ЖЭТФ, 1998, том 113, вып. 3, стр. 1094–1100

IS SUPERDENSE FLUID HYDROGEN A MOLECULAR METAL?

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Submitted 18 July 1997

Recent experiments on the compression of liquid hydrogen in reverberating shock waves indicating the transition into a metallic state at about nine times liquid-H_2 density [4] have been interpreted by a microscopic percolation in a virtual molecular structure with a continuous spectrum of the electron excitations. The scaling dependence of the electron mobility on the energy above the percolation threshold has been used to qualitatively describe the electrical conductivity of fluid molecular hydrogen in the vicinity of the insulator–metal transition point.

Metallic hydrogen, the simplest element in the periodic system and the most abundant in the Universe, has been extensively studied as the prototype of the insulator–metal transition for over half a century [1]. The current research is mainly motivated by the significance of metallic hydrogen in astrophysics, especially for the magnetic-dynamo models of Jupiter and Saturn [2]. Although in this field the disordered phases are actually interesting, the insulator–metal transition is traditionally considered in solids, and most experiments have been done in diamond anvil cells at very low temperatures. At ninefold compression a phase transition indicated by the appearance of a strong infrared absorption band has been recovered, but the onset of metallization because of the band gap closure in solid molecular hydrogen is still a subject of controversy [3]. Recently, Weir, Mitchell, and Nellis [4] have reached almost the same densities in a fluid phase at much higher but still moderate temperatures by strongly compressing liquid hydrogen in reverberating shock waves. Under these conditions, a qualitative change of the electronic structure is revealed by strongly changing electronic properties, despite the thermal excitations which play a masking role. In the density range $(1.7–2.1)\cdot 10^{23}\,\mathrm{cm}^{-3}$, at temperatures in the range 2000–4000 K the electrical conductivity of shock-compressed fluid hydrogen increases by more than three orders of magnitude to 2000 $\Omega^{-1}\cdot\mathrm{cm}^{-1}$, a value characteristic of metals. When the densities are lower, there is activation energy, which goes to zero at approximately $1.9\cdot 10^{23}\,\mathrm{cm}^{-3}$, marking the onset of metallization.

If even solid hydrogen is nonmetallic, the liquid can be metallic as is the case of silicon. Therefore, analysis of the insulator–metal transition in fluid hydrogen is based on the theory of disordered electron systems [5, 6] rather than on the theory of crystalline solids. Recently, Ross [7] has proposed the metallization of H-atom subsystem in partially dissociated fluid hydrogen. We show that more naturally molecular hydrogen is metallized wholly.

Strong electron–ion interaction makes the structure near the insulator–metal transition in fluid hydrogen close to the neutral molecular fluid. Therefore, analysis can be based on a microscopic percolation model [8] which has been applied to expanded fluid mercury [9], sodium–ammonia solutions [10], and doped semiconductors Si : P [11]. The underlying idea is a virtual atomic-like structure which is retained in such systems in the transition region where atoms are in mixed states described by the density matrix. Since classically accessible spheres of

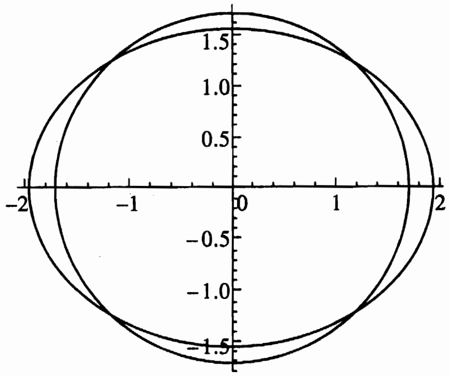

Fig. 1. Classically accessible region of the molecular orbital of hydrogen on the atomic unit scale. The mean sphere of the same volume is also shown

valence electrons of neighboring atoms overlap, screening leads to admixing of free-like electron states. In the microscopic percolation model a sharp change of the electrical conductivity below the insulator–metal transition is governed by a high coupling parameter, namely, the ionization potential of atoms in expanded metals, or admixture states in ammonia solutions and semiconductors to the temperature. Applying this model to hydrogen, which consists of strongly bound two-atomic molecules, we assume a virtual molecular structure. Otherwise, near the insulator–metal transition point we consider fluid hydrogen a molecular metal with partially free electrons in bonding quasimolecular orbitals admixed with free electron states (in contrast, nearly free metallic electrons could not bound the molecules). Two electrons of H_2 quasimolecules in a virtual molecular structure are equivalent and contribute equally to the conductivity. We show that the percolation model of the insulator–metal transition is capable to qualitatively describing the electronic properties of such a virtual molecular structure. The model of a virtual molecular structure can also shed light on a plasma phase transition, whose existence in hydrogen is still strongly questionable [12].

Presumably, a virtual molecular structure exists at temperatures much lower than the ionization or dissociation energy of molecules and at moderately high densities, at which the molecular orbitals are not strongly overlapped. In such a structure, the transition point can be identified with a percolation threshold of the classically accessible regions of electrons in the ground-level molecular orbitals. Since electrons are mainly localized within the classically accessible region, the effective one-electron potential near the boundary of this region is close to the molecular ion potential. Thus, the boundary surface is determined by the equation

$$-\frac{e^2}{2r_1}-\frac{e^2}{2r_2}=-J, \qquad (1)$$

where e is the electron charge, r_1 and r_2 are the distances of an electron from the nuclei, $J \approx 16$ eV is the vertical ionization potential of the molecules. This surface, which is close to the prolate ellipsoid with half-axes $1.55a_0$ and $1.95a_0$, where a_0 is the Bohr radius (Fig. 1), bounds almost the same volume as a mean sphere of radius

$$R_m=\frac{e^2}{J}. \qquad (2)$$

The upper limit for the percolation threshold corresponds to ellipsoids with the parallel rotational axes, which coincides with that of spheres of the same volume. Furthermore, for the strongly correlated fluids like hard spheres with very thin overlapping shells [13], the percolation threshold corresponds to the random close packing fraction,

$$\frac{4\pi}{3}R_m^3\, n_m = \zeta_{th}, \tag{3}$$

where n_m is the molecule number density, and $\zeta_{th} \approx 0.64$. We note that Eq. (3) can be rewritten as the Edwards–Sienko correlation for the insulator–metal transitions in doped semiconductors [14]:

$$\frac{e^2 n_m^{1/3}}{J} = 0.534.$$

From Eqs. (2) and (3) we obtain the number density of hydrogen molecules at the insulator–metal transition point:

$$n_m \approx 2.1 \times 10^{23}\ \ \mathrm{cm}^{-3},$$

which corresponds to the mass density 0.7 g/cm^3. This value agrees within the experimental uncertainty with the above-mentioned estimate from the disappearance of the activation energy [4].

The Coulomb interaction in a strongly coupled plasma above the insulator–metal transition point is characterized by the coupling parameter

$$\Gamma = \frac{z^2e^2}{R_sT} = \zeta_{th}^{1/3} z^2 \frac{J}{T}, \tag{4}$$

where $z = 2$ is the total charge number of tightly bound protons, and $R_s = (4\pi n_m/3)^{-1/3}$ is the Wigner–Seitz radius of the molecular cell. Although the classical Coulomb parameter is higher than 10^2, it does not necessarily strongly influence the structure of compressed fluid determined by the repulsion between quasimolecules. Evidently, strongly repulsive exchange interaction between quasimolecules in the dense hydrogen plasma precludes a plasma phase transition, which is induced otherwise by the Coulomb attraction.

The overlap of the classically accessible regions of electrons in neighboring molecules qualitatively changes the electronic states. The number of electrons screening the nuclei can fluctuate; i.e., the nuclei are virtually screened by electrons of neighboring molecules. Therefore, in mixed quasimolecular states electrons are partially free, and the spectrum of excitations is continuous. According to the variational principle of quantum mechanics, an internal energy spectrum of a quasimolecule (i.e., without the energy of the intermolecular interactions) is bound from below by the ground energy level of the free molecule. Using molecular orbitals, we write the one-electron energy spectrum in a form

$$E_p = -J + \varepsilon_p, \quad \varepsilon_p = p^2/2m, \tag{5}$$

where ε_p is the electron excitation energy, p is the momentum of an electron far from the virtually screened nuclei, and m is the electron mass. On the other hand, the mean internal energy of the quasimolecule in a mixed state is

$$E_p = -a_{00}J + a_{pp}\varepsilon_p, \tag{6}$$

where a_{pp} and a_{00} are the diagonal elements of the density matrix normalized by the condition $a_{pp} + a_{00} = 1$. From Eqs. (5) and (6), it follows that the admixture of free motion in the quasimolecular orbitals, which is determined by the ratio of the matrix elements, is

$$a_{pp}/a_{00} = \varepsilon_p/J. \tag{7}$$

Therefore, low-lying quasimolecular states, which are preferably occupied, contain only a small admixture of free motion. The lifetime and the extension of the quasimolecular states, which in neighboring molecules can overlap, are bound by transitions of electrons between molecules [8].

In the vicinity of the insulator–metal transition point the electric current is carried by electrons which transfer between overlapping, classically accessible spheres in a virtual molecular structure. Although below the transition point the electrons in the ground-level state are localized in finite clusters, classically accessible regions of electrons excited over a mobility gap could form an infinite cluster. At still higher energies practically the entire volume becomes classically accessible, and the electron mobility increases to the minimal gas-kinetic value. By definition, the absolute mobility gap Δ_1 is determined by the appearance of the mobility, and soft mobility gap Δ_2 is determined by its increase to the gas-kinetic value. This two-parameter gap is

$$\Delta_k = J - e^2 \left(4\pi n_m/3\zeta_k\right)^{1/3}, \quad k = 1, 2, \tag{8}$$

where $\zeta_1 \simeq 0.64$ is the percolation threshold equal to the random close packing fraction, and ζ_2 $(> \zeta_1)$ is an accessible volume fraction of the same order of magnitude. The latter parameter is of less importance since it does not lead to the exponential dependence of the conductivity. One can use the regular close packing fraction $\zeta_2 = 0.74$. In the scaling theory, the mobility is a power function of the distance from the threshold [15]:

$$\mu(\varepsilon_p) = \frac{e\tau}{m}\left(\frac{\varepsilon_p - \Delta_1}{\Delta_2 - \Delta_1}\right)^{\nu}, \quad \varepsilon_p < \Delta_2, \tag{9}$$

where $\nu \approx 0.9$ is the critical exponent, $\tau = l/v_T$ is the relaxation time, $l \approx R_s$ is the minimal free path length, and $v_T = \sqrt{8T/\pi m}$ is the mean thermal velocity. Below and at the transition point the Boltzmann statistics of the quasiatomic excitations has been shown to apply even at very low temperatures [11]. By averaging with the density of states corresponding to free motion in a major part of the quasimolecular-state volume, we obtain the electrical conductivity

$$\sigma = \frac{ze^2 n_m \tau \vartheta}{m}, \tag{10}$$

where the factor $\vartheta < 1$ describes the partial localization of the electrons. This factor is expressed by the following combination of the incomplete gamma-functions $\Gamma(m, x)$,:

$$F_k = \frac{2}{\sqrt{\pi}}\left[\Gamma\left(\frac{5}{2}, \frac{\Delta_k}{T}\right) - \frac{\Delta_k}{T}\Gamma\left(\frac{3}{2}, \frac{\Delta_k}{T}\right)\right].$$

Below the insulator–metal transition point the localization factor is

$$\vartheta = \frac{T(F_1 - F_2)}{\Delta_2 - \Delta_1} \approx \frac{2}{\sqrt{\pi}}\frac{\sqrt{\Delta_1 T}}{(\Delta_2 - \Delta_1)}\exp\left(-\frac{\Delta_1}{T}\right), \qquad \Delta_2 > \Delta_1 \gg T, \tag{11}$$

which is exponentially small. On the metallic side

$$\vartheta = \frac{3T/2 - \Delta_1 - TF_2}{\Delta_2 - \Delta_1} \approx \frac{3T/2 - \Delta_1}{\Delta_2 - \Delta_1}, \qquad \Delta_1 \leq 0, \ \ \Delta_2 \gg T. \tag{12}$$

Taking into account the electron degeneracy above the insulator–metal transition point, the thermal energy $3T/2$ in the last formula must be substituted by a renormalized Fermi-energy

$$\varepsilon'_F = \hbar^2 k_F^2 \vartheta^2 / 2m, \tag{13}$$

where the prime indicates the difference from the electron gas, and $k_F = \left(6\pi^2 n_m\right)^{1/3}$ is the Fermi wave-vector. In practice, the localization factor in this case goes to unity. Moreover, this factor drops out in the expression of conductivity. Indeed, for the degenerated electrons the relaxation time is

$$\tau = l/v'_F, \ \ v'_F = v_F \vartheta, \tag{14}$$

where v'_F is a renormalized Fermi velocity, and v_F is the Fermi velocity of the electron gas. By substituting Eq. (14) into Eq. (10) we reduce the localization factor. Therefore, we obtain the minimal metallic conductivity

$$\sigma = \frac{e^2 n_e l}{m v_F}. \tag{15}$$

In fact, for the degenerated electrons the electric conductivity can be described in gas-kinetic terms. We use the Ioffe–Regel criterion for the minimal free path length

$$l \sim \hbar / \Delta p, \tag{16}$$

where Δp is the quantum uncertainty of the electron momentum. At high temperatures the momentum uncertainty can be substituted by the thermal momentum $m v_T$. The minimal free path is then the thermal wave length. From Eq. (10) we then obtain

$$\sigma \approx \frac{e^2 n_e}{k_F m v_T} \approx \frac{e^2 n_e R_s}{m v_T}. \tag{17}$$

Except for a numerical coefficient of the order of unity, this expression is the same as it would be in the case of Boltzmann statistics if the free path length were equal to R_s. With such an accuracy, Eqs. (10)–(12) for the percolation conductivity can also be directly extrapolated for the degenerated electrons on the metallic side of the transition.

In the case of strong degeneracy the momentum uncertainty can be only expressed by the Fermi momentum

$$\Delta p = \gamma m v_F,$$

where γ is a coefficient, and the free path length is

$$l \sim 1/\gamma k_F.$$

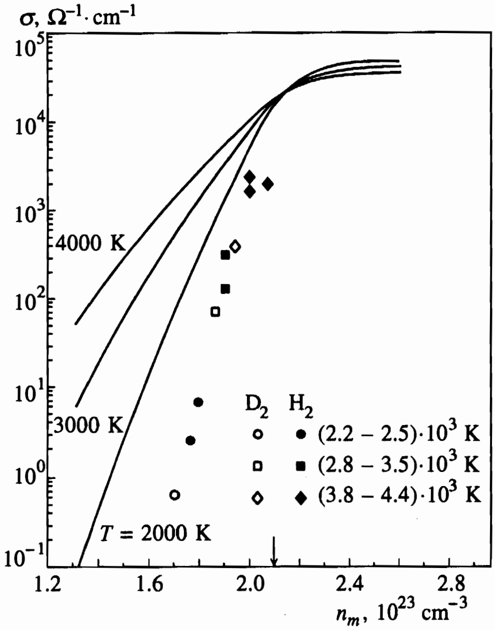

Fig. 2. Electric conductivity of dense fluid hydrogen in the insulator–metal transition range. Experimental dots from Ref. [4] and solid lines by the microscopic percolation theory are shown. The estimated insulator–metal transition point is shown by the arrow. The γ parameter is 0.1

Matching it to the extrapolated Boltzmann formula on the metallic side of the transition (at the point at which $v_T = \gamma v_F$), we obtain

$$l = R_s/\gamma, \tag{18}$$

i.e., the parameter γ is the inverse free path length of the intermolecular spacing. For a rough estimate of the parameter γ, applying the $v_T = \gamma v$ equality to the transition point, we obtain $\gamma \sim 0.1$. Of course, the uncertainty of this parameter does not influence the Boltzmann conductivity below the insulator–metal transition point.

The percolation conductivity of dense molecular hydrogen in the insulator–metal transition region is shown in Fig. 2 to qualitatively agree with the experiment. Thus, an idea of a microscopic percolation can be actually instructive for understanding of the insulator–metal transition in the strongly compressed dielectric liquid. Obviously, the theory based on a virtual molecular structure is limited to the vicinity of the transition point, in particular, because deep into metallic state hydrogen molecules dissociate. While the metallic state is reasonably well understood [16], the transition is still a subject of study.

In conclusion, we apply a microscopic percolation theory for the description of the insulator–metal transition in dense fluid hydrogen with a virtual molecular structure and show that molecular bonding can still be consistent with the metallic properties.

This work was partially supported by the Russian Foundation for Basic Research (grant №97-02-16222). A part of this work has been done during my visit in Iinstitut für Niedertemperatur-Plasmaphysik, Greifswald (Deutschland) with a partial financial support of Deutscher Akademischer Austauschdients. I am grateful to H. Schneidenbach for help in programming and to H. Hess for help and hospitality.

References

1. N. F. Mott, *Metal-Insulator Transition*, London, Taylor & Francis 1991).
2. D. Saumon, W. B. Hubbard, G. Chabrier, and H. M. van Horn, Astrophys. J. **391**, 827 (1992).
3. H. K. Mao and R. J. Hemley, Rev. Mod. Phys. **66**, 671 (1994).
4. S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996).
5. J. M. Ziman, *Models of Disorder*, Cambridge University Press (1979).
6. B. I. Shklovsky and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Springer-Verlag, New York (1989) [Russ. original, Nauka, Moscow, 1979)].
7. M. Ross, Phys. Rev. B **54**, R9589 (1996).
8. A. A. Likalter, Sov. Phys. Usp. **35**(7), 591 (1992) [Usp. Fiz. Nauk, **162**, 119 (1992)].
9. A. A. Likalter, Sov. Phys. JETP **67**(12), 2478 (1988) [Zh. Eksp. Teor. Fiz. **94**, 157 (1988)].
10. A. A. Likalter, JETP **84**(3), 516 (1997) [Zh. Eksp. Teor. Fiz. **111**, 938 (1997)].
11. A. A. Likalter, JETP **80**(6), 1105 (1995) [Zh. Eksp. Teor. Fiz. **107**, 1996 (1995)].
12. H. Reinholz, R. Redmer, and S. Nagel, Phys. Rev. E **52**, 5368 (1995).
13. A. L. Bug, S. A. Safran, and G. S. Grest, Phys. Rev. Lett. **55**, 1896 (1985).
14. P. P. Edwards and M. J. Sienko, Phys. Rev. B **17**, 2575 (1978).
15. P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
16. A. A. Abrikosov, Astron. Zh. **31**, 112 (1954).