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Picosecond Melting of Peptide Nanotubes with Infrared Laser: A Nonequilibrium Simulation Study

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Abstract

Here we show the details of the construction and characterization of the FFC, equilibrium and NEMD simulations.

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Construction of the FF channel

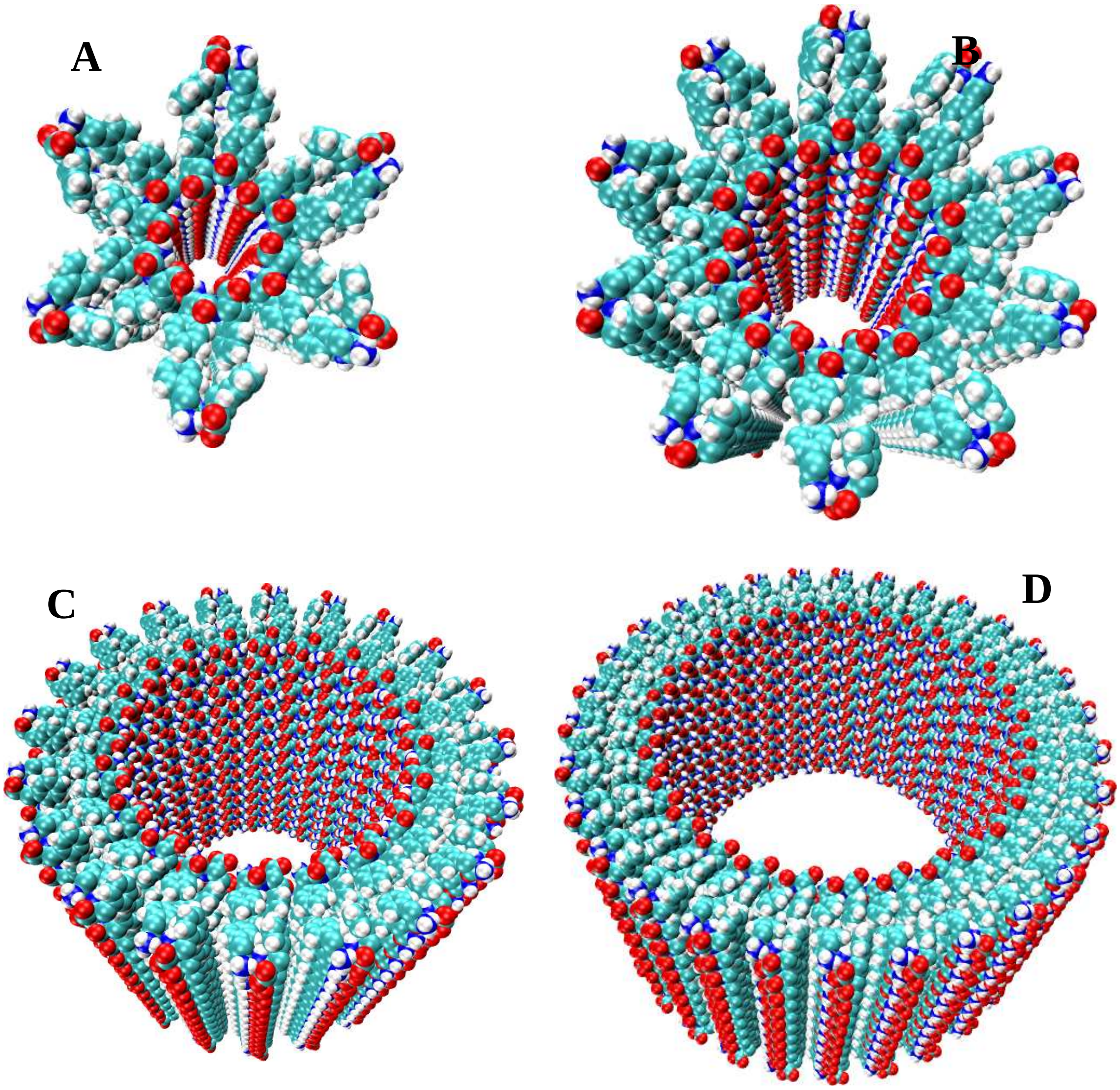

Figure 1: The FF channels constructed in 12 complete circles with the optimized lattice constants ($a = 6.0$, $b = 8.3$,$\gamma = 90°$) and $n_1 = 6$ (A), 10 (B), 20 (C) and 30 (D).

Recently, Nussninov and coworkers have proposed a method called 2D lattice wrapping system to construct a framework of a peptide nanotube from peptide building blocks.[1,2] In this approach, only five parameters ($\vec{a}, \vec{b}, \gamma, n_1, n_2$) are needed to define a 2D lattice: ($\vec{a}, \vec{b}$) are two lattice vectors and γ is the angle between them. The number n_1 defines how many lattice cells are used to wrap one full round along the axis $\vec{a}$ and n_2 indicates how many cells are shifted along the axis $\vec{b}$ after one complete wrapping. Given these five parameters, a 2D lattice is generated where a lattice site is occupied by a building block. This 2D sheet is then wrapped onto a cylinder surface along a rotating axis $\vec{w} = n_1.\vec{a} + n_2.\vec{b}$ to generate 3D tube. In the case of FF channel (FFC), the X-ray crystallographic analysis has shown that each individual FF channel can be formed by merely six FF peptides with the termini NH_3^+ and COO^- points toward the center of the tube and the two phenyl rings pointing outward.[3] Also, tubes with different sizes with thickness's consisting of only two FFs should be feasible to generate. In this case, the two phenyl rings of one FF point to the other two rings of another FF. Guided by this experimental information, the FFNTs are constructed as the following. First, we take a single FF peptide, which is in the *cis*-state, from the crystal structure (Cambridge Crystallographic Data Centre, no. CCDC 163340). Then the second FF is generated such that two phenyl rings point head-to-head toward their counterparts of the first FF, and the shortest distance between heavy atoms of two FFs is 1 nm. Having generated this building block, we construct four tubes each has twelve ($n_2 = 12$) complete round and each round contains $n_1 = 6, 10, 20$ and 30 building blocks. In the following tubes are named as T6, T10, T20 and T30. For all tubes, our optimized lattice constants are: $a = 6.0$, $b = 8.3$ and angle $\gamma = 90°$ which are close to the values obtained by Nussinov et al. using the all-atom CHARMM force-field.[4]

Equilibrium simulation

Each constructed FFC is centered in a cubic simulation box filed with explicit water molecules, allowing a minimum distance between the tube and the edge of the box of 0.8 nm. We use the SPC water model to describe the solvent. Each system is energy minimized using the steepest descent method, then a short simulation of 1 ns is carried out in NPT ensemble, followed by the production run in NVT ensemble. The GROMACS program[5] is used to perform the simulations. The bond lengths with hydrogen atoms are fixed with the SHAKE algorithm[6] and the equations of motion are integrated with a time step of 2 fs using the velocity Verlet integrator.[7] The electrostatic interactions are calculated using the particle mesh Ewald method and a cutoff of 1.1 nm.[8] A cutoff of 1.2 nm is used for the Van der Waals interactions. The nonbonded pair lists are updated every 10 fs. Temperature is controlled by the velocity-rescaling thermostat.[9]

Nonequilibrium laser-induced FFNT dissociation

For each FFC system, we select 100 independent structures from their equilibrium trajectory and then use for laser-induced NEMD simulation. In this approach, a time-dependent electric field

$$E(t) = E_0 \exp[-\frac{(t-t_0)^2}{2\sigma^2}] \cos[2\pi c\omega(t-t_0)], \tag{1}$$

was applied to mimic a laser pulse. Here, E_0 represents amplitude of the electric field, σ is the pulse width, t is the time after the pulse maximum t_0, c is the speed of light and ω is the frequency. This technique has been implemented in the GROMACS simulation package.[5] In these simulations only the waters are coupled to the heat bath in order to maintain the temperature of 310 K with a coupling constant of 0.1 ps. To ensure stability, a time step of 0.2 fs was used, and data collected every 1 ps. All other simulation parameters are the same with those used in the equilibrium simulation.

Data analysis

To characterize the tube geometry, we calculate the tube inner and outer diameters as $\langle D\rangle = (1/12)\sum_{i=1}^{12}(1/3)\sum_{j=1}^{3} d_i^{j,j+3}$ where $d_i^{j,j+3}$ is the distance between the centers of mass of two opposite FF peptides j, $j+3$ on the inner- or outer circle i-th. The length is defined as $\langle L\rangle = (1/11)\sum_{i=1}^{11} l_{i,i+1}$ where $l_{i,i+1}$ is the distance between the centers of mass of two consecutive circles i and $i+1$.

A hydrogen bond (HB) was considered formed when the acceptor-donor distance is not more than 0.35 nm, and the acceptor-donor-hydrogen angle is not more than 30.

The vibrational spectrum of the FFC is calculated only for initial structures in gas phase. We first perform normal mode analysis, then the vibrational spectrum is calculated within the normal mode harmonic approximation using the standard theory.[10] This is done using the GROMACS simulation package.[5] The vibrational modes associated to the spectrum is

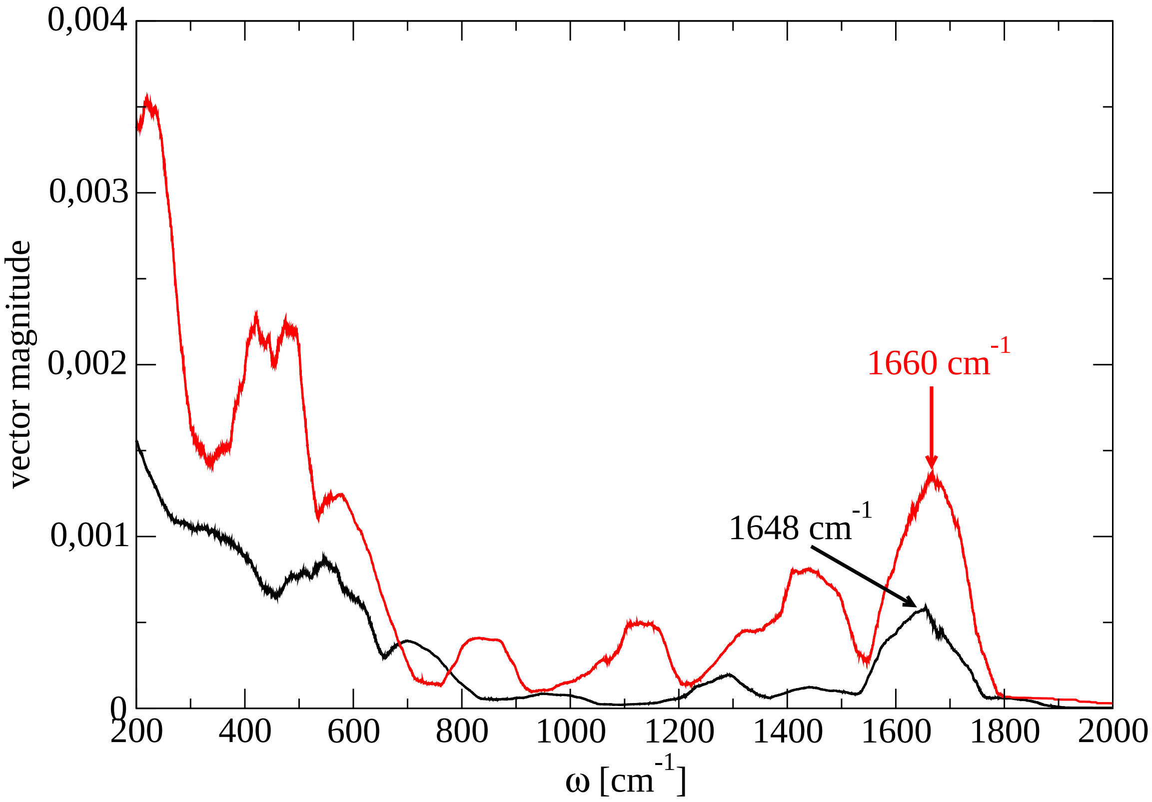

Figure 2: The vector magnitude of the atoms C and O motions in different normal mode vibrations. Shown are results of the COO- groups (black) and C=O groups (red).

assigned as follows. Let $\mathbf{U_k} = (u_{1k}, u_{2k}, u_{3k}, \cdots, u_{3N-8k}, u_{3N-7k}, u_{3N-6k})$ be the eigenvector which represens the direction of motion of the normal mode k-th obtained from the normal mode analysis. In our case, the FFC contains $N = 5328$ atoms, thus there are $5328 \times 3 - 6 = 15978$ normal modes. Here, (u_{1k}, u_{2k}, u_{3k}) are three Cartesian vector components which tell us the direction of motion of atom 1 in the mode k-th, and so on. To estimate the contribution of motion of atom i-th to the vibration of mode k-th, we define the vector magitude $V_{ik} = \sqrt{u_{ik}^2 + u_{ik}^2 + u_{ik}^2}$. Larger value of V_{ik} reflects larger contribution of atom i-th to mode k-th, that is, the vibration is more localized on atom i-th. To assign two peaks shown in Fig.2(B) of the paper, we calculate V_{ik} for all normal modes $k = 1 \cdots 15978$ for different atoms i: the oxygen atoms of the COO- groups, the carbone atoms of the COO- groups, the oxygen atoms of the C=O groups, the carbone atoms of the C=O groups. Fig.2 shows the sum of the vector magnitude of the C, O atoms of the COO- and C=O groups. As seen, at low frequencies ($\omega \leq 600$ cm^{-1}), the vector magnitudes are large because these are associated with the relative motions between FF units. The vector magnitude of the C, O motions of the COO- groups shows a peak at 1648 cm^{-1}, indicating that this mode is primarily contributed by the C-O- stretching. thus we assign this frequency to the C-O stretching of the COO- groups. Similarly, the vectors of the C, O motions of the C=O groups shows a peak at 1660 cm^{-1} which reflects the C=O stretching.

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