Quantum fluctuations increase the self-diffusive motion of para-hydrogen in narrow carbon nanotubes

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THEORY AND METHODS

A. Path Integral Action

According to Feynman's path integral formalism we mapped each para-hydrogen (p-H_2) molecule onto an equivalent polymer chain or 'necklace' of P classical 'beads' $\mathbf{r}_i^{(1)}$, $\mathbf{r}_i^{(2)}$,…, $\mathbf{r}_i^{(P)}$ [1-5]. The vector $\mathbf{r}$ denotes the position of a bead belonging to the i-th molecule. In our simulations of p-H_2 in the bulk phase we have used the primitive action, given by[1-5]:

$$W = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{\alpha=1}^{P}\left(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_i^{(\alpha+1)}\right)^2 + \frac{1}{P}\sum_{i<j}\sum_{\alpha=1}^{P}V_{ff}\left(\mathbf{r}_{ij}^{(\alpha)}\right) \tag{1S}$$

where N is the number of p-H_2 molecules, $\beta = \left(k_B T\right)^{-1}$ is the inverse of the temperature, m denotes mass of p-H_2, and $\hbar$ is Planck's constant divided by 2π. Owing to the cyclic condition of the polymer chains, if $\alpha = P$, then $\alpha + 1 = 1$. The interaction potential between p-H_2 molecules, $V_{ff}(r)$, is taken from Silvera and Goldman[6]. In all performed path integral Monte Carlo simulations we quantized p-H_2 molecules by 128 beads.

In our simulations of p-H_2 adsorbed in carbon nanotubes we used the primitive action, given by[7-8]:

$$W = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{\alpha=1}^{P}\left(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_i^{(\alpha+1)}\right)^2 + \frac{1}{P}\sum_{i<j}\sum_{\alpha=1}^{P}V_{ff}\left(\mathbf{r}_{ij}^{(\alpha)}\right) + \frac{1}{P}\sum_{i=1}^{N}\sum_{\alpha=1}^{P}V_{sf}\left(\mathbf{r}_i^{(\alpha)}\right) \tag{2S}$$

The first two terms in Eq.2S correspond to fluid-fluid interactions, and the last term results from an additional fluid-solid interactions.

As previously, we computed the solid-fluid potential between the spherical p-H_2 bead and infinitely-long structureless cylindrical carbon tube from the following the equation[9,10]:

$$V_{sf}(x)=\pi^2\rho_s\varepsilon_{sf}\sigma_{sf}^2\left[\frac{63}{32}\frac{F\left(-\frac{9}{2},-\frac{9}{2},1,\delta^2\right)}{\left(\left(1-\delta^2\right)R^*\right)^{10}}\delta^{11}-3\frac{F\left(-\frac{3}{2},-\frac{3}{2},1,\delta^2\right)}{\left(\left(1-\delta^2\right)R^*\right)^4}\delta^5\right] \quad (3S)$$

Where $\delta=R/x$, $R^*=R/\sigma_{sf}$, R denotes the carbon tube radius, x is the distance from the pore centre to the centre of spherical bead, ρ_s is the density of carbon atoms in the pore wall (0.382 Å^{-2}), σ_{ff}=2.958 Å, ε_{ff}/k_b=36.7 K, σ_{ss}=3.4 Å, ε_{ss}/k_b=28 K, $\sigma_{sf}=\left(\sigma_{ss}+\sigma_{ff}\right)/2$, $\varepsilon_{sf}=\sqrt{\left(\varepsilon_{ss}/k_b\right)\left(\varepsilon_{ff}/k_b\right)}$, and $F(a,b,c,z)$ is the hypergeometric function given by[10]:

$$F(a,b,c,z)=1+\frac{ab}{c}z+2!\frac{a(a+1)(b+1)}{c(c+1)}z^2+\ldots \quad (4S)$$

In the current study we investigated the thermodynamic and dynamics properties of p-H$_2$ molecules as well as their classical counterparts (i.e., P = 1 in Eqs. 1S-2S) adsorbed in four infinitely-long structureless carbon nanotubes at 30 K. We selected the pore sizes of structureless carbon cylinders in agreement with atomistic configurations of the following armchair nanotubes: (6,6) – pore radius of 4.07 Å, (7,7) – pore radius of 4.713 Å, (10,10) – pore radius of 6.7326 Å, (12,12) – pore radius of 8.0794 Å. The free energies computed at zero coverage for classical p-H$_2$ molecule (i.e., solid-fluid interaction potentials) are displayed in Figure 1S. Note that the free energy barrier at the pore centre strongly depends on the nanotube size. For all adsorption systems we define the pore density as follows: $\rho=N/V$, where N denotes the number of adsorbed molecules, and $V=\pi R_{in}^2 L$. Here, L is the length of the unit cell along the tube axis, and the internal radius of carbon cylinder is given by: $R_{in}=R-\sigma_{ss}/2$ Å, where σ_{ss}=3.4 Å is the collision diameter of carbon atom.

B. Simulation Details

B.I. Grand Canonical Path Integral Monte Carlo method

We used grand canonical path integral Monte Carlo (GCPIMC) simulations to generate initial configurations of adsorbed p-H_2 molecules in studied carbon nanotubes at 30 K[11,12]. The chemical potential computed from Widom's particle insertion method in canonical ensemble was an input in the GCPIMC simulations[13]. Our simulation systems consist of a single infinitely-long structureless carbon nanotube with periodic boundary conditions in axial direction. All studied nanotubes were kept rigid during GCPIMC simulations. The size of nanotubes was adjusted to ensure that at least 60 paths were adsorbed for each studied pore density. As in our previous studies, fluid-fluid interactions between the adsorbed molecules were cut off at $r_{cut} = 5\sigma_H$ (σ_H = 2.958 Å)[8]. Thermalization of the adsorbed p-H_2 is performed by path-displacement trials (i.e., centroid displacement and bisection[2,3]) whereas chemical equilibration between adsorbed p-H_2 and the reservoir is realized by the patch-exchange trials. The acceptance probabilities are given by the Metropolis algorithm. In all GCPIMC simulations 10^8 configurations were used, of which we discarded the first $6 \cdot 10^7$ to guarantee equilibration. The stability of the simulation results was confirmed by additional longer runs of $5 \cdot 10^8$ configurations. The equilibrium configurations of p-H_2 classical counterpart were obtained from GCPIMC simulation in the classical limit (i.e., for the number of beads $P = 1$).

B.II. Canonical Path Integral Monte Carlo method

In order to obtain imaginary-time correlation functions, we have performed a series of path integral simulations in NVT ensemble. In our simulations we used at least 60 adsorbed p-H_2 molecules interacting via spherically-symmetric potential due to Silvera and Goldman[6]. All initial p-H_2 configurations were taken from GCPIMC simulations. For each studied system we performed $2 \cdot 10^6$ Monte Carlo steps using the staging algorithm[2,3,5]. The kinetic and potential energy was computed from thermodynamics estimator[5]. High-temperature density matrix as well as displacement correlation function was extracted from equilibrium configurations of adsorbed p-H_2 molecules. Free energy profiles were computed from Widom's particle insertion method[13].

B.III. Inversion of frequency-dependent diffusion constant from Tikhonov's first-order regularizing functional

We determined the frequency-dependent diffusion constant, $D(\omega)$, from the following integral equation (see Rabani et al.[14], Kowalczyk et al.[15]),

$$G_v(\tau) = \frac{1}{2\pi}\int_0^\infty \left[e^{-\omega\tau} + e^{-(\tau-\beta)\omega}\right] D(\omega)\, d\omega \tag{5S}$$

where $G_v(\tau)$ denotes the imaginary-time correlation function, $\beta = (k_b T)^{-1}$ is the inverse temperature, $0 < \tau < \beta$ is the imaginary time and P is the number of Trotter slices.

For isotropic bulk p-H_2, we computed imaginary-time correlation function from PIMC simulations in the canonical ensemble[14,15],

$$G_v(\tau_j) = \delta_{j1}\frac{1}{3m\varepsilon} - \frac{1}{N\varepsilon^2}\sum_{\alpha=1}^{N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_P P(\mathbf{r}_1,\ldots,\mathbf{r}_P)\times\left(\mathbf{r}_\alpha^j - \mathbf{r}_\alpha^{j\text{-}1}\right)\cdot\left(\mathbf{r}_\alpha^2 - \mathbf{r}_\alpha^1\right) \tag{6S}$$

where δ is the Kronecker delta function, $\varepsilon = \beta / P$, N is the total number of particles, r_j is a shorthand notation for the position vectors of all particles assisted with bead j, $\mathbf{r}_\alpha^j$ is the position vector of liquid particle α of bead j and $P(\mathbf{r}_1,\ldots,\mathbf{r}_P)$ is the regular sampling function used in standard cyclic PIMC method (with $\mathbf{r}_0 = \mathbf{r}_P$). In our PIMC, imaginary-time correlation function was collected every 10 configurations. For p-H_2 molecules adsorbed in narrow carbon nanotubes, we averaged the imaginary-time correlations only in axial direction (i.e., we computed self-diffusion of adsorbed p-H_2 along the nanotube). Following to our previous work[15], we inverted ill-posed integral equation given by Eq .5S by using first-order Tikhonov's regularizing functional (see Kowalczyk et al.[15] for more details).

To validate our computational methodology, we computed the imaginary-time correlation function and the frequency-dependent diffusion constant for liquid p-H_2 at 14 and 25 K. Both systems have been extensively studied by different methods of quantum dynamics. Moreover, the self-diffusion constants for those systems are known from experiment[14]. The results presented in Figures 2S-3S are in full agreement with previous calculations due to Rabani et al.[14]. The self-diffusion constants are in good agreement with experimental data (see Figure 2S and 3S).

B.IV. Mean square displacement correlation function

We evaluated the mean square displacement correlation function for the free p-H_2 molecule from the following relation[16]:

$$R^2_{free}(\tau) = 3\lambda^2\tau(\beta\hbar - \tau)/(\beta\tau)^2 \tag{7S}$$

where $\lambda = (\hbar\beta/m)^{1/2}$, m denotes the mass of p-H_2 molecule, and $0 < \tau < \beta$ is the imaginary time. $R^2(\beta\hbar/2)$ is a measure of the spatial extend of free p-H_2[16-19]. For all p-H_2 fluids adsorbed in carbon nanotubes, we computed the mean square displacement correlation function from NVT path integral Monte Carlo simulations[18].

B.V. Classical Molecular Dynamics simulations

Molecular dynamics (MD) simulations were performed using home-made code. All MD simulations were performed in NVT ensemble with a stochastic dissipative particle dynamics thermostat (DPD)[12]. All studied nanotubes were kept rigid in our MD simulations. During equilibration MD time, the confined fluid was attached to the DPD thermostat to maintain 30 K. The DPD thermostat adds pairwise random and dissipative forces to all adsorbed p-H_2 molecules, and has been shown to preserve momentum transport[12]. We removed DPD thermostat during production MD time. We used Verlet integrator with a time step of 1 fs[11,12]. All studied adsorption systems consist of at least 60 classical p-H_2 molecules. The initial configurations of adsorbed p-H_2 molecules were taken from GCMC simulations. We used periodic boundary conditions in axial direction. Fluid-fluid interactions between the adsorbed molecules were cut off at $5\sigma_H$ (σ_H = 2.958 Å). MD simulations were performed for the total time of 16 ns, of which we discarded the first 8 ns to guarantee equilibration at 30 K. For each studied MD system, we computed the velocity distribution histogram from time sampling of the momentum of adsorbed classical p-H_2 molecules[12]. MD velocity profiles were in full agreement with theoretical Maxwell-Boltzmann ones, as is shown in Figure 4S. This indicates correct equilibration of adsorbed fluids[12]. To further validate our MD simulation results, we collected high-temperature density matrix of adsorbed classical p-H_2 (see comparison of MD results with PIMC at the classical limit shown in Figure 5S). Self-diffusion coefficients corresponding to axial direction were computed from standard Green-Kubo integration of the velocity autocorrelation function[11,12].

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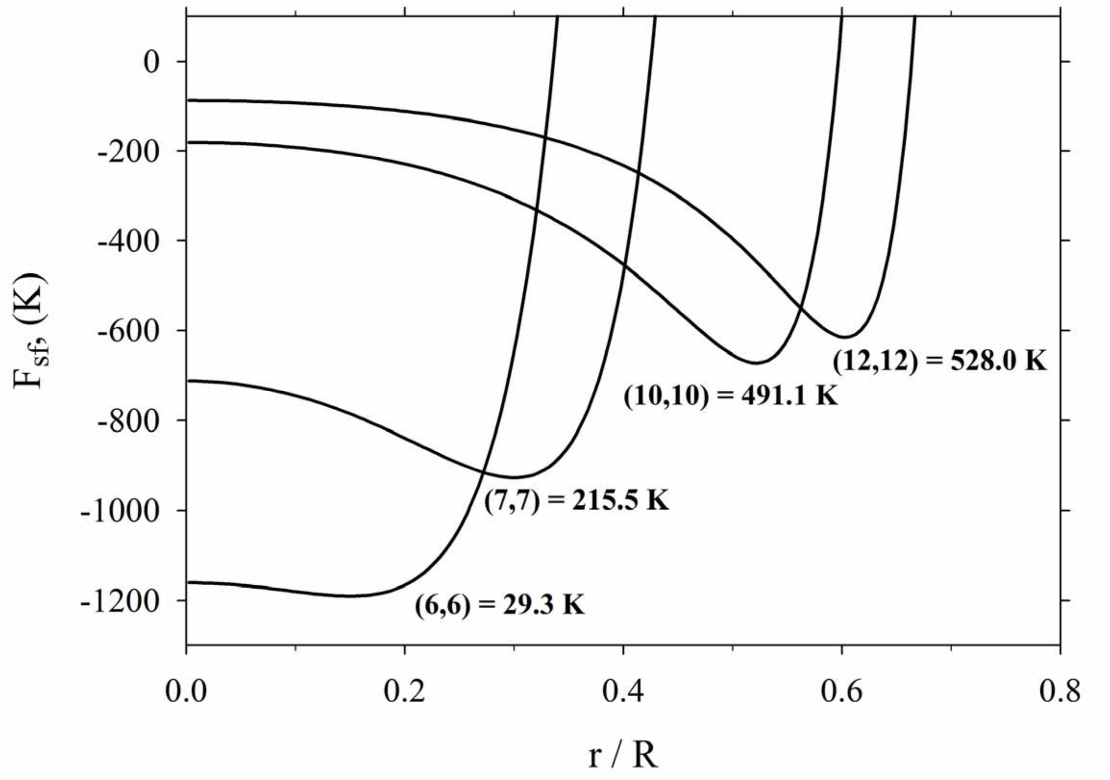

Figure 1S. Free energy of classical p-H_2 computed at 30 K and zero coverage for all studied carbon nanotubes. The height of the free energy barriers are displayed on the plot.

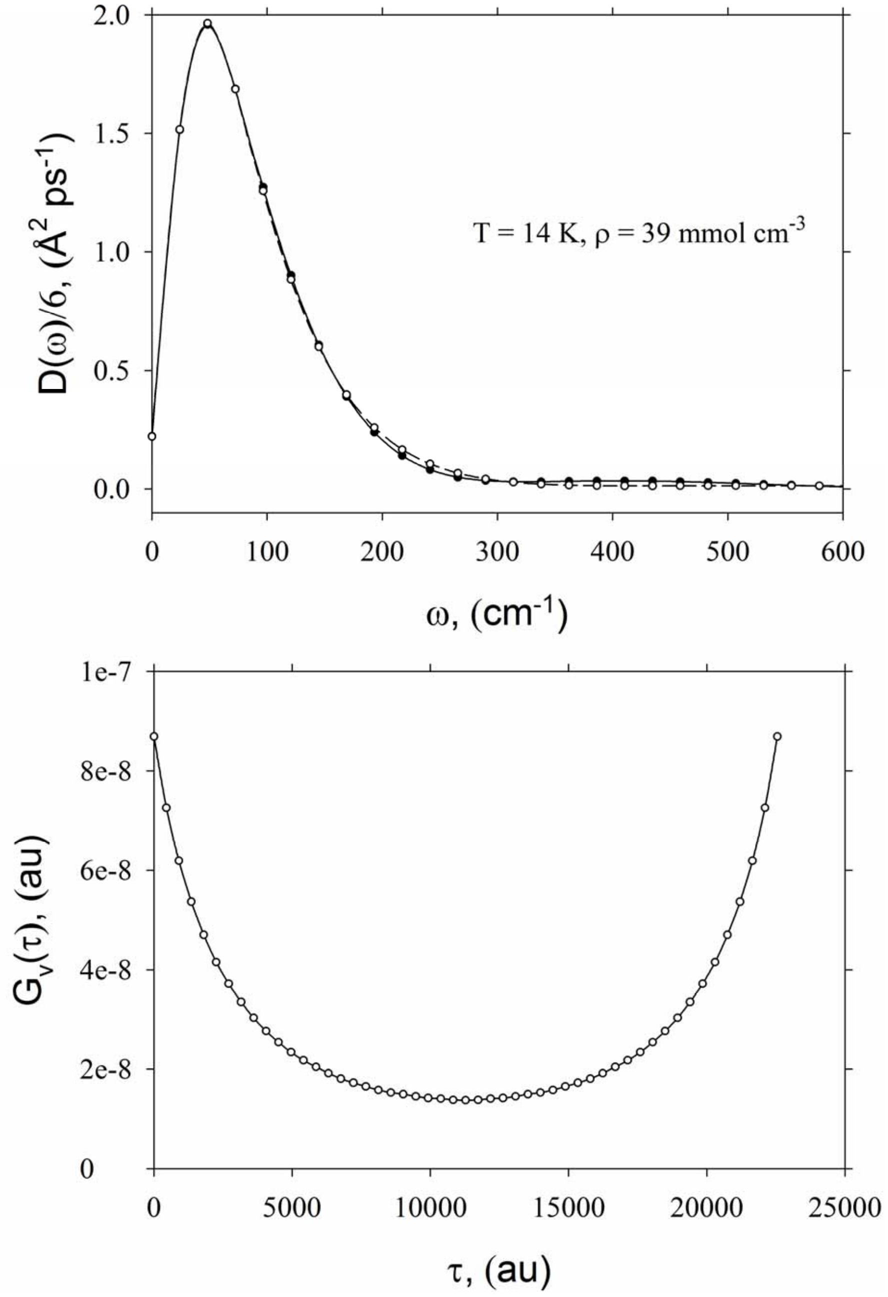

Figure 2S. Plots of imaginary-time correlation function and the frequency-dependent diffusion constant for liquid p-H_2 at 14 K. Frequency-dependent diffusion power spectrums were computed from the first-order Tikhonov's regularizing functional using L-curve (open circles) and quasi-optimality criterion (close circles) for automatic selection of the regularisation parameter[15]. The value of the self-diffusion constant obtained from the analytic continuation method 0.22 Å^2 ps^{-1} is in good agreement with the experimental result 0.4 Å^2 ps^{-1} (see Reference 14).

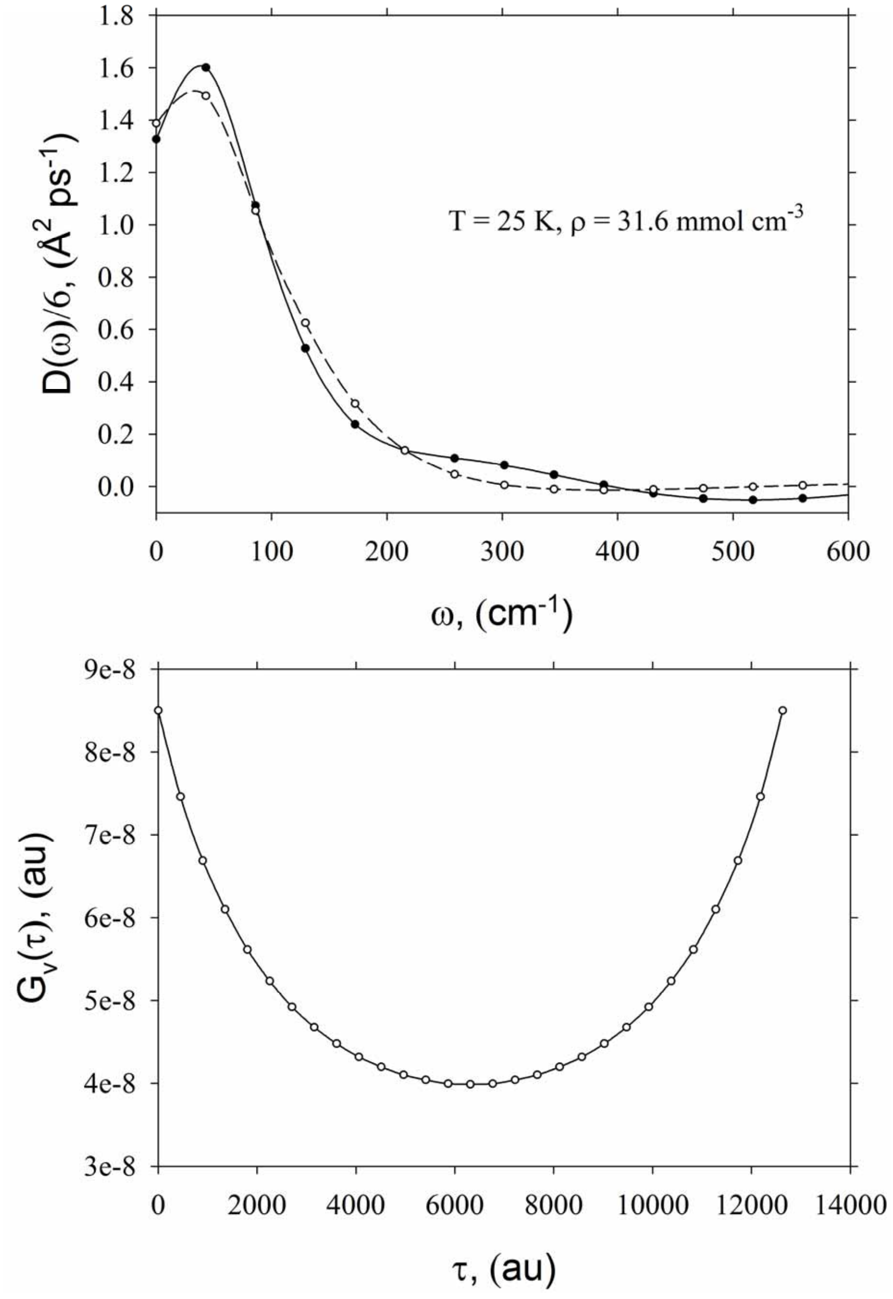

Figure 3S. Plots of imaginary-time correlation function and the frequency-dependent diffusion constant for liquid p-H_2 at 25 K. Frequency-dependent diffusion power spectrums were computed from the first-order Tikhonov's regularizing functional using L-curve (open circles) and quasi-optimality criterion (close circles) for automatic selection of the regularisation parameter[15]. The value of the self-diffusion constant obtained from the analytic continuation method 1.39 Å^2 ps^{-1} is in good agreement with the experimental result 1.6 Å^2 ps^{-1} (see Reference 14).

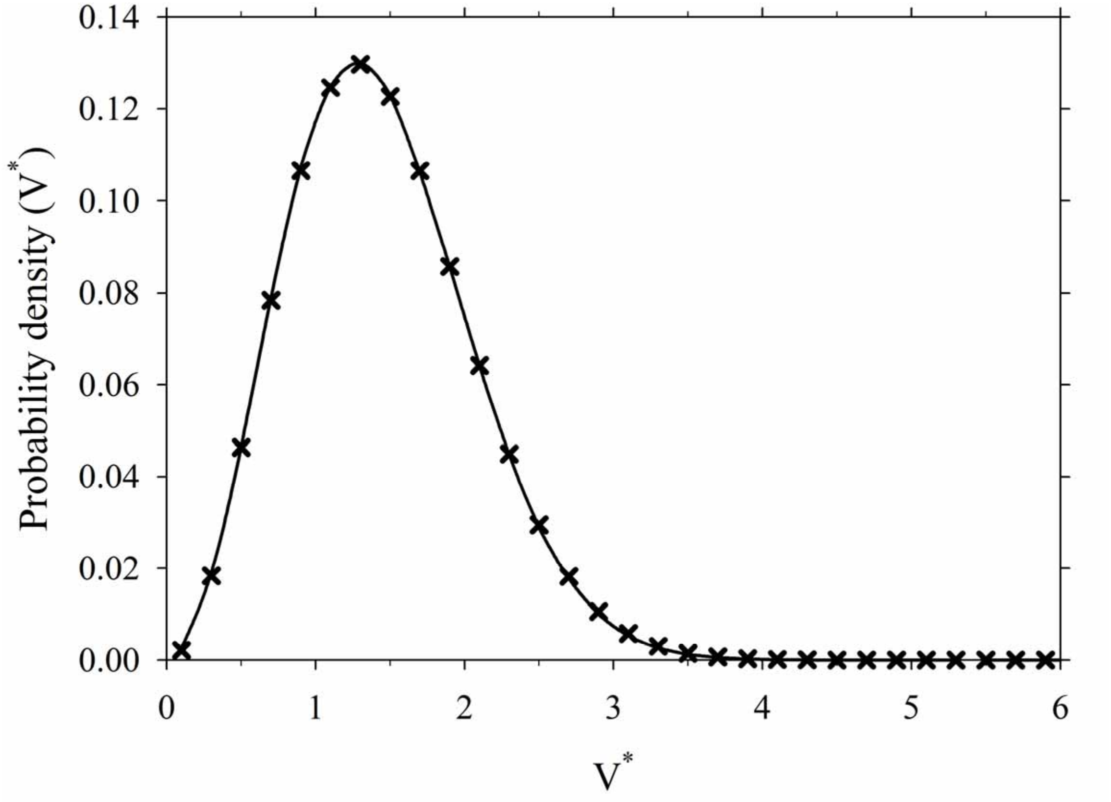

Figure 4S. Comparison of MD (crosses) and Maxwell-Boltzmann (solid line) velocity distribution computed for classical p-H_2 (20.34 mmol cm^{-3}, 30 K) adsorbed in (7,7) carbon nanotube. The velocity, V^*, is presented in reduced Lennard-Jones units[11,12].

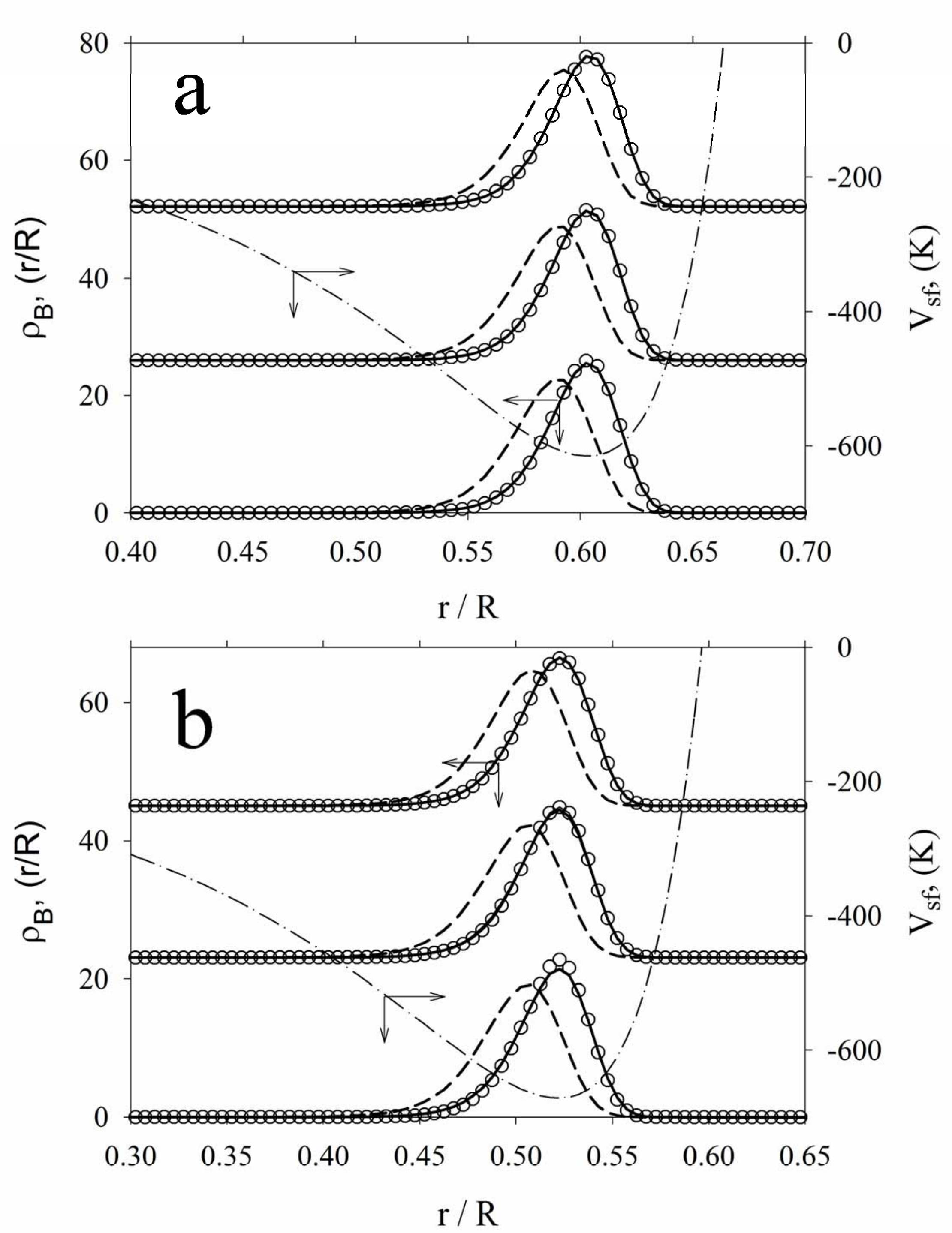

Figure 5S. Density dependence of PIMC (dashed lines) and classical (MC-solid lines and MD-open circles) high-temperature density matrix of p-H_2 adsorbed in (12,12) (panel a) and (10,10) (panel b) carbon nanotube at 30 K. Studied densities are: 7 (bottom panel), 20 (middle panel), and 32 mmol cm^{-3} (upper panel). The solid-fluid interaction potential is displayed by dashed-dot lines.