An analysis of the quantum effect on the thermodynamic and transport properties of cryogenic hydrogen using molecular dynamics method

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Abstract. In this paper, we have analysed an effect of quantum nature of the hydrogen molecule on its thermodynamic and transport properties using molecular dynamics (MD) method based on the path integral method. We performed *NVE* constant MD simulation and the quantum effect on the molecular mechanism was analysed. The simulation results were compared with experimental data. As a result, we clarified that the quantum nature makes the virial pressure larger than in classical mechanics and taking account the quantum nature makes smaller intermolecular interaction energy and larger repulsive force than classical representation. Besides, we have confirmed that the path-integral-based MD method well reproduces the thermal conductivity and quantum effect on the transport properties is also large.

1. Introduction

Analyses of nanosacle thermal flow properties of hydrogen using molecular dynamics (MD) method are important for the safe and efficient use of hydrogen. However, in the case of hydrogen molecules, their quantum nature, that is, the uncertainty or wave nature of the nucleus resulting from its small mass cannot be neglected. Because the molecular motion of hydrogen cannot be treated by classical mechanics, it is difficult to reproduce nanoscale thermal flow properties of hydrogen using the classical MD method [1]. Recently, some quantum MD methods those are able to reproduce the time evolution of the molecules whose quantum effect cannot be neglected were proposed. However, because this quantum nature affects not only microscopic thermal flow properties but also macroscopic thermodynamic properties, it is needed to comprehend the quantum effect on the both sides of property in detail. Therefore, in this study, we investigated the effect of the quantum nature on the thermodynamic properties of liquid hydrogen and its molecular mechanism using classical MD method and a MD method based on the path integral method.

2. Simulation method

In this paper, we applied the molecular dynamics methods which are based on the path integral method. Using the path integral method, the quantum partition function becomes the same form as the

classical partition function which consists of L particles ring polymer [2]. In short, the quantum partition function is described as the Trotter product discretization,

$$Q(\beta,N) = \lim_{L\to\infty} \frac{1}{N!} \left(\frac{mL}{2\pi\beta\hbar^2}\right)^{\frac{3NL}{2}} \int\cdots\int \prod_{i=1}^{N}\prod_{j=1}^{L} dr_i^{(j)} \exp\left[-\beta\left(\sum_{i=1}^{N}\sum_{j=1}^{L}\frac{mL}{2\beta^2\hbar^2}\left(r_i^{(j)}-r_i^{(j+1)}\right)^2 + \frac{1}{L}\phi\left(r_i^{(j)}\right)\right)\right], \tag{1}$$

where m is the mass of molecule, N is the number of molecules, L is the number of discretized points, that is, the number of beads composed a ring polymer, $\beta (= 1/k_B T)$ is the inverse temperature, $r_i^{(j)}$ is the jth bead position of molecular i, ϕ is the interaction of beads. The centroid MD (CMD) [3] is one of the new quantum MD method which is able to reproduce the time evolution of the molecules whose quantum effect cannot be neglected. The CMD method can reproduce the thermodynamic characteristics of liquid hydrogen as compared with other methods [4]. The centroid position and momentum are defined as

$$\bar{r}_i = \frac{1}{L}\sum_{j=1}^{L} r_i^{(j)}, \; \bar{p}_i = \frac{1}{L}\sum_{j=1}^{L} p_i^{(j)}. \tag{2}$$

Where $p_i^{(j)}$ is the jth bead momentum of molecular i. Using the centroid information, the centroid distribution function becomes classical like form,

$$\rho_c(\bar{r},\bar{p}) = \rho_c(\bar{r})\rho_c(\bar{p}) = \exp\left(-\beta\frac{\bar{p}^2}{2m}\right)\exp\left(-\beta\phi_c(\bar{r})\right), \tag{3}$$

where $\phi_c(r^c)$ is the centroid potential of mean force. The equation of motion of hydrogen molecule also can be expressed by a classical like form [3],

$$m_i\ddot{r}_i^c = -\frac{\partial\phi_c\left(r_1^c,\cdots,r_N^c\right)}{\partial r_i^c} = -\frac{\int\cdots\int\prod_{i=1}^{N}\prod_{j=1}^{L} dr_i^{(j)}\delta\left(r_i^c-\bar{r}_i\right)\frac{\partial\phi\left(\bar{r}_1,\cdots,\bar{r}_N\right)}{\partial r_i^0}\exp\left(-\beta S\left[r_i^{(j)}\right]\right)}{\int\cdots\int\prod_{i=1}^{N}\prod_{j=1}^{L} dr_i^{(j)}\delta\left(r_i^c-\bar{r}_i\right)\exp\left(-\beta S\left[r_i^{(j)}\right]\right)}, \tag{4}$$

Moreover, centroid correlation function $<\hat{B}_c(0)\hat{A}_c(t)>$ can be exactly related to the Kubo-transformed quantum correlation function,

$$\left\langle \hat{B}_c(0)\hat{A}_c(t)\right\rangle = \frac{1}{Z}\int\int\frac{d\bar{r}d\bar{p}}{2\pi\hbar}\rho(\bar{r},\bar{p})B_c A_c(t) = \frac{1}{\beta Z}\int_0^\beta d\lambda \mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{B}e^{-\lambda\hat{H}}e^{iHt/\hbar}\hat{A}e^{-iHt/\hbar}\right], \tag{5}$$

where the operator $\hat{B}_c$ and $\hat{A}_c$ are restricted in a linear function of the position and/or momentum [5]. Because of this restriction, it is being pointed out that in the case of nonlinear operator, for example heat flux operator [6], CMD is difficult to apply for the calculation. Therefore, in this study, we applied the maximum entropy numerical analytic continuation (MEAC) method [7] with imaginary-time path integral MD method for the calculation of the thermal conductivity of liquid hydrogen. The quantum correlation function $C(t)$ is related to its spectral density, $I(\omega)$, by a Fourier transform,

$$C(t) = \int_{-\infty}^{\infty} d\omega e^{-i\omega t} I(\omega). \tag{6}$$

The imaginary time correlation function $G(\tau)$ can be written as

$$G(\tau) = \int_{-\infty}^{\infty} d\omega e^{-\omega\tau} I(\omega). \tag{7}$$

by substituting $-i\tau$ into t of equation (6). The same spectral density $I(\omega)$ can be obtained by inverse Laplace transform of the imaginary time correlation function of equation (7). Because the inversion is an ill-posed problem, however, the MEAC method is applied for the inversion. The quantum correlation function can be obtained by the inverse Fourier transform of equation (6) using the $I(\omega)$ which derived by inversion of equation (7). The imaginary time heat flux correlation function can be written using heat flux operator $\hat{J}$ [6] as

$$G_J(\tau) = \frac{1}{Z}\mathrm{Tr}\left[e^{-\beta H}e^{\tau H}\hat{J}e^{-\tau H}\cdot\hat{J}\right]. \tag{8}$$

In the case of the CMD simulation, the number of molecules and the number of beads were 256 and 64 respectively. The REference System Propagator Algorithm (RESPA) [8] was used for the numerical

integration method. The time steps for the centroids motion was 0.2 fs, and the number of Trotter expansion was set at 10, that is, the time step for the beads motion of 0.02 fs. Silvera-Goldman (SG) [9] was applied for the bead interaction. We have performed *NVE* constant classical MD and CMD simulations at constant density (ρ = 80 kg/m^3) by changing temperature. The pressure formulation using the path integral representation can be obtained from the equation (1) [10] as

$$P = \frac{N}{V\beta} + \frac{1}{3V}\sum_{i=1}^{N} \boldsymbol{r}_i^c \cdot \boldsymbol{F}_i^c \,. \tag{10}$$

Here $\boldsymbol{F}_i^c$ is the force which acts on the centroid and *V* is the volume of the system. In this study, the quantum effect on the molecular mechanism of pressure is analysed.

In the case of the MEAC simulation, first we have performed path integral MD simulation [11] to evaluate the imaginary time heat flux auto correlation function. The number of molecules and the number of beads were 256 and 48, respectively. The time step was 0.5 fs. At every 10 steps, we calculated the imaginary time heat flux correlation function of equation (8) and we repeated this calculation 1000 times. We considered this data as a set and we calculated 1000 data sets. These data sets were used for the inverse Laplace transform of equation (7). We applied the same procedure as described in Ref. [7] to obtain the spectral density using the MEAC method. The simulation conditions were saturation points at 14 K and 30 K. We calculated the thermal conductivity of liquid hydrogen using the spectral density and clarified the quantum effect on the transport properties.

3. Results and discussion

Temperature dependence of the pressure formula of classical MD and CMD at constant density ρ = 80 kg/m^3 is shown in figure 1. In this figure, the total pressure of the CMD is consistent with experimental data [12] in whole temperature region. By contrast, there are disagreements between the classical MD results and experimental data in the low temperature region. Moreover, from the comparison of the each term of the pressure formula, it is found that although the kinetic pressure of each method agrees well with each other in whole temperature region, the virial pressure of the CMD is larger than classical case and the difference of the virial pressure is equivalent to the total pressure difference. From these results it is clarified that taking account of the quantum nature produces the virial pressure larger than classical case. To clarify the quantum nature on the virial term in detail, intermolecular potential of hydrogen is derived using force matching method [13]. In this method, the force which acts on the centroid is expressed by classical like force using least squares approximation. The fitted results are shown in figure 2. As shown in this figure, the potential which acts on the centroid depends on the temperature. Additionally, in the case of the lower temperature, the potential well is shallower than and the well positions are much more far away from the original SG potential well position. These results suggest that taking into account the quantum nature makes weaker intermolecular interaction energy and broader repulsive force than classical representation. This is the
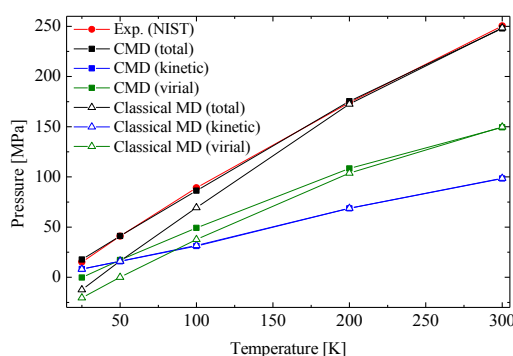

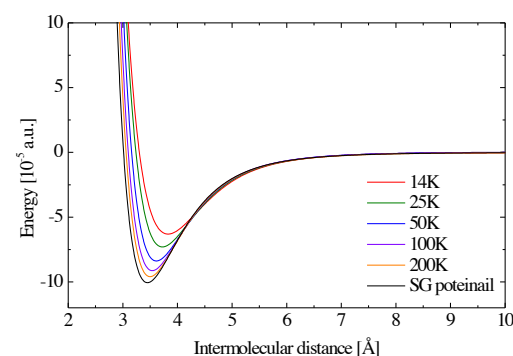**Figure 1.** Comparison of temperature dependence of pressure at constant density (80 kg/m^3)

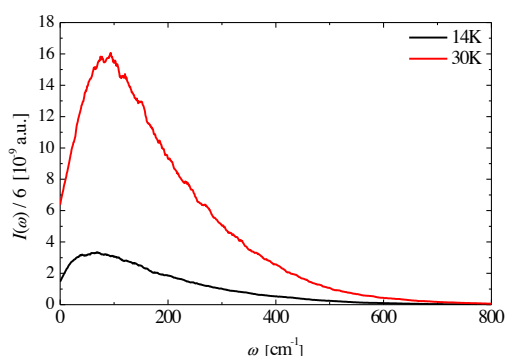**Figure 2.** Comparison of mean intermolecular potential between hydrogen molecules.

Figure 3. Comparison of spectral density of heat flux correlation function at 14 K and 30 K.
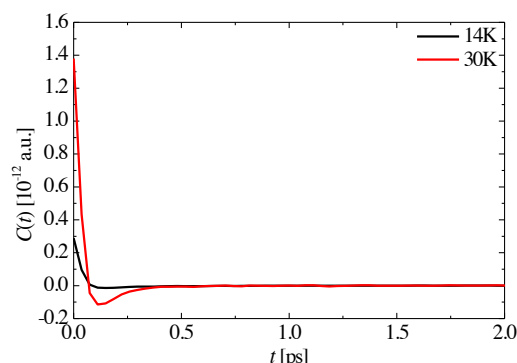

Figure 4. The quantum heat flux correlation functions at 14 K and 30 K.

reason why the virial pressure increase.

Next, the comparison of the spectral density of heat flux correlation function is shown in figure 3 and its quantum correlation function is shown in figure 4. The thermal conductivity can be obtained from the heat flux correlation through the Green-Kubo method. The thermal conductivity result of each temperature is 0.105 W/m/K and 0.0650 W/m/K, respectively. These results are in good agreement with the experimental data (0.0767 W/m/K and 0.0937 W/m/K) [12] as compared with those of the classical method results (0.239 W/m/K and 0.110 W/m/K) especially in low temperature region. From these results we found that the quantum effect of hydrogen molecule on its transport properties is large. However, it is need to more detailed analysis of quantum effect on the thermal conductivity, for example the quantum effect on the molecular mechanism of energy transport.

4. Concluding remarks

In this paper, we have analyzed the quantum effect of the hydrogen molecule on its thermodynamic and transport properties using molecular dynamics (MD) method based on the path integral method. We calcified that the quantum effect is large and taking into account the quantum nature makes weaker intermolecular interaction energy and broader repulsive force than classical representation.

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