1860 (1996)]. Various mechanisms such as band gap closure, self-doping, or thermally activated transport have been proposed to explain this nonmetal-to-metal transition. We perform an exploratory calculation of the hopping conductivity in dense hydrogen fluid which is considered as a partially dissociated system of H atoms and H<sub>2</sub> molecules. It is shown that hopping processes between H atoms play an important role in this nonmetal-to-metal transition.

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The equation of state (EOS) and the electrical conductivity of fluid hydrogen were determined in single and multiple shock-compression experiments up to high pressures. The exponential increase of the electrical conductivity is typical for thermally activated transport in semiconductors and was explained with a decrease of the band gap with increasing pressure.<sup>1</sup> For ultrahigh pressures above 1.4 Mbar, conductivities of about  $2 \times 10^5$  ( $\Omega \text{ m}$ )<sup>-1</sup> as characteristic for simple metallic fluids such as Cs have been observed experimentally around 3000 K.<sup>2</sup>

The concept of band gap closure, which is strictly valid only for solid insulators at  $T=0$  K, has been generalized for finite temperatures to treat this nonmetal-to-metal transition. However, the mechanism of this electronic transition in a strongly correlated, disordered fluid at finite temperatures is not clear yet. For instance, dissociation of hydrogen molecules becomes important in the megabar region due to the lowering of the dissociation energy. Corresponding dissociation models yield a reasonable agreement with the measured EOS data and the Hugoniot curves.<sup>3-6</sup>

Ross<sup>4</sup> has proposed a self-doping process such that atoms generated by pressure dissociation of molecules act as donor states which are easily thermally activated so that metallic-like conductivities may occur.

Within a partially ionized plasma (PIP) model, free electrons are generated by dissociation of molecules,  $\text{H}_2 \rightleftharpoons 2 \text{H}$ , and a subsequent ionization of atoms,  $\text{H} \rightleftharpoons \text{e} + \text{p}$ . This model yields a strong increase of the conductivity with the pressure but does not match the experimental data at ultrahigh pressures very well.<sup>7</sup>

Percolation theory has been applied to the region of the nonmetal-to-metal transition in fluid hydrogen as well.<sup>8</sup> Assuming that a virtual molecular structure exists, the electrical conductivity shows also a strong increase with the pressure but saturates at values which are two orders of magnitude higher than the experimental ones.

On the other hand, quantum molecular dynamics simulations have shown that hydrogen displays a highly transient nature at high pressures.<sup>9</sup> The lifetime of diatomic molecules is of the order of only few vibrational periods. While the

equilibrium properties are well described by time averaged quantities, the transport properties may be strongly influenced by fluctuations of the charge density. New simulations underline the importance of atoms for the nonmetal-to-metal transition considering the relation between conductivity and dissociation fraction and the behavior of the density of states (DOS) near the Fermi level.<sup>10</sup> It was concluded that *hopping processes* between atoms are important for electronic conduction under megabar pressures, see also Refs. 2(b) and 7. The calculated resistivity<sup>10</sup> shows qualitative agreement with the experimental trends.

We apply a model which treats both delocalized (free) and localized (bound) states so that thermally activated transport as well as hopping transport can be described simultaneously. While the treatment of free electron transport is well developed, the calculation of the hopping contribution is still in an exploratory stage but will lead into more insight about the nature of the nonmetal-to-metal transition in fluid hydrogen under megabar pressures.

We start with an effective Hamiltonian which can be derived by summing up certain classes of Feynman diagrams, Refs. 11 and 12, yielding the PIP model within the chemical picture:

$$\begin{aligned}
 H_S = & \sum_k E_k a_k^\dagger a_k + \frac{1}{2} \sum_{kk'q} V_q a_{k+q}^\dagger a_{k'-q}^\dagger a_k' a_k \\
 & + \sum_{m\sigma, kq} (V_q + M_{q,m} a_{m,\sigma}^\dagger a_{m,\sigma}) \exp(i\mathbf{q} \cdot \mathbf{R}_m) a_{k+q}^\dagger a_k \\
 & + \sum_{m\sigma} E_m a_{m,\sigma}^\dagger a_{m,\sigma} + \sum_{mm'\sigma} t_{mm'} a_{m',\sigma}^\dagger a_{m,\sigma} \\
 & + \frac{U}{2} \sum_{m\sigma} a_{m,\sigma}^\dagger a_{m,\sigma} a_{m,-\sigma}^\dagger a_{m,-\sigma}. \quad (1)
 \end{aligned}$$

We define the kinetic energy  $E_k = \hbar^2 k^2 / (2m_e)$  of delocalized electrons,  $k$  contains the wave number  $\mathbf{k}$  and spin. Elastic scattering of these electrons with ions and other free electrons is described by the Coulomb potential  $V_q$

TABLE I. Composition of dense hydrogen fluid along the 2500 K isotherm according to the PIP model.

$\varrho$ in g/cm <sup>3</sup>	$\alpha_{\text{dis}}$	$\alpha_{\text{ion}}$
0.10	$0.80 \times 10^{-4}$	$0.90 \times 10^{-15}$
0.20	$0.19 \times 10^{-3}$	$0.71 \times 10^{-13}$
0.30	$0.58 \times 10^{-3}$	$0.76 \times 10^{-11}$
0.40	$0.14 \times 10^{-2}$	$0.78 \times 10^{-9}$
0.50	$0.62 \times 10^{-2}$	$0.10 \times 10^{-6}$
0.60	$0.26 \times 10^{-1}$	$0.58 \times 10^{-5}$
0.70	$0.76 \times 10^{-1}$	$0.55 \times 10^{-4}$
0.75	0.10	$0.10 \times 10^{-3}$
0.82	0.12	0.12
0.88	0.14	0.24
0.90	0.15	0.25
0.95	0.18	0.27
1.00	0.20	0.28

$=e^2/(\epsilon_0 q^2 \Omega_0)$ . The atomic form factor for elastic scattering at localized states with wave function  $\psi_m(p)$  reads  $M_{q,m} = V_q \sum_p \psi_m^*(p) [\psi_m(p) - \psi_m(p-q)]$ . Localized electrons with energies  $E_m$  independent of the position at site  $\mathbf{R}_m$  are described by the hopping matrix element  $t_{mm'} = t(\mathbf{R}_m' - \mathbf{R}_m)$  and the Coulomb repulsion term  $U$  for two electrons of opposite spin  $\sigma$  on the same site. Recombination and ionization processes are assumed as not contributing to conducting processes, and hydrogen atoms and molecules are considered to be in the ground state,  $E_m = E_0^{\text{H}}, E_0^{\text{H}_2}$ .

An important quantity in the PIP model is the composition which can be given in terms of the degree of ionization  $\alpha_{\text{ion}} = N_e/N$  and dissociation  $\alpha_{\text{dis}} = N_{\text{H}}/N$ .  $N_e = N_p$ ,  $N_{\text{H}}$ , and  $N_{\text{H}_2}$  denote the number of free electrons, protons, H atoms, and H<sub>2</sub> molecules, respectively, and  $N = N_e + N_{\text{H}} + 2N_{\text{H}_2}$  is the total number of electrons. The composition can be determined by combining equations of state for the dense, partially dissociated fluid and the fully ionized plasma, see Ref. 13. The respective dissociation and ionization degrees serve as input for the calculation of the electrical conductivity and are given in Table I for densities up to 1 g/cm<sup>3</sup> and a temperature of 2500 K which is close to the experimental conditions.<sup>2</sup> Comparison with other EOS data and Hugoniot curves shows reasonable agreement for low temperatures  $T \leq 5000$  K, see Ref. 6. Therefore, we give an accuracy of about 10% in the presented EOS.

We can define three regions: A partially dissociated fluid below 0.75 g/cm<sup>3</sup> with almost no ionization ( $\alpha_{\text{ion}} \leq 10^{-4}$ ), the instability region of the plasma phase transition (PPT) between 0.75 g/cm<sup>3</sup> and 0.88 g/cm<sup>3</sup>, and a partially ionized fluid ( $\alpha_{\text{ion}} \geq 0.25$ ) for higher densities. In the coexistence region, a two-phase mixture was considered to obtain the dissociation and ionization degrees.

The electrical conductivity of a system with delocalized and localized electrons can be treated within linear response theory.<sup>11,14,15</sup> The total Hamiltonian  $H = H_S + H_F + H_B$  consists of the system Hamiltonian  $H_S$  given by Eq. (1), the coupling to a constant external electric field  $H_F = -e\mathbf{E} \cdot \mathbf{R}$

with the position operator for the electrons  $\mathbf{R} = \sum_i \mathbf{r}_i$ , and a bath  $H_B$  which represents the possibility of particle and heat transfer through the system. The total current density of such a system exposed to an external field  $\mathbf{E}$  is given by

$$\langle \mathbf{j} \rangle = \text{Tr}\{\varrho \mathbf{j}\} = \frac{e}{\Omega_0} \text{Tr}\{\varrho \dot{\mathbf{R}}\} \equiv \sigma \mathbf{E}. \quad (2)$$

$\varrho$  is the nonequilibrium statistical operator,  $\Omega_0$  the system volume, and  $\sigma$  the electrical conductivity. The time derivative of the position operator of localized and delocalized electrons,

$$\mathbf{R} = \sum_{m\sigma} \mathbf{R}_m a_{m,\sigma}^\dagger a_{m,\sigma} - \sum_{k,k'} i \frac{\partial}{\partial \mathbf{k}} \delta(\mathbf{k} - \mathbf{k}') a_{k'}^\dagger a_k, \quad (3)$$

is calculated via  $\dot{\mathbf{R}} = i[H_S, \mathbf{R}]/\hbar = \dot{\mathbf{R}}_{\text{hop}} + \dot{\mathbf{R}}_{\text{del}}$  with

$$\begin{aligned} \dot{\mathbf{R}}_{\text{hop}} &= \frac{i}{\hbar} \sum_{mm'\sigma} t_{mm'} (\mathbf{R}_m - \mathbf{R}_{m'}) a_{m'}^\dagger a_{m,\sigma} \\ \dot{\mathbf{R}}_{\text{del}} &= \frac{1}{\hbar} \sum_k \frac{\partial}{\partial \mathbf{k}} E_k a_k^\dagger a_k. \end{aligned} \quad (4)$$

The total current density (2) is the sum of the hopping current of localized states and the current of thermally activated delocalized states, i.e.,  $\langle \mathbf{j} \rangle = \langle \mathbf{j}_{\text{hop}} \rangle + \langle \mathbf{j}_{\text{del}} \rangle$ . The total conductivity is also additive if ionization and recombination processes are neglected,  $\sigma = \sigma_{\text{hop}} + \sigma_{\text{del}}$ .

We apply linear response theory to construct the nonequilibrium statistical operator  $\varrho$ . For the electrical conductivity of delocalized states, we find a Chapman-Enskog type determinant representation,<sup>15,16</sup>

$$\sigma_{\text{del}} = - \frac{\beta e^2}{m_e^2 \Omega_0} \frac{1}{|(D_{nm})|} \begin{vmatrix} 0 & (N_{0m}) \\ (N_{n0}) & (D_{nm}) \end{vmatrix}, \quad (5)$$

where  $\beta = 1/(k_B T)$ . The elements of the matrices, the correlation functions  $N_{nm} = (\mathbf{P}_n, \mathbf{P}_m)$  and  $D_{nm} = \langle \dot{\mathbf{P}}_n(\tau), \dot{\mathbf{P}}_m \rangle + (\dot{\mathbf{P}}_n, \mathbf{P}_m)$ , are defined in Refs. 12, 15, and 16. The moments of the distribution function  $\mathbf{P}_n = \sum_k \hbar \mathbf{k} (\beta E_k)^n a_k^\dagger a_k$  characterize, as a set of relevant observables, the nonequilibrium state. The electrical conductivity (5) is determined here within a three-moment approximation:  $n, m = \{0, 1, 2\}$ .

The correlation functions  $N_{nm}$  and  $D_{nm}$  can be evaluated for arbitrary degeneracy using Wick's theorem. The  $N_{nm}$  are given by multiples of the particle number. The force-force correlation functions  $D_{nm}$  are determined by the system Hamiltonian (1) via  $\dot{\mathbf{P}}_n = i[H_S, \mathbf{P}_n]/\hbar$  and contain contributions due to electron-proton, electron-electron, and electron-atom scattering within a molecular background:  $D_{nm} = D_{nm}^{ep} + D_{nm}^{ee} + D_{nm}^{eH}$ . The scattering processes between charged particles are treated on  $T$  matrix level performing a phase shift analysis with respect to the Debye potential. Elastic electron-atom scattering is treated in  $T$  matrix approximation with respect to a screened polarization potential. In the case of large ionization degrees, i.e., if free electrons dominate the

conduction process, a Ziman type expression for the electrical conductivity should be applicable, see Ref. 17.

The hopping conductivity derived from Eq. (4) is proportional to the squares of the hopping matrix element and the distance between the sites  $m$  and  $m'$ ,<sup>11</sup>

$$\sigma_{\text{hop}} = \frac{\pi\beta e^2}{3\hbar\Omega_0} \sum_{mm'} |t_{mm'}|^2 (\mathbf{R}_m - \mathbf{R}_{m'})^2 f_m(1-f_m) \times \delta(E_m - E_{m'}). \quad (6)$$

The distribution function of initial and final states is given by  $f_m = [1 + e^{\beta(E_m - \mu)}]^{-1}$ . Introducing the DOS  $D(E)$  for the energy distribution, we get

$$\sigma_{\text{hop}} = -\frac{\pi e^2}{3\hbar\Omega_0} \sum_{mm'} |t_{mm'}|^2 \times (\mathbf{R}_m - \mathbf{R}_{m'})^2 \int dE [D(E)]^2 \frac{d}{dE} f(E). \quad (7)$$

At zero temperature, the derivative of the Fermi distribution function can be replaced by a  $\delta$ -function,  $(d/dE)f(E) = -\delta(E - E_F)$ , so that only states near the Fermi energy contribute to the hopping conductivity. This coincides with the random phase model as it was applied to expanded fluid alkali metals.<sup>18,19</sup>

The configurational average over all atomic sites  $m$  and  $m'$  in Eq. (7) yields the pair distribution function  $g_{\text{HH}}$  and we have

$$\sigma_{\text{hop}} = \frac{\pi}{3} \sigma_0 J_4 \int dE [D(E)]^2 \frac{d}{dE} f(E), \quad (8)$$

with a density-dependent integral

$$J_l = 4\pi [n_{\text{H}} a_{\text{B}}^3]^{l/2} \int_0^\infty dx x^l g_{\text{HH}}(x) |t(x)|^2. \quad (9)$$

The unit of the conductivity is  $\sigma_0 = e^2/\hbar a_{\text{B}} = 4.6 \times 10^6 (\Omega \text{ m})^{-1}$  with the Bohr radius  $a_{\text{B}}$  and  $x = r/a_{\text{B}}$ .

Considering the Hubbard part of the Hamiltonian (1) for the electrons bound in atoms, a DOS can be derived from the configurationally averaged Green function  $\bar{G}(z)$  via  $D(E) = -\text{Im} \bar{G}(E + i0)/\pi$ . A graph-theoretical analysis of the configurationally averaged Green function for a random tight-binding model characterized by quenched liquid-like disorder was performed in Refs. 20 and 21. In simplest approximation, the DOS is given as a semi-elliptic band centered at  $\omega = E - E_0^{\text{H}} = 0$  with the bandwidth  $4\sqrt{J_2}$ . Taking into account the exchange term  $U$  leads to a further split of this band. A solution for the Green function is obtained within the Hubbard-III approximation,<sup>22</sup>

$$\bar{G}(\omega) = \frac{1}{2J_2} [F(\omega) \pm \sqrt{4J_2 - F(\omega)^2}], \quad (10)$$

where the complex function  $F(\omega)$  is density dependent via  $J_2$  and the fraction of bound electrons with spin  $\sigma$ ,  $n_\sigma = 0.5 N_{\text{H}}/(N_{\text{H}} + N_e)$ , which are able to move by hopping

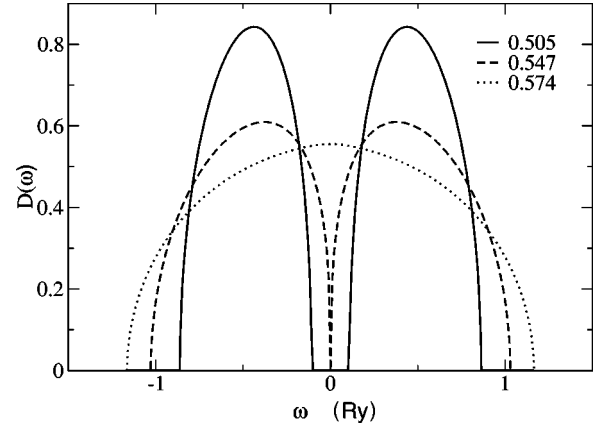


FIG. 1. Density of state for hydrogen fluid within the disordered Hubbard approximation for  $\rho = 0.505, 0.547,$  and  $0.574 \text{ g/cm}^3$ .

processes within the band.  $F(\omega)$  takes into account higher order corrections and leads to band gap closure for an increasing ratio  $J_2/U$ .

We estimate the hopping matrix element  $t(x)$  by the overlap integral of the ground state wave functions for hydrogen,  $t(x) = t_0(1+x)\exp(-x)$ , where  $t_0 = 2 \text{ Ry}$  sets the energy scale. The on-site exchange energy  $U$  can be estimated from the lowest energy for a state with two electrons at one site, the binding energy of  $\text{H}^-$ ,  $E_b(\text{H}^-) = 0.75 \text{ eV}$ , and we have  $U = [1 - (0.75/13.6)] \text{ Ry} = 0.945 \text{ Ry}$ . The pair distribution function  $g_{\text{HH}}$  is taken from Monte Carlo simulations for partially dissociated, fluid hydrogen.<sup>5,6,23</sup> The resulting DOS is shown for three densities in Fig. 1. Band gap closure occurs above  $0.547 \text{ g/cm}^3$ . The hopping conductivity is then obtained via Eq. (8).

Figure 2 shows the electrical conductivity of fluid hydrogen as a function of the mass density for 2500 K. The transition from semiconducting behavior to metallic-like conductivities is observed experimentally at about  $0.65 \text{ g/cm}^3$  where the conductivity saturates at values which are typical for fluid metals like cesium.

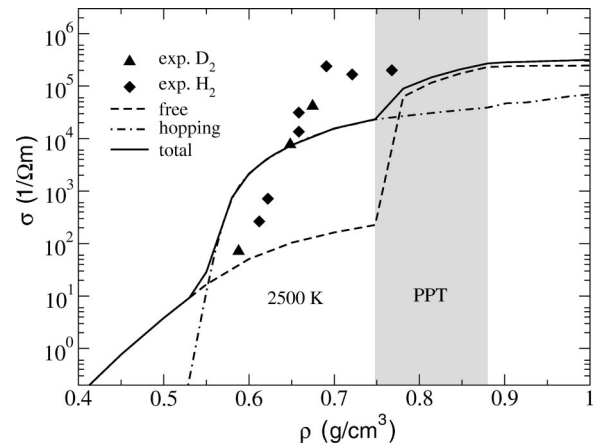


FIG. 2. Electrical conductivity of fluid hydrogen at 2500 K: Experiments (Ref. 2), conductivity of free electrons (5) (dashed line), hopping conductivity (8) between H atoms (dash-dotted line), and total conductivity (solid line). The coexistence region of the PPT is indicated by the shaded area; see Ref. 13.

Below  $0.5 \text{ g/cm}^3$ , the conductivity of delocalized states (5) shows a strong increase with the density according to the composition, see Table I. Reasonable agreement with the single shock experiments<sup>1</sup> has been achieved in that region.<sup>24</sup> For densities up to  $0.75 \text{ g/cm}^3$ , this contribution to the total conductivity is substantially smaller than the experimental values because the ionization degree remains less than 0.1%.

The hopping conductivity (8) shows an even stronger increase with the density in the transition region from semiconducting to metallic-like behavior between  $0.5$  and  $0.7 \text{ g/cm}^3$  because H atoms are created by pressure dissociation which is a density effect and the DOS is also density dependent, see Fig. 1. There, the hopping conductivity is up to two orders of magnitude higher than that of delocalized electrons.

The shaded area in Fig. 2 between  $0.75$  and  $0.88 \text{ g/cm}^3$  describes an instability region of the EOS which is usually interpreted as a PPT: A semiconducting, partially dissociated phase coexists with a partially ionized phase with plasma-like conductivity. For densities above  $0.88 \text{ g/cm}^3$ , delocalized electrons dominate the conduction process again due to a relatively high but almost constant ionization degree of about 25% so that the conductivity saturates as found experimentally.

We conclude that the electrical conductivity in dense hydrogen fluid follows different regimes. Thermally activated electron transport as in semiconductors is clearly relevant below  $0.5 \text{ g/cm}^3$ . The transition to metallic-like conductivities which occurs between  $0.5$  and  $0.7 \text{ g/cm}^3$  can be explained by hopping processes between H atoms in a partially dissociated fluid as it has been discussed in Refs. 2(b), 7, and 10. Plasma-like conductivities occur near  $1 \text{ g/cm}^3$  in the partially ionized fluid domain.

Our results for the conductivity are not strongly dependent on the parameters of the Hubbard model. The closure of the Coulomb gap responsible for the steep increase of the conductivity derives from the concentration of hydrogen atoms given in Table I. A better treatment of the configurational average when calculating the DOS and of the hopping conductivity similar to the disordered tight-binding model<sup>18–20</sup> should lead to a continuous transition from hopping to itinerant electron transport with increasing density. This is of relevance in order to perform a quantitative comparison with the experimental data.

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