Supporting Information

Carbon Nanotubes in Benzene: Internal and External Solvation

Simulation methodology and calculations:

Here we present details of our MD simulations of SWNTs in benzene. The simulation cell is comprised of a rigid and immobile SWNT in liquid benzene consisting of 512 C_6H_6 molecules. Five different SWNTs in the (n, n) armchair configuration, i.e., $n = 7, 8, 9, 10$ and 12, were considered. As in Ref. 1, both ends of the nanotubes are terminated with hydrogen atoms, modeled by the Lennard-Jones (LJ) parameters $\epsilon = 15.2\,\mathrm{K}$ and $\sigma = 0.242\,\mathrm{nm}$ and partial charge $+0.1\,e$. The C–H bond length employed for the termination is $0.109\,\mathrm{nm}$. The C atoms directly bonded to the terminal H atoms have a partial charge $-0.1\,e$, while all others are assumed to be electrically neutral. The LJ parameters employed for C atoms of the nanotubes are $\epsilon = 43.2\,\mathrm{K}$ and $\sigma = 0.340\,\mathrm{nm}$.[2] During the simulations, the nanotubes were held immobile and rigid with carbon-carbon bond length $l_{CC} = 0.1415\,\mathrm{nm}$,[3] and the nanotube length $h = 3.742\,\mathrm{nm}$, defined as the end-to-end, hydrogen-to-hydrogen distance. A 12-site all-atom representation was employed to describe benzene. The LJ parameters of benzene were taken from the OPLS-AA force field,[4] while its geometry and partial charges were employed from the work of Kumar and Maroncelli.[5]

The simulations were performed using the DL_POLY program (version 2.13).[6] Periodic, orthorhombic boundary conditions were employed. The long-range electrostatic interactions were computed via the standard Ewald method.[7] The precision parameter and real space cutoff employed for Ewald calculations were 10^{-6} and $14\,\text{Å}$, respectively. The same $14\,\text{Å}$ was used for the cutoff distance of LJ interactions while the width of the neighbor list was set at $1.2\,\text{Å}$. The trajectories were integrated via the Verlet leapfrog algorithm using a time step of $2\,\mathrm{fs}$. To determine the density of the combined nanotube-benzene system, we first conducted simulations in the *NPT* ensemble at $298\,\mathrm{K}$ and $1\,\mathrm{atm}$ for $2\,\mathrm{ns}$ using the Nosé-Hoover barostat.[8] The time constants used for T and P fluctuations were $0.5\,\mathrm{ps}$ and $2\,\mathrm{ps}$, respectively. Benzene molecules were allowed to move in and out of the nanotube during the simulations. The results for the simulation box size determined as an average in the *NPT* ensemble are compiled in Table S1. Using these results, we simulated molecular dynamics of the SWNT-benzene systems in the canonical ensemble at $298\,\mathrm{K}$ employing the Nosé-Hoover thermostat[8,9] with the time constant $0.5\,\mathrm{ps}$. The simulations were carried out with $1\,\mathrm{ns}$ equilibration, followed by a $4\,\mathrm{ns}$ production run. Angular velocity correlation functions were computed by sampling the trajectory every $40\,\mathrm{fs}$. For all other quantities, the trajectory was sampled at the $1\,\mathrm{ps}$ interval.

Table S1: Simulation box size of the combined (n, n) nanotube-benzene system

n	d_0 (nm)	L_x	L_y	L_z
7	0.95	39.10	39.10	50.12
8	1.08	39.12	39.12	50.13
9	1.22	39.14	39.14	50.16
10	1.35	39.17	39.17	50.20
12	1.62	39.30	39.30	50.40
bulk[a)]		31.80	31.80	31.80

[a)]Pure liquid benzene consisting of 216 benzene molecules.

Angular velocity autocorrelation function:

Though not presented in our paper, we have also considered angular velocity autocorrelation functions, $C_\parallel^\omega(t)$ and $C_\perp^\omega(t)$, and their correlation times

$$C_\parallel^\omega(t) = \frac{\sum_i \langle \omega_{i,\parallel}(0) \cdot \omega_{i,\parallel}(t) \rangle}{\sum_i \langle \omega_{i,\parallel}(0) \cdot \omega_{i,\parallel}(0) \rangle} \;\; ; \qquad \tau_\parallel^\omega = \int_0^\infty C_\parallel^\omega(t) \, dt,$$

$$C_\perp^\omega(t) = \frac{\sum_i \langle \omega_{i,\perp}(0) \cdot \omega_{i,\perp}(t) \rangle}{\sum_i \langle \omega_{i,\perp}(0) \cdot \omega_{i,\perp}(0) \rangle} \;\; ; \qquad \tau_\perp^\omega = \int_0^\infty C_\perp^\omega(t) \, dt, \qquad (1)$$

where $\omega_{i,\parallel}$ and $\omega_{i,\perp}$ are the components of the angular velocity of the i-th benzene molecule, respectively, parallel and perpendicular to its C_6-axis in the body-fixed frame. Thus $C_\parallel^\omega(t)$ and $C_\perp^\omega(t)$ describe rotations about the C_6-axis (spinning) and C_2-axes (tumbling), respectively. We note that reorientation of the C_6-axis of benzene occurs via tumbling, while both spinning and tumbling contribute to reorientations of the C_2-axes.

The MD results for the angular velocity autocorrelation functions are presented in Fig. S1. The corresponding results for $\tau_\parallel^\omega$ and $\tau_\perp^\omega$ are compiled in Table S2. Overall the oscillatory behavior of $C_\parallel^\omega(t)$ and $C_\perp^\omega(t)$ inside the SWNTs is more pronounced than in the bulk. Furthermore, with the exception of $(8, 8)$, the librational character measured as the amplitude and/or duration of these oscillations tends to increase as the pore size decreases. By contrast, the angular velocity relaxation in the bulk is completed without much libration in less than 1 ps for both spinning and tumbling motions [Fig. S1(f)]. This indicates that confinement inside of small micropores enhances the librational character of benzene rotations at short times. In the case of the $(8, 8)$ nanotube in Fig. S1(b), the extremely slow and monotonic decay of $C_\parallel^\omega(t)$ without oscillations indicates that its internal benzene molecules undergo free spinning motions. The associated angular velocity correlation time, $\tau_\parallel^\omega = 16$ ps, is longer than other correlation times by more than two orders of magnitude. This is due to closely-packed,

columnar π-stacking structure of internal benzene (see Figs. 4 and 5(b) of the main paper), which allows only spinning motions inside $(8,8)$.

Table S2: MD results for angular velocity correlation times of internal benzene[a)]

n	$\tau_\parallel^\omega$	$\tau_\perp^\omega$
7	0.063	0.038
8	16	0.022
9	0.029	0.020
10	0.071	0.020
12	0.063	0.023
bulk[b)]	0.12	0.032

[a)]Units: ps
[b)]In liquid benzene.

References

[1] Y. Shim and H. J. Kim, *ACS Nano*, 2009, **3**, 1693–1702.

[2] G. Hummer, J. C. Rasaiah and J. P. Noworyta, *Nature*, 2001, **414**, 188–190.

[3] T. W. Odom, J.L. Huang, P. Kim and C. M. Lieber, *Nature*, 1998, **391**, 62–64.

[4] J. Pranata, S. G. Wierschke and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1991, **113**, 2810–2819.

[5] P. V. Kumar and M. Maroncelli, *J. Chem. Phys.*, 1995, **103**, 3038–3060.

[6] T. R. Forester and W. Smith, *DL_POLY 2.13 user manual*, CCLRC, Daresbury Laboratory: Daresbury, Warrington, U.K., 2001.

[7] D. M. Heyes, *J. Chem. Phys.*, 1982, **74**, 1924–1929.

[8] W. G. Hoover, *Phys. Rev.* 1985, **A31**, 511–519.
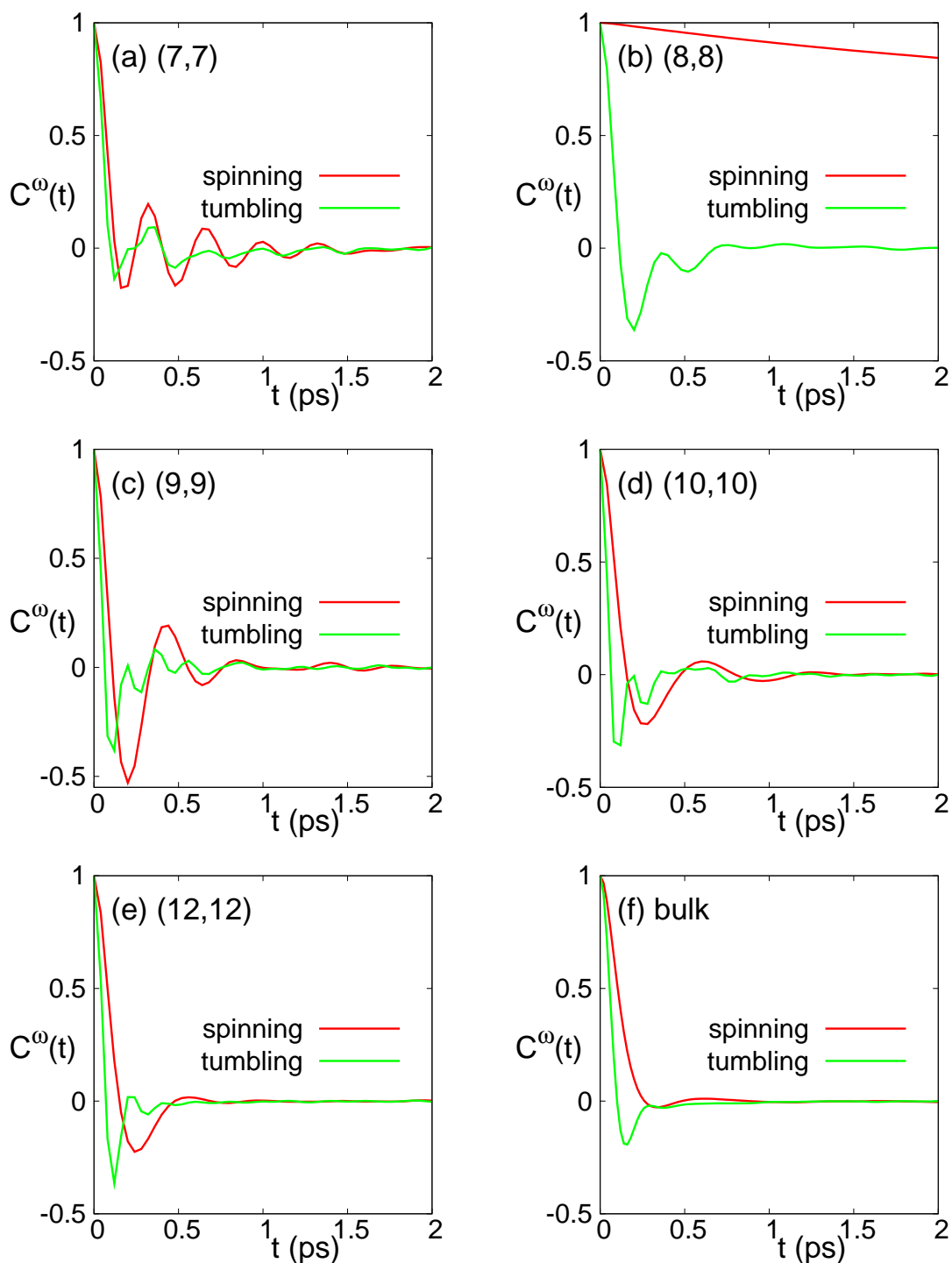
[9] S. Nose, *J. Chem. Phys.* 1984, **81**, 1695.

Figure S1: MD results for $C_\parallel^\omega(t)$ (spinning) and $C_\perp^\omega(t)$ (tumbling) in the interior of (n,n) SWNTs at 298 K. For comparison, $C_\parallel^\omega(t)$ and $C_\perp^\omega(t)$ in the bulk liquid are shown in (f).

4