Significant reduction of the internuclear potential in superconductive solid metallic hydrogen

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Abstract
Hydrogen varies its stable state in accordance with its temperature and density. Though molecular gas is stable in the environment, the monatomic state is stable in high density ranges of more than about 1 g cm^{-3}. Such dense hydrogen has many aspects never seen in the molecular state. For example, in the range over about 10^8 K temperature and over 10^3 g cm^{-3} density, great efforts are being made to realize inertial confinement fusion (ICF). Additionally, in the range of temperature lower than about 10^5 K and of density more than 10^4 g cm^{-3} pycno nuclear fusion is supposed to occur. Here for the first time we have derived the expression for the Debye screening length of the interionic potential, taking into account correlated electron pairs, and investigated the nuclear reaction rate in superconductive solid metallic hydrogen. It is revealed that the screening length is shortened by correlated electron pairs that follow the Bose–Einstein distribution in the superconductive state. The bosonization increases the number of lower energy states of the electrons to increase the screening effects on the potential with decreases in the temperature, resulting in a significant enhancement of the nuclear reaction rate by more than 10 orders of magnitude.

1. Introduction

Hydrogen exhibits a strong quantum effect at low temperature and ultra-high pressure due to its low nuclear mass [1–3]. One of the most characteristic states, solid metallic hydrogen, was predicted in 1935 [4] and experimental research has been ongoing since then. A state known as monatomic solid metallic hydrogen (MSMH) is expected to form at pressures over 400 GPa [5–8]. Liquid metallic hydrogen has been realized [9] but the temperature and pressure ranges over which it exists are far from the predicted stability region of MSMH. The physical properties of MSMH are still little known because it has not been generated experimentally. Due to the light mass and lack of closed shell electrons surrounding the nucleus, MSMH should be very different from the other alkali metals as it is predicted to be a high-temperature elemental superconductor [10] and the effect of the state of conductive electrons on the crystal structure will be much greater than in other elements. Therefore it is important to reveal the characteristic properties of MSMH. We have been looking at the superconductive state of MSMH. In the superconductive state, a proportion of the electrons form correlated electron pairs. The mass-center motion of a correlated pair follows Bose–Einstein (BE) statistics, in contrast to normal electrons which follow Fermi–Dirac (FD) statistics. Therefore, it would be valuable to determine the influence of the electronic state in superconductive MSMH. One approach is to evaluate the Debye length, which represents the degree of screening of the ionic Coulomb potential.

2. Derivation of the Debye length in MSMH

Generally in an ordinary solid other than metallic hydrogen, each nucleus opposes closed shell electrons. If a solid is an insulator, the internuclear potential can be approximated by the Lennard-Jones potential. If a solid is a metal, conductive electrons also affect the screening of the interionic potential. By taking into account that most solids have a similar density, closed shell electrons are always important for sustaining the crystal. As for metallic hydrogen, which does

not have orbital electrons, interionic interaction is described by a Coulomb potential screened by conductive electrons. Such a screened Coulomb potential $\phi(r)$ is represented by $\phi(r) = e \exp(-r/\lambda)/4\pi\varepsilon_0 r$, where r is the distance from the nucleus, e is the electric charge, ε_0 is the electric constant and λ is the Debye length which shows the degree of screening. This approximation appears in many fields. For example, in the classical state electrons follow the Maxwell–Boltzmann distribution with temperature T such that $\lambda = \sqrt{\varepsilon_0 k_B T / e^2 n_e}$, where k_B is the Boltzmann constant and n_e is the average electron number density. In the same way, in metals the electron temperature is represented by the Fermi temperature T_F, and degenerate electrons follow the Fermi–Dirac distribution such that $\lambda = \sqrt{2\varepsilon_0 k_B T_F / 3 e^2 n_e} \equiv \lambda_e$ [11], where λ_e is the Debye length of free electrons in a metal. This quantity λ must be modified for the superconductive state because a proportion of the free electrons form correlated electron pairs. The screening effect of the correlated pairs is described by λ_c. Though the number of correlated pairs is much smaller than that of total conductive electrons, the free electrons and the correlated pairs coexist in the superconductive state. Therefore the total Debye length λ is synthesized from λ_e and λ_c. First, we derive an expression for λ and then determine the average density of the correlated pairs n_c, together with other necessary values. We treat a correlated pair as a quasi-particle and assume that it follows the BE distribution [12]. The energy of a correlated pair is $\varepsilon = v_F p / 2 - 2e\phi$, where v_F is the Fermi velocity [13] and p is the momentum. To treat the chemical potential μ, we introduce the quantity $z = \exp(\mu / k_B T)$, and then Bose–Einstein (BE) distribution is given as

$$f_{BE}(\varepsilon(\vec{x}, \vec{p})) = \frac{1}{z^{-1}e^{\beta\varepsilon(\vec{x},\vec{p})} - 1}, \qquad (1)$$

where $(\vec{x}, \vec{p})$ is the mass center of a correlated pair and its momentum, z, is decided from the equation

$$N_c = \frac{1}{V}\int f_{BE}(\varepsilon(\vec{x}, \vec{0}))\,\mathrm{d}\vec{x} + \frac{1}{(2\pi\hbar)^3}\int f_{BE}(\varepsilon(\vec{x}, \vec{p}))\,\mathrm{d}\vec{x}\,\mathrm{d}\vec{p}. \qquad (2)$$

Here $N_c = V n_c$ is the total number of pairs and $\beta = \frac{1}{k_B T}$. To integrate equation (2), we approximate ϕ as its average value ϕ_0 ($\phi_0 = 0$ in quasineutrality). Using definite integration of the Riemann-zeta function

$$\frac{1}{n!}\int_0^\infty \frac{x^n \mathrm{d}x}{\alpha^{-1}e^x - 1} = \zeta_{n+1}(\alpha) \qquad (0 \leqslant \alpha \leqslant 1), \qquad (3)$$

the integration is executed and

$$N_c = \frac{1}{z^{-1} - 1} + \frac{V}{(2\pi\hbar)^3}\frac{8\pi}{(\beta\frac{v_F}{2})^3}\zeta_3(z). \qquad (4)$$

z and β relate one to one and z increases monotonically when β increases. First, we think $\beta \to \infty$ ($T \to 0$) which leads to

$$z = \frac{N_c}{1 + N_c} \simeq 1. \qquad (5)$$

When $\beta \to 0$ ($T \to \infty$), it means $z \to 0$ (because $\frac{\zeta_3(z)}{\beta^3} < \infty$). And so we expand $\zeta_3(z) \simeq z + \mathrm{O}(z^2)$ and

$$N_c = \frac{z}{1 - z} + \frac{V}{(2\pi\hbar)^3}\frac{8\pi}{(\beta\frac{v_F}{2})^3}(z + \mathrm{O}(z^2)). \qquad (6)$$

Re-forming the equation,

$$N_c = \left(1 + N_c + \frac{V}{(2\pi\hbar)^3}\frac{8\pi}{(\beta\frac{v_F}{2})^3}\right)z + \mathrm{O}(z^2), \qquad (7)$$

and finally

$$z = \frac{N_c}{1 + N_c + \frac{V}{(2\pi\hbar)^3}\frac{8\pi}{(\beta\frac{v_F}{2})^3}} \simeq \frac{1}{1 + \frac{1}{\zeta_3(1)}\left(\frac{T}{T_c}\right)^3}. \qquad (8)$$

Here T_c is the critical temperature defined as

$$T_c = \sqrt[3]{\frac{\pi^2}{\zeta_3(1)}}\frac{\hbar}{k_B}\frac{v_F}{2}n_c^{\frac{1}{3}}. \qquad (9)$$

When we take $T \to 0$ in equation (8), it approaches equation (5). This means that equation (8) is a good approximation at almost all temperatures. Therefore we use equation (8) as the approximation of z. By expanding the BE distribution function about ϕ to first order, we obtain an expression for the local density of the correlated pairs

$$n_c'(x) = n_c\left(1 + \frac{g(z)}{k_B T}2e\phi(x)\right). \qquad (10)$$

Here,

$$g(z) = \frac{1}{1 - z} + \frac{1 - z}{z}\zeta_2(z) - \frac{\zeta_3(z)}{z}. \qquad (11)$$

Regarding the local free electron density, since $n_e \gg n_c$, we neglect the change in n_e induced by the creation of correlated pairs. By expanding the FD distribution function in the same way, the local free electron density $n_e'(\vec{x})$ is given as

$$n_e'(\vec{x}) = n_e\left(1 + \frac{3e\phi(\vec{x})}{2k_B T_F}\right). \qquad (12)$$

Setting the screening effects of the correlated pairs as $\lambda_c^2 = \varepsilon_0 k_B T / (2e)^2 g(z) n_c$, by substituting equations (10) and (12) for the Poisson equation

$$\triangle\phi = -\frac{1}{\varepsilon_0}\left(-e(n_e' - 2n_c) - 2en_c' + en_e\right), \qquad (13)$$

the total Debye length in the superconductive solid metallic hydrogen λ_{sc} can be expressed as

$$\frac{1}{\lambda_{sc}^2} = \frac{1}{\lambda_e^2} + \frac{1}{\lambda_c^2} = \frac{3e^2 n_e}{2\varepsilon_0 k_B T_F} + \frac{(2e)^2 g(z)n_c}{\varepsilon_0 k_B T}. \qquad (14)$$

The first term on the right-hand side represents screening from the normal conductive electrons which follow FD statistics. The second is a new term that represents the effect of the correlated pairs and is important in our subsequent analysis of MSMH. It is not a simple expression for the reason that λ_c is a valid parameter at all temperatures, even outside the

superconductive region. For example, as $T \to \infty$, the expression shows that $z \to 0$, $g(z) \to 1$ and $\lambda_c \to \sqrt{\varepsilon_0 k_B T/(2e)^2 n_c}$, which is the Debye length of a classical particle. Conversely at $T < T_c$, $g(z) \approx ((T/T_c)^3/\zeta_3(1))^{-1}$. So the Debye length λ_c becomes

$$\lambda_c = \sqrt{\frac{\varepsilon_0 k_B T}{(2e)^2 g(z) n_c}} \approx \sqrt{\frac{\varepsilon_0 k_B T^4}{\zeta_3(1)(2e)^2 T_c^3 n_c}}. \quad (15)$$

Next we need to determine n_c. By using a correction factor γ to express the difference between the actual Fermi surface and the ideal Fermi sphere, n_c is given by

$$n_c = \frac{3\hbar w_D}{4 k_B T_F} n_e \gamma, \quad (16)$$

where $\hbar$ is Planck's constant divided by 2π, and w_D is the Debye frequency. By using equation (9), expression (16) becomes

$$\frac{T_c}{T_F} = \left(\frac{\Theta_D}{4\zeta_3(1) T_F}\right)^{1/3} \gamma^{1/3}, \quad (17)$$

where the Debye temperature is $\Theta_D = \hbar w_D/k_B$. MSMH is predicted to have $T_c \approx 10^2$ K and $\Theta_D \approx 10^3$ K [10]. For the majority of metals $T_F \approx 10^5$ K. We assume that the Fermi temperature for MSMH is of the same order, and consequently $\gamma \approx 10^{-7}$. To determine w_D, we use one-dimensional coupled oscillations and the harmonic approximation: $w_D = \frac{16}{9\pi}\sqrt{e^2/2\pi\varepsilon_0 m a^3} \exp(-a/2\lambda)\sqrt{1 + a/\lambda + (a/\lambda)^2/2}$ where m is the nuclear mass and a is a lattice constant. Based on the equations and parameters derived so far, we now investigate how the characteristic quantities for MSMH will change. We assume γ does not depend on the density.

Figure 1 shows temperature dependence of the Debye length λ_e, λ_c and λ_{sc}. The calculations were performed in solid metallic deuterium in order to calculate the nuclear reaction rate afterwards. At $T/T_c > 0.1$, $\lambda_{sc} \approx \lambda_e$ and at $T/T_c < 0.1$, λ_{sc} decreases from λ_e and asymptotically approaches to λ_c. λ_e is the screening effect of the Fermi-degenerate electron and is constant with respect to the temperature in the region of $T \ll T_F$. λ_c is the effect of the correlated pairs and $\lambda_c \propto T^2$ under the critical temperature, as shown in equation (15). When the temperature is higher than $0.1T_c$, λ_c in equation (14) is insignificant because $n_e \gg n_c$. On the other hand, λ_c becomes important at lower temperatures because $\lambda_c \propto T^2$.

In other materials, the crystal density and structure are sustained by closed shell electrons. However, solid metallic hydrogen does not oppose any closed shells so the Debye length affects lattice constants strongly and the lattice constant would be shortened as temperature goes down. Additionally, internuclear reaction would be strengthened below the critical temperature.

Then we calculate the nuclear reaction rate for superconductive MSMH. Because the nuclei in the crystal do not diffuse from their equilibrium positions due to zero-point oscillation, we estimate the reaction rate using the procedure outlined below rather than using the S-matrix. A similar idea was put forward in [14], but differed in that penetration probability was used. To simplify the calculation of reaction rate, we consider
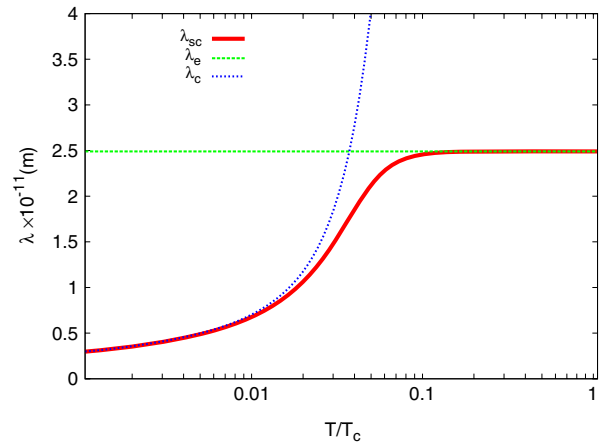

Figure 1. Temperature dependence of the Debye length. The calculations were done in deuterium. λ_{sc} is the total Debye length, λ_e and λ_c are that of the Fermi-degenerate electron and the correlated electron pairs, respectively. The calculations were performed at $n = 10^{31}$ m^{-3}, where T_c is expected to be 945 K.

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

deuterium (a Bose particle) instead of hydrogen (a Fermi particle). Despite their different mass, both hydrogen and deuterium have the same electric charge and do not oppose closed shells in the metallic state. Therefore, it is reasonable to consider that the effect of changes of electric state on the crystals may be similar. In this case, we treat the crystal as a simple cube and then $n \approx n_e = a^{-3}$. The reaction rate per unit volume and unit time R is given by multiplication of the inverse of the vibrational period, the density of pairs of nearest-neighbor nuclei, the probability that the two nearest nuclei can collide and the penetration probability. The frequency of the relative motion of a nuclear pair is then regarded as w_D and the oscillation period is consequently $t = 2\pi/w_D$. Putting the number of nearest-neighbor nuclei as N, the density of a pair of nearest-neighbor nuclei is $nN/2$. We assume each nucleus oscillates in an approximately isotropic potential. Because the internuclear distance is much larger than the nuclear radius r_a, the solid angle over which two nuclei can collide is $\Omega \approx \pi r_a^2/4\pi a^2 = r_a^2/4a^2$. A reaction can occur when the direction of motion is within the angle Ω, which implies that the contribution of direction to the reaction rate is $\Omega/4\pi$. Denoting the penetration probability as P, R is

$$R \approx \frac{1}{t} \times \frac{nN}{2} \times \frac{\Omega}{4\pi} \times P = \frac{w_D n N \Omega P}{16\pi^2}. \quad (18)$$

When the relative motion of two nuclei is one-dimensional, P can be expressed as

$$P = \exp\left(-\frac{2\sqrt{2m^*}}{\hbar} \int_{2r_a}^{r'} \sqrt{e\phi(x) - K}\, dx\right) \quad (19)$$

by using the Wentzel–Kramers–Brillouin approximation. Here, m^* is the reduced mass, the energy of the nucleus K consists of a density term $e^2 \exp(-a/\lambda)/4\pi\varepsilon_0 a$ and a zero-point energy term $\hbar w_D/2$, and r' is a classical turning point that satisfies $e\phi(r') - K = 0$. The reaction rate can be expressed as $R(\lambda)$ because it varies with λ through w_D and P.
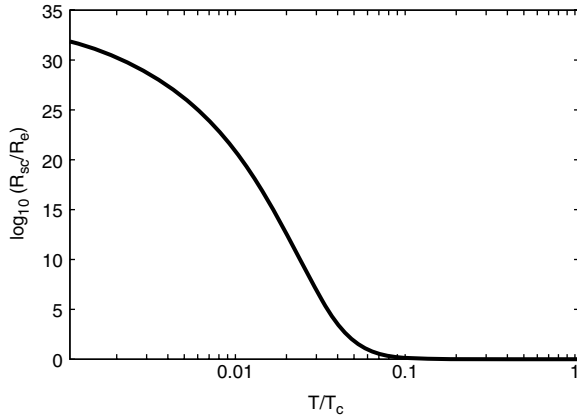
Figure 2. Temperature dependence of the nuclear reaction rate ratio R_{sc}/R_e. R_e and R_{sc} are the reaction rates supposing normal conducting and the superconductive state, respectively. R_{sc}/R_e indicates the enhancement effects due to the correlated electron pairs, and the ratio increases at lower temperature. The calculations were performed at $n = 10^{31}$ m^{-3}, as in figure 1.

Figure 3. Density dependence of the reaction rate ratio R_{sc}/R_e. A peak emerges due to the existence of the correlated electron pairs. The density is normalized by $n_0 = 10^{30}$ m^{-3} which is a typical value for common solids. The calculations were performed at $T = 10$ K. Because T_c increases monotonically with density, $T_c > 10$ K for all $n > n_0$, hence the superconductive state spans the whole range of the figure if the density range corresponds to the metallic state.

3. Results and discussion

Figure 2 shows the temperature dependence of the reaction rate taking into account the correlated electron pairs. $R_e \equiv R(\lambda_e)$ and $R_{sc} \equiv R(\lambda_{sc})$ respectively. R_e is constant with respect to the temperature like λ_e in figure 1. R_{sc} changes at a temperature of about $T/T_c = 0.1$ because λ_{sc} changes at the same temperature. The reaction rate is enhanced by the presence of correlated pairs. The temperature dependence of R_{sc} is always $dR_{sc}/dT < 0$. This is because the screening effect is much stronger than decreases in the kinetic energy of the nuclei.

Figure 3 shows the density dependence of the reaction rate taking into account the correlated electron pairs. There is a peak in the ratio R_{sc}/R_e. This is due to it being a superconductive state. To prove this argument, we define $R_0 \equiv R(\infty)$ as the reaction rate without screening (the Debye length is regarded as ∞) and show the density dependence of R_e and R_{sc} normalized by R_0 in figure 4. There are different changes on R_e/R_0 and R_{sc}/R_0. As for R_e/R_0, because $a \propto n^{-1/3}$ and $\lambda_e \propto n^{-1/6}$, the effect of λ_e diminishes with increasing density and R_e/R_0 decreases monotonically to unity. On the other hand, R_{sc}/R_0 has a peak as R_{sc}/R_e in figure 3. The peak arises from two conflicting changes induced in R_{sc} by an increase in density. The first is a weakening of the screening, the same effect as for R_e/R_0, while the second is a strengthening of the screening caused by the growth of n_c. Growth of n_c shortens λ_c and λ_{sc} and enhances the nuclear reaction rate.

4. Conclusion

In summary, we have investigated monatomic solid metallic hydrogen in the superconductive state taking into account changes in the statistical electron distribution. We have derived an expression for the Debye length including two components, one of which is normal electrons and the other correlated electron pairs. As the temperature decreases, effects of the
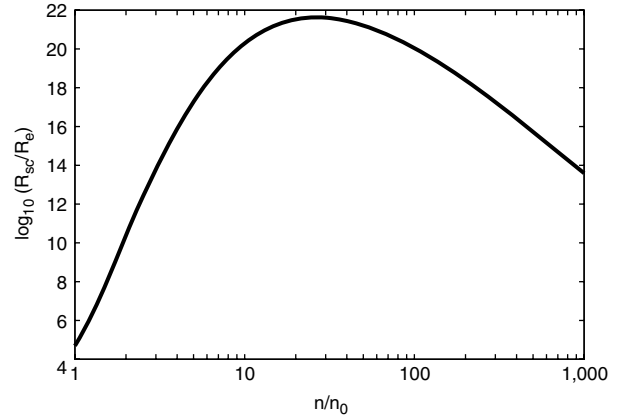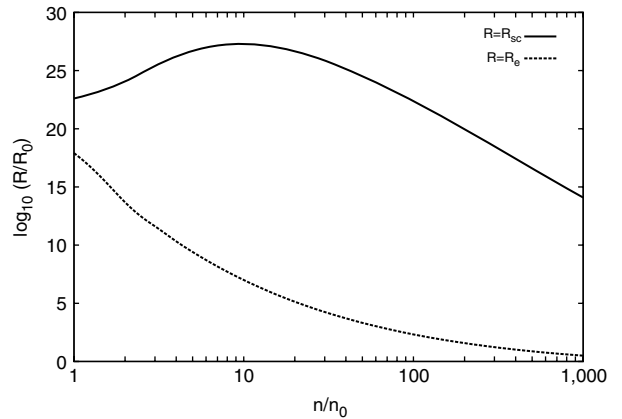

Figure 4. Density dependence of the reaction rate ratio normalized by R_0. R_0 is defined for the condition $\lambda = \infty$ to see the different screening effects between the normal conducting and the superconductive state. The calculations were performed at $T = 10$ K as in figure 3.

superconductive state appear, shortening the Debye length. In solid metallic hydrogen, the Debye length is inseparably related to the lattice constant and ionic state. Therefore the result that the reaction rate R_{sc} increases at lower temperatures is unique to MSMH in the superconductive state and implies peculiar ionic dynamics. The generation of solid metallic hydrogen is very challenging, so the ultimate test of the results is beyond current experimental techniques, but is nevertheless interesting and would be of help in research into high pressure metals in astrophysics.

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