

Supplementary Information

Ordered and disordered packing of coronene molecules in carbon nanotubes

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I. SIMULATION DETAILS

We simulated coronene@SWCNT and dicoronylene@SWCNT systems by means of the Monte Carlo method in the canonical (NVT) ensemble, i.e. thermodynamic averages are calculated from a large set of randomly generated configurations — obeying equilibrium statistics — for a given number of molecules N , volume V and temperature T .

For coronene@SWCNT systems with diameters $D = 1.45 - 1.7$, we took $N = 25$, a value combining reasonable cluster size with reasonable computation times. The number of Monte Carlo steps used for sampling was $N_{MC} = 10^6$. For coronene@SWCNT with diameters $D = 1.8 - 2$ nm we took $N = 10$, the number of Monte Carlo steps used for sampling was $N_{MC} = 10^6$.

At the start of the simulation, the coronene molecules were placed with their molecular planes perpendicular to the tube axis (molecular 6-fold symmetry axis parallel to the tube axis), their centers of mass on the tube axis, with a nearest-neighbour (center-of-mass-to-

center-of-mass) distance of $a_0 = 5 \text{ \AA}$. (Figure 1a,b). Starting configurations with random molecular orientations or molecules oriented with their molecular planes parallel to the nanotube axis did not lead to configurations with lower energies. Introducing a cartesian coordinate system (O, X, Y, Z) with the long axis of the nanotube coinciding with the Z -axis, the molecules were thus initially located at sites $\vec{X}(j) = (j - 1)a_0\vec{e}_Z$, $j = 1, \dots, N$. Periodic boundary conditions along the z -axis were imposed, the repeated tube fragment has length $L = Na_0 + \Delta L$, where $\Delta L = 27.28 \text{ \AA}$ is an offset chosen so that i) the molecules have some space left to move along the tube axis (so that they can cluster and decluster) and ii) molecules at a distance ΔL apart do not interact. This results in a linear density $\rho = N/L = 0.16 \text{ \AA}^{-1}$ for $N = 25$ and $\rho = 0.13 \text{ \AA}^{-1}$ for $N = 10$. In reality, values of the linear density will vary throughout the tube, since one typically has sections with a lot of molecules, and sections without molecules. It is important point to have a density that is not too high, so that molecules have space to move around. In our simulations, this is implemented by taking the minimal separation between two molecules required for molecules not interacting with each other as an offset and by building in additional free space by initially putting the molecules further apart (5 \AA) than in actual equilibrium ($\lesssim 4 \text{ \AA}$, see Fig. 2b).

We adopt the smooth-nanotube approximation — characterizing a nanotube by its radius rather than its chiral indices, see below — so that the periodically repeated tube fragment can indeed have any length. The coronene molecules are assumed to be rigid and to display perfect D_{6h} symmetry; we generated atomic C and H positions based on interatomic C–C and C–H bond lengths of 1.39 \AA and 1.08 \AA [1, 2]. This leaves 6 degrees of freedom for each molecule (3 translational and 3 rotational). In a Monte Carlo simulation, configurations are generated by changing these degrees of freedom; a newly generated configuration is accepted if $E^n \leq E^o$, where E^n stands for the energy of the new configuration and E^o for the energy of the old configuration. Otherwise, the new configuration is accepted with probability $P = e^{-\frac{E^n - E^o}{k_B T}}$ (k_B is the Boltzmann constant).

The core component of a Monte Carlo simulation is the recipe for calculating interaction energies. We model coronene-coronene interactions by considering C and H atoms as charged sites; intermolecular interactions are then the result of the sum of van der Waals and Coulomb interactions between these sites. A popular way of describing the van der Waals interactions is to use the Lennard-Jones (12,6) potential, resulting in the following

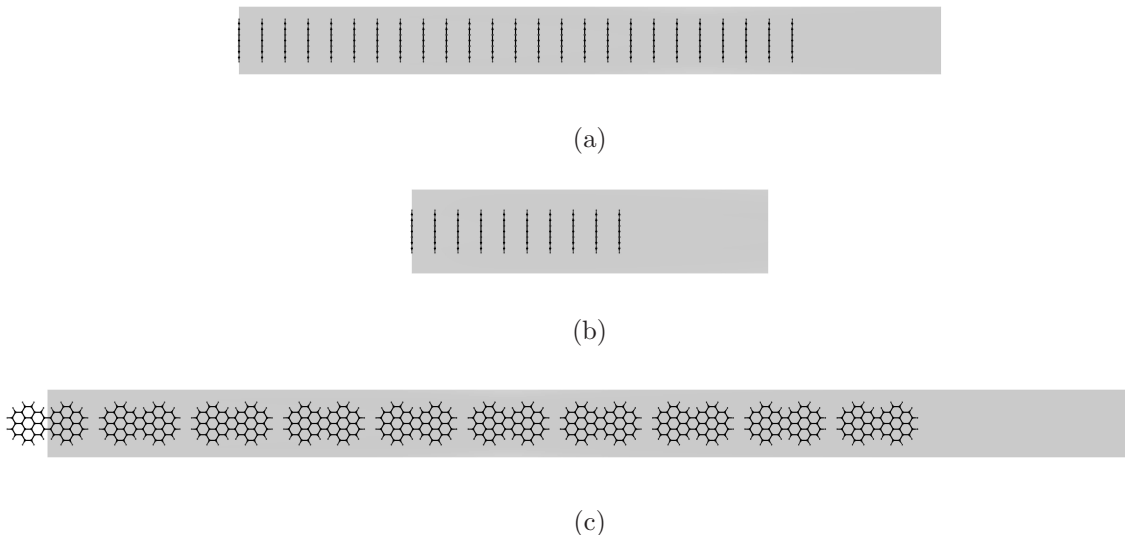


FIG. 1: Starting configurations for (a) coronene@SWCNT, 25 molecules, (b) coronene@SWCNT, 10 molecules and (c) dicoronylene@SWCNT, 10 molecules.

coronene-coronene interaction energy:

$$E_{C_{24}H_{12} - C_{24}H_{12}} = \sum_{s=C,H} \sum_{s'=C,H} \sum_{i=1}^{n_s} \sum_{i'=1}^{n_{s'}} V_{ss'}(r_{ss'}(i, i')), \quad (1.1)$$

$$V_{ss'}(r) = \begin{cases} 4\varepsilon_{ss'} \left[\left(\frac{\sigma_{ss'}}{r} \right)^{12} - \left(\frac{\sigma_{ss'}}{r} \right)^6 \right] + F \frac{q_s q_{s'}}{r} + v_{ss'}^c & \text{if } r \leq r_{ss'}^c, \\ 0 & \text{if } r > r_{ss'}^c, \end{cases}, \quad (1.2)$$

$$v_{ss'}^c = -4\varepsilon_{ss'} \left[\left(\frac{\sigma_{ss'}}{r_{ss'}^c} \right)^{12} - \left(\frac{\sigma_{ss'}}{r_{ss'}^c} \right)^6 \right] - F \frac{q_s q_{s'}}{r_{ss'}^c}. \quad (1.3)$$

Here, the indices s and s' run over the two occurring types of atoms, C and H, and the indices i and i' run over the atoms of types s and s' in the first and the second molecule, respectively ($n_C = 24$, $n_H = 12$). $r_{ss'}(i, i')$ stands for the distance between atom i of type s of the first molecule and atom i' of type s' of the second molecule. To every atom-atom pair potential, a cut-off value $v_{ss'}^c$ is added, so that beyond a certain distance $r_{ss'}^c$, the interaction energy is zero. The cut-offs are set at $r_{ss'}^c = 5r_{ss'}^{\min}$, with $r_{ss'}^{\min}$ the location of the minimum of $V_{ss'}(r)$. For the potential constants ε_{CC} , ε_{CH} , ε_{HH} , σ_{CC} , σ_{CH} , σ_{HH} , q_C and q_H we took the values from Refs. [3] and [4] used for simulating benzene-benzene interactions; they are quoted in Table I. The value of the constant F is $503.217 \text{ K} \times k_B$.

Coronene-nanotube interactions are calculated with the approximation of a smooth nanotube: rather than taking the discrete (chiral) structure of the nanotube characterised with

TABLE I: Potential constants used for modelling coronene-coronene (or dicoronylene-dicoronylene) and coronene-nanotube (or dicoronylene-nanotube) interactions.

coronene-coronene / dicoronylene-dicoronylene			
ss'	CC	CH	HH
$\varepsilon_{ss'}$ ($k_B \times K$)	35.2	23.0	15.0
$\sigma_{ss'}$ (Å)	3.55	3.01	2.47
$q_s q_{s'}$ (Å)	0.00330625	-0.0066125	0.013225
coronene-nanotube / dicoronylene-nanotube			
s	C	H	
ε_s ($k_B \times K$)	31.6	21.7	
σ_s (Å)	3.40	3.00	

indices n and m , we consider a cylinder of diameter $D = \frac{l}{\pi} \sqrt{n^2 + nm + m^2}$ with a continuous surface density ρ_S of carbon atoms, $\rho_S = \frac{4}{\sqrt{3}l} = 0.372 \text{ \AA}^{-2}$ ($l = \sqrt{3}d_{C-C} = 2.49 \text{ \AA}$ with $d_{C-C} = 1.44 \text{ \AA}$ the C-C bond length in a carbon nanotube). The smooth-nanotube approach has proven to be a justified approximation for the simulation of C_{60} and C_{70} molecules in SWCNTs [5, 6]. Note that characterising a nanotube by its diameter rather than its chiral indices reflects the experimental nanotube synthesis situation: nanotube samples are usually described as displaying a distribution of diameters rather than a single (n, m) chirality. The interaction energy is then obtained as

$$E_{C_{24}H_{12} - \text{SWCNT}} = \sum_{s=C,H} \rho_S \frac{D}{2} \sum_{i=1}^{n_s} \int_0^{2\pi} d\Phi \int_{-\infty}^{+\infty} dZ V_s(|\vec{r}_s(i) - \vec{\rho}|) \quad (1.4)$$

where the index i runs over the n_s atoms of type s of the coronene molecule. The vector $\vec{\rho} = (\frac{D}{2} \cos \Phi, \frac{D}{2} \sin \Phi, Z)$ addresses a point on the nanotube, and V_s is the pair potential for interactions between an atom of type s of the coronene molecule and a “nanotube atom”. For the pair potentials we take truncated-and-shifted Lennard-Jones (12, 6) potentials:

$$V_s(r) = \begin{cases} 4\varepsilon_s \left[\left(\frac{\sigma_s}{r}\right)^{12} - \left(\frac{\sigma_s}{r}\right)^6 \right] + v_s^c & \text{if } r \leq r_s^c \\ 0 & \text{if } r > r_s^c \end{cases}, \quad (1.5)$$

$$v_s^c = -4\varepsilon_s \left[\left(\frac{\sigma_s}{r_s^c}\right)^{12} - \left(\frac{\sigma_s}{r_s^c}\right)^6 \right]. \quad (1.6)$$

There are no charges associated with the atoms here. The potential constants ε_s and σ_s are taken from Ref. [7] where benzene-graphite interactions were studied; their values are listed in Table I. The additions v_s^c ensure continuity at the cut-off distances r_s^c , set at $5r_s^{\min}$ with $r_s^{\min} = \sqrt[6]{2}\sigma_s$ the location of the minimum of $V_s(r)$.

The total system energy E of a configuration used for deciding upon acceptance or rejection according to the Monte Carlo scheme is then given by

$$E = \frac{1}{2} \sum_{j_1=1}^N \sum_{\substack{j_2=1 \\ j_1 \neq j_2}}^N E_{C_{24}H_{12} - C_{24}H_{12}}(j_1, j_2) + \sum_{j_1=1}^N E_{C_{24}H_{12} - SWCNT}(j_1), \quad (1.7)$$

where $E_{C_{24}H_{12} - C_{24}H_{12}}(j_1, j_2)$ stands for the intermolecular interaction energy of molecules j_1 and j_2 given by Eqs. (1.1) – (1.3) and $E_{C_{24}H_{12} - SWCNT}(j_1)$ for the interaction energy of molecule j_1 with the surrounding nanotube given by Eqs. (1.4) – (1.6).

We call a Monte Carlo *trial move* a change of the configuration where either the position or the orientation of one — randomly chosen — of the N molecules is changed. A Monte Carlo *step* is defined as a series of $(5 + 5)N$ trial moves, so that on average every molecule undergoes 5 translational and 5 orientational trial moves in one Monte Carlo step. The amplitudes for positional and rotational trial moves were adjusted on-the-fly during preliminary Monte Carlo runs to yield an acceptance rate of approximately 50%, and then fixed. After equilibration has set in (the total system energy then fluctuates around an average value), quantities of interest were sampled. Results (averages of sampled quantities) were collected for $N_{MC} = 10^6$ Monte Carlo steps.

Simulations for dicoronylene@SWCNT were done in a completely analogous way. The same phenomenological potential model as for coronene@SWCNT [Eqs. (1.1) – (1.7), Table I] was used. The atomic coordinates of the dicoronylene molecule ($n_C = 48$, $n_H = 20$) were determined from the structure of the coronene molecule, with the same C–C and C–H bond lengths and resulting in D_{2h} symmetry. For reasons of computational feasibility, only $N = 10$ molecules were taken. The molecules were placed with their centers of mass on the nanotube axis and all oriented in the same way with the molecular plane parallel to the nanotube’s long axis, with a center-of-mass-to-center-of-mass distance of $a_0 = 20 \text{ \AA}$ and a set-off of $\Delta L = 35.41 \text{ \AA}$. We started with configurations where the molecules are parallel to the tube axis (Figure 1c). The number of Monte Carlo steps used for sampling was $N_{MC} = 10^6$.

II. ADDITIONAL DATA FOR CORONENE@SWCNT

Figure 2 shows a typical pair correlation function $g(r)$ for a coronene@SWCNT system displaying 1D order (columnar stack of molecules). For the determination of the location of the first peak of $g(r)$, which we use as a measure for the average distance between neighboring molecules, a separate histogram was recorded for the interval $2 - 6 \text{ \AA}$, with 900 bins, resulting in a bin width of $0.00444 \dots \text{ \AA}$, so that the location of the peak maximum is correct up to $\pm 0.00222 \dots \text{ \AA}$. The inset in Figure 2 shows a part of that histogram (for $D = 1.5 \text{ nm}$ and $T = 300 \text{ K}$).

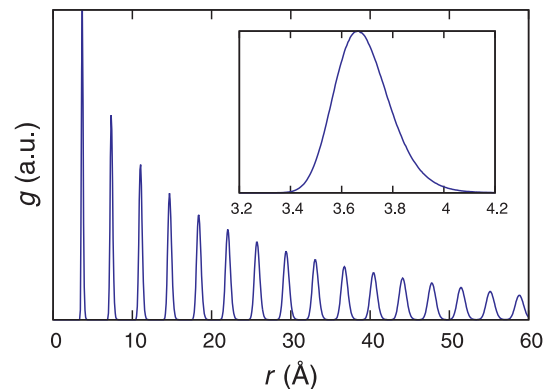


FIG. 2: Pair correlation function $g(r)$ (in arbitrary units) for coronene@SWCNT with $D = 1.5 \text{ nm}$ and $T = 300 \text{ K}$. Inset: zoom of the first peak, the location of the maximum of which serves as a measure for the average intermolecular distance d_1 .

Figure 3 shows the pair correlation functions $g(r)$ for the cases for which snapshots are shown in Figure 3 of the main text.

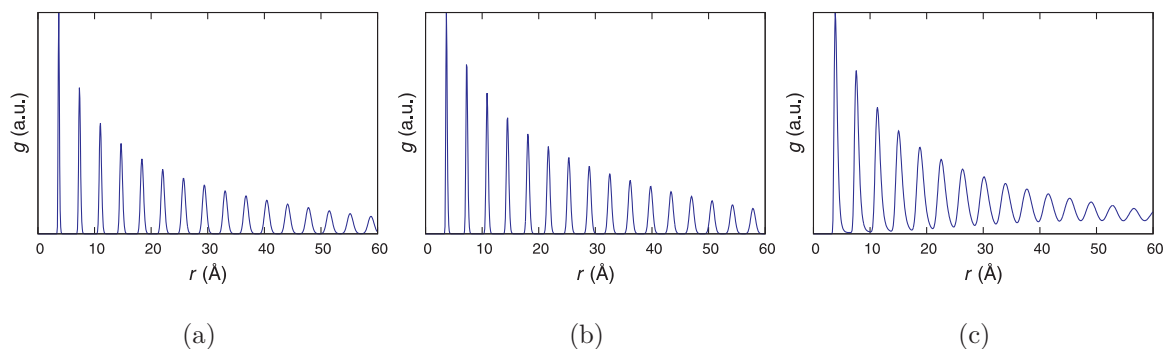


FIG. 3: Pair correlation functions $g(r)$ (in arbitrary units) for coronene@SWCNT with (a) $D = 1.5 \text{ nm}$ and $T = 300 \text{ K}$, (b) $D = 1.65 \text{ nm}$ and $T = 300 \text{ K}$, and (c) $D = 1.7 \text{ nm}$ and $T = 800 \text{ K}$.

Figure 4 shows the average molecular mean-squared radial distances $\langle\langle\rho^2\rangle\rangle$ for coronene@SWCNT as a function of temperature for diameters in the range $1.45 \text{ nm} \leq D \leq 1.7 \text{ nm}$.

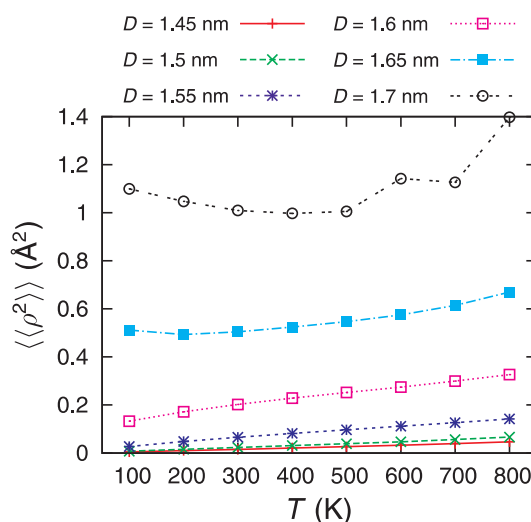


FIG. 4: Average molecular mean-squared radial distances $\langle\langle\rho^2\rangle\rangle$ for coronene@SWCNT as a function of temperature.

Next, we include some results of additional simulations addressing the role of the starting configuration, and of the density and the number of molecules in the simulations.

Fig. 5 shows the starting configuration and a snapshot at equilibrium for a simulation with 3 coronene molecules for $D = 1.5 \text{ nm}$ and $T = 300 \text{ K}$. This demonstrates, as mentioned above, that the starting configuration does not play any role in reaching the equilibrium configuration.



FIG. 5: (a) Starting configuration with 3 molecules aligned parallel to the tube axis in a tube with $D = 1.5 \text{ nm}$ and (b) a snapshot of a configuration resulting from equilibrating the configuration shown in a) for $T = 300 \text{ K}$.

In Fig. 6 we show equilibrium snapshots for simulations with 10 coronene molecules, for $D = 1.5 \text{ nm}$ and $T = 300 \text{ K}$, $D = 1.65 \text{ nm}$ and $T = 300 \text{ K}$, and $D = 1.7 \text{ nm}$ and

$T = 800$ K (to be compared with Fig. 3 of the main text). A comparison between all snapshots for $N = 10$ and $N = 25$, and a comparison of the calculated quantities shown in Fig. 2 of the main text (average total energy per molecule E/N , average distance between neighbouring molecules d_1 , average molecular tilt angles $\langle\theta\rangle$ and average molecular mean-squared displacements $\langle\langle u^2 \rangle\rangle$), for varying tube diameter ($D = 1.45 - 1.7$ nm) and varying temperature ($T = 100 - 800$ K), shows that our conclusions are the same for these two case studies. More importantly, this comparison shows that the number of molecules and the molecular density don't play any role of importance.

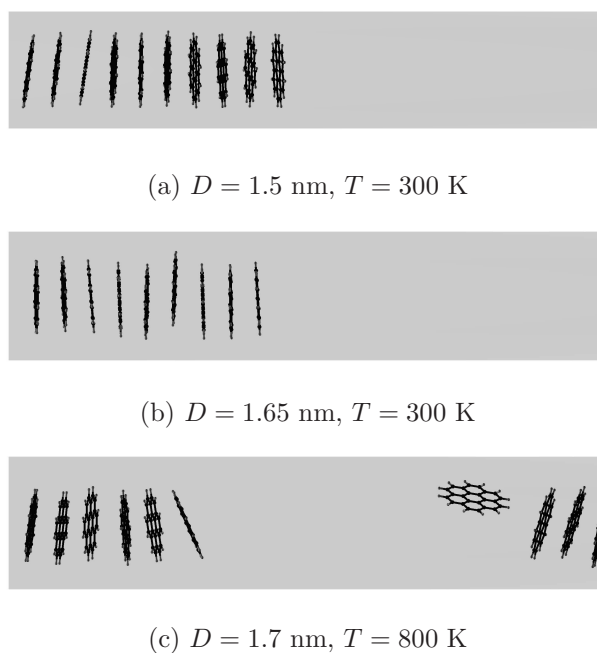


FIG. 6: Equilibrium snapshots for simulations with 10 coronene molecules.

Finally, we note that simulations without confinement in a tube do not result in the regular stacks observed for in-tube confinement.

III. ADDITIONAL DATA FOR DICORONYLENE@SWCNT

For $D = 1.5 - 1.7$ nm, regular clusters of stacked tilted dicoronylene molecules are observed (see Figure 8b of the main text). This follows unambiguously from the distributions of the tilt angle values $\phi(j)$ shown in Figure 7. The two peaks at ϕ_1 and $180^\circ - \phi_1$, broadening with increasing temperature, correspond to one and the same molecular orientation (molecules tilted by $\theta = |90^\circ - \phi_1|$ with respect to the nanotube axis). For this diameter

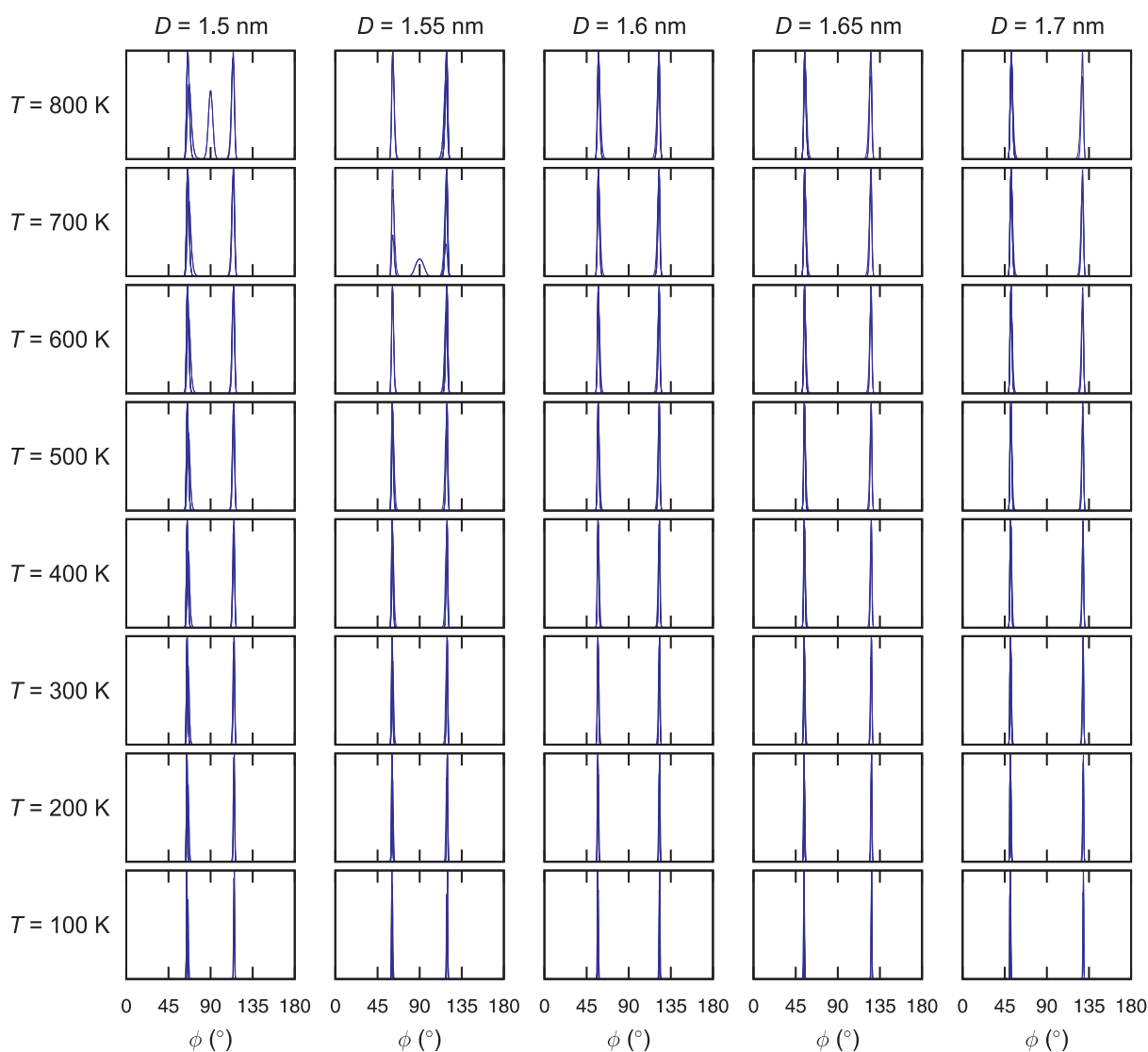


FIG. 7: Distributions of $\phi(j)$ values (in arbitrary units) for the $N = 10$ dicoronylene molecules of simulated dicoronylene@SWCNT systems for nanotube diameters $D = 1.5 - 1.7$ nm (left to right) and temperatures $T = 100 - 800$ K (bottom to top).

range, the evolution of the average tilt angles $\langle\theta\rangle$ with temperature is shown in Figure 8. For $D = 1.5$ nm and $T = 800$ K, and for $D = 1.55$ nm and $T = 700$ K, two molecules align more or less parallel to the nanotube axis (tilt angle $\sim 0^\circ$); the other molecules form a regular cluster. For $D = 1.5$ nm and $D = 1.55$ nm, the temperature evolution of the tilt angle has been obtained by excluding the two molecules oriented more or less parallel to the nanotube axis.

Figures 9 and 11 show the average total energy per molecule E/N and the average

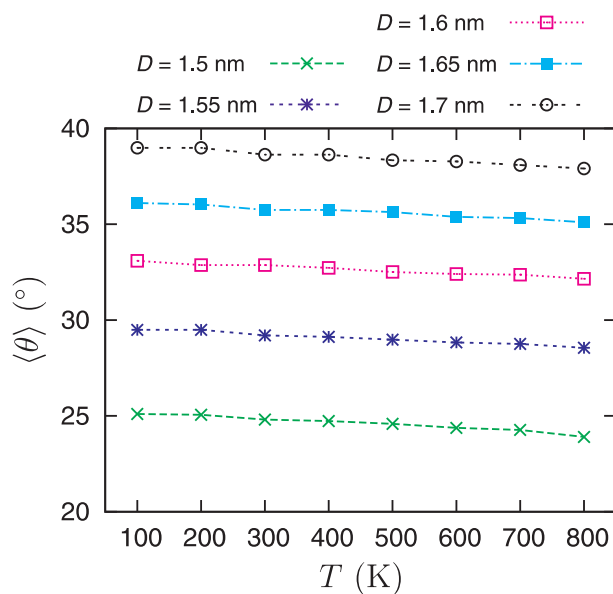


FIG. 8: Average molecular tilt angles $\langle \theta \rangle$ for dicoronylene@SWCNT as a function of temperature.

molecular mean-squared displacements $\langle \langle u^2 \rangle \rangle$ for dicoronylene@SWCNT as a function of temperature. Note that the outlying value of E/N for $D = 1.55$ nm at $T = 700$ K corresponds to the case with two parallel-lying molecules, suggesting that the true ground state has only tilted molecules as observed for the other temperatures.

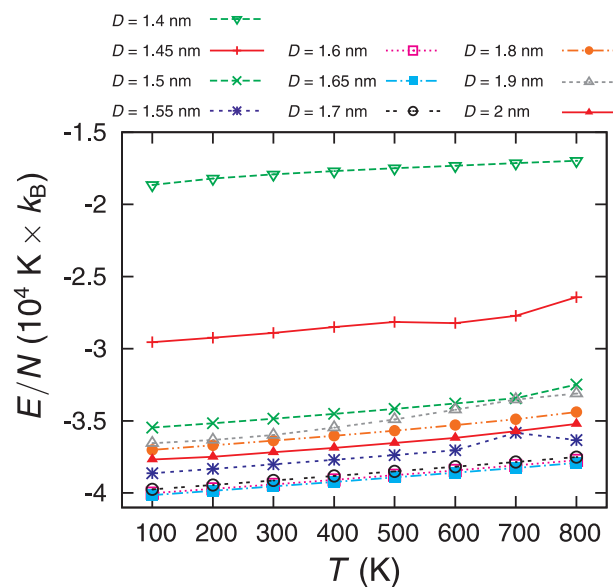


FIG. 9: Average total energy per molecule E/N for dicoronylene@SWCNT as a function of temperature.

Figure 10 shows a snapshot of a typical dicoronylene@SWCNT configuration for the extra

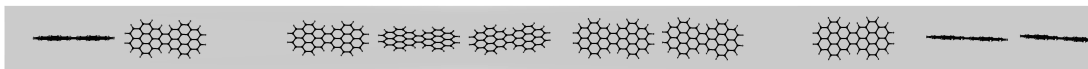


FIG. 10: Snapshot of a dicoronylene@SWCNT configuration for $D = 1.4$ nm and $T = 300$ K.

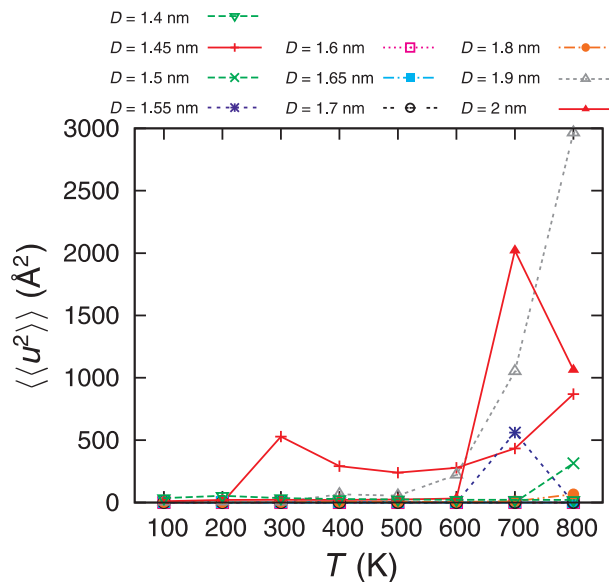


FIG. 11: Average molecular mean-squared displacements $\langle\langle u^2 \rangle\rangle$ for dicoronylene@SWCNT as a function of temperature.

small diameter value $D = 1.4$ nm.

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