Nuclear Quantum Effects in the Layering and Diffusion of Hydrogen Isotopes in Carbon Nanotubes

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RPMD Simulations

We perform RPMD simulations of pure and binary H$_2$, D$_2$, and T$_2$ mixtures confined in relatively wide carbon nanotube (2.72 nm pore diameter) at 25 K in NVT ensemble$^{1-3}$. The total interactions are computed using$^{4,5}$

$$U = U^{\text{int}} + U^{\text{ext}}$$ (S1)

$$U^{\text{int}} = \frac{mP}{2(\beta \hbar)^2} \sum_{i=1}^{N} \sum_{k=1}^{P} \left| E_i^{(k)} - E_i^{(k+1)} \right|$$ (S2)

$$U^{\text{ext}} = \frac{1}{P} \sum_{i<j}^{P} \sum_{k=1}^{P} \varphi_{ij} \left( r_{ij}^{(k)} \right) + \frac{1}{P} \sum_{i=1}^{N} \sum_{k=1}^{P} \varphi_{i} \left( r_{i}^{(k)} \right)$$ (S3)

where $r_{ij}^{k} = \left| E_j^{(k)} - E_i^{(k)} \right|$, $P = 32$ is the number of ring polymer beads is imaginary-time path-integral discretization, $N$ is the number of hydrogen isotopes in the nanotube, $\beta = (k_B T)^{-1}$ is the inverse of thermal energy, $m$ denotes the mass of hydrogen isotope, and $\hbar = \hbar / 2\pi$ is Planck’s constant. Owing to the cyclic condition of the ring polymer, if $k = P$, then $k + 1 = 1^4$.

Interaction between hydrogen isotopes are computed from spherically symmetric Silvera-Goldman (SG) potential$^6$:

$$\varphi_{ij}(r) = \exp(\alpha - \delta r - \gamma r^2) - \left( \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) f_c(r) + \frac{C_9}{r^9} f_c(r)$$ (S4)

where the first term on the right-hand side (RHS) accounts for short-range repulsive interactions, the second set of terms on the RHS account for long-range attractive dispersion interactions, and the last term on the RHS is an effective three-body correction. The last two terms are multiplied by a damping function, which turns off these interactions at short distances and is given by$^6$

$$f_c(r) = e^{-\left( r / r_c - 1 \right)^2} \theta(r_c - r) + \theta(r - r_c)$$ (S5)
where $\theta(r)$ is the Heaviside function. The parameters for the SG potential are given in Table S1.

The interactions between hydrogen isotopes and an infinitely long, cylindrically symmetric carbon nanotube are computed using

$$\varphi_{sf}(r) = \pi^2 \rho_s \varepsilon_{sf}^2 \sigma_{sf}^2 \left[ \frac{63}{32} \left( \frac{4.5 - 4.5 \cdot 1.0; \delta^2}{1 - \delta^2} \right) - 3 \left( \frac{1.5 - 1.5 \cdot 1.0; \delta^2}{1 - \delta^2} \right) \right]$$

(S6)

where $F(\alpha, \beta, \gamma; \chi)$ is a hypergeometric function, $R = 13.6$ Å is the radius of the nanotube (this pore size corresponds to (20,20) armchair single-walled carbon nanotube), $\rho_s = 0.382$ Å$^{-2}$ is the density of carbon atoms in the nanotube wall, $\delta = r / R$, and $\zeta = R / \sigma_{sf}$. The parameters $\sigma_{sf} = 3.179$ Å and $\varepsilon_{sf} / k_B = 32.056$ K are obtained via mixing rules from self-interaction parameters for carbon atoms and molecular hydrogen.

The initial configurations of pure and binary mixtures of hydrogen isotopes in carbon nanotube (29.58 Å long) are generated from path integral grand canonical Monte Carlo simulations. The system consists of 30-250 hydrogen molecules, depending on the studied pore density. In RPMD, we apply periodic boundary conditions and minimum image convention for computing the interactions between hydrogen isotopes in the longitudinal direction. We truncate all interactions between neighboring ring-polymers at centroid-to-centroid distance of 14.79 Å. We equilibrated the system for 50 ps, and then calculated ensemble averages, mean square displacement, ring-polymer radius of gyration, and ring-polymer centroid density for 10 ps (production time) by averaging over 1000 consecutive 4 ps ring polymer trajectories with a time step of 0.5 fs. For selected densities, we performed 10 independent RPMD runs with longer production time of 25 ps. The averages computed for 10 and 25 s production runs are within statistical error of RPMD simulations (see Figs. 1-S1). The equations of motion were integrated using a symplectic integrator based on alternating free energy harmonic ring polymer and external force steps. The temperature was controlled by resampling the ring polymer momenta from the Maxwell distribution at inverse temperature between each trajectory.
References


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<th>Parameter</th>
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**Table S1.** Parameters of the Silvera-Goldman model potential in atomic units$^6$. 
Figure S1. Pore density variation of H$_2$ (top) and D$_2$ (bottom) ring-polymer radius of gyration, obtained using RPMD trajectories. Open and filled symbols correspond to 10 and 25 ps production runs, respectively.
Figure S2. Self-diffusion coefficients for H$_2$ and the heavy isotope as a function of H$_2$ mole fraction in the H$_2$/D$_2$ (top) and H$_2$/T$_2$ (bottom) mixtures at a fixed pore density of 16.4 mmol/cm$^3$ and 25 K.