Supporting Information for:

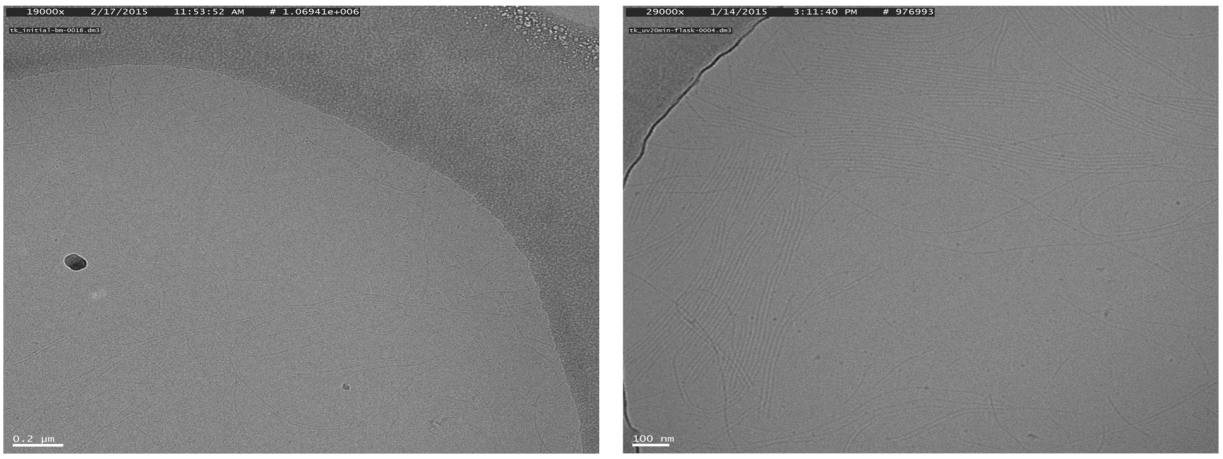
How Defects Control the Out-of-Equilibrium Dissipative Evolution of a Supramolecular Tubule

Davide Bochicchio,[a] *Supaporn Kwangmettatam,*[b] *Tibor Kudernac*[b] *and Giovanni M. Pavan*[a,]*

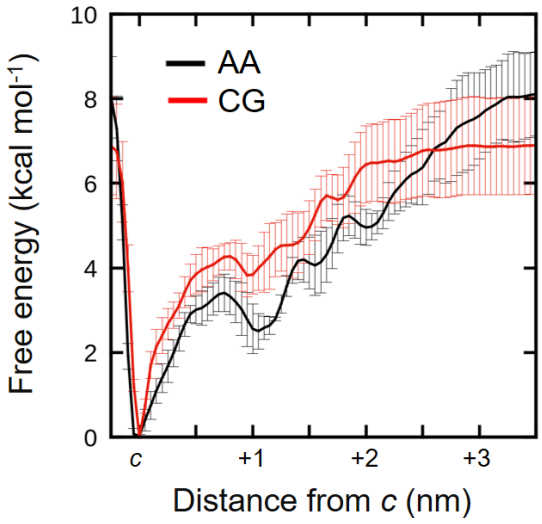
[a] Department of Innovative Technologies, University of Applied Sciences and Arts of Southern Switzerland, Galleria 2, Via Cantonale 2c, CH-6928 Manno, Switzerland

giovanni.pavan@supsi.ch

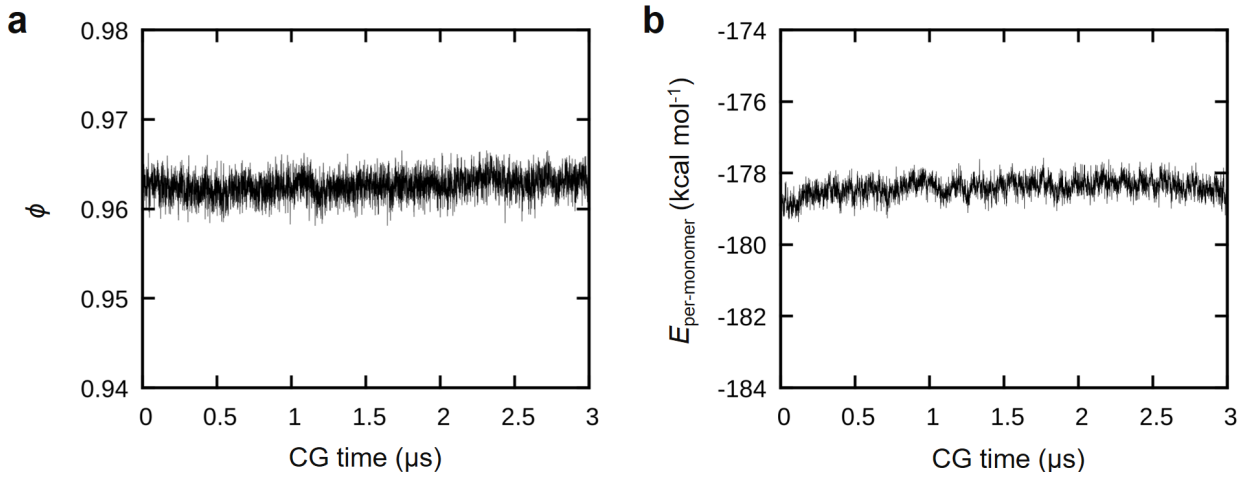
[b] Molecular Nanofabrication Group, MESA+ Institute for Nanotechnology, University of Twente, PO Box 207, 7500 AE Enschede, The Netherlands



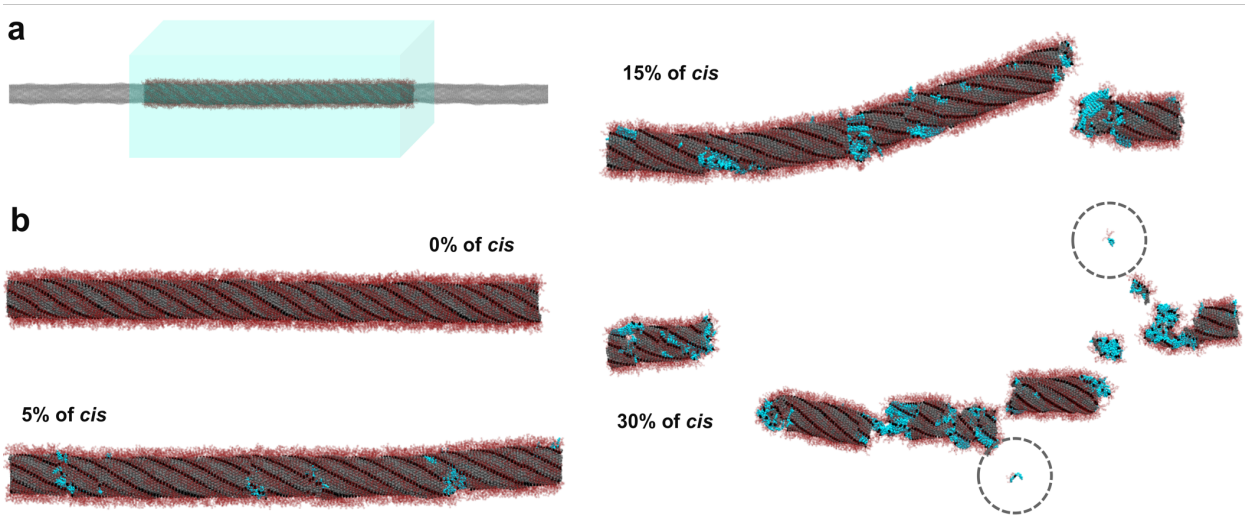
Supporting Figure 1 Additional TEM image of the self-assembled tubules in water.



Supporting Figure 2 Dimerization free energy profiles of two V-shaped monomer tails in their *trans* form, calculated via Metadynamics simulations for the atomistic model (AA, black) and the coarse-grained (CG, red) model. The AA and CG free energy profiles are in good agreement within the error bars.

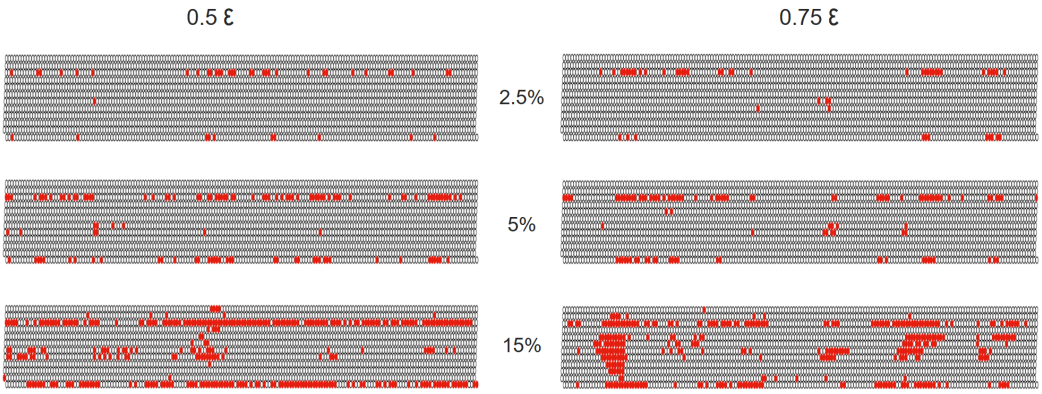


Supporting Figure 3 Equilibration of the CG supramolecular tubule (all tails in non-excited *trans* form) in terms of order parameter ϕ (**a**) and monomer-monomer interaction energy E (**b**). The tubule appears as stable during the CG simulations time. **a** The order parameter equilibrates at $\phi \approx 0.96$, indicating that the tubule is well ordered, with a deviation from the initially perfect configuration ($\phi = 1$) of less than 4%.

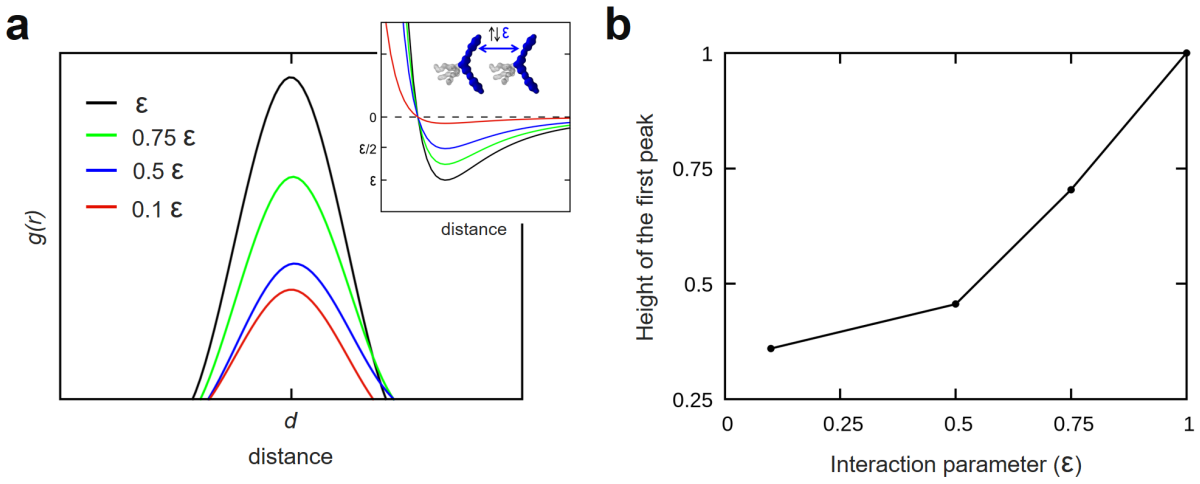


Supporting Figure 4. Breakage and disassembly of the supramolecular tubule equilibrated at

various *cis* percentages. **a** Initial configuration for the tubule model. This models a section (~80 nm of length) of an infinite tubule spanning through a simulation box filled with water (cyan). **b** Configurations of the tubule equilibrated via CG-MD at different (static) *cis* percentages: 0% (native unperturbed tubule), 5%, 15% and 30% of *cis*. The central ring of the monomers is colored in black, *trans* tails are in gray, *cis* ones in cyan and oligoether hydrophilic chains are in transparent red. At 15% of cis the tubule starts breaking spontaneously during the CG-MD. At 30% of *cis* we could observe breakage in correspondence of the cyan (*cis*) areas and spontaneous monomer disassembly (grey circles) during the CG-MD simulation.



Supporting Figure 5. Spatial distribution of transited *cis* tails in the tubule during the **CG$_i$**-MD simulations when the interaction parameter ε is halved (0.5 ε) or reduced to 0.75 ε.



Supporting Figure 6. Spatial correlation of defects as a function of the strength of the interactions between the monomers tails. **a** Height of the first *g(r)* peak (*g(d)*, where *d* is the distance between closest neighbor tails in the stack) at different interaction strengths (see inset). The *g(d)* peaks indicates the relative probability for the transition to occur close to other *cis* tails (defects correlation). **b** Relative height of *g(d)* as a function of the interaction strength (fractions of ε: monomer interaction strength in the native tubule) – the spatial correlation of defects increases with the interaction strength, revealing the origin of the "crowding" effect in our supramolecular tubule.

CG force-field parameters for the monomers

Here we report the .itp file (GROMACS format – energies in kJ mol^{-1}) for all developed CG monomer models used in this work. The 2nd column in the [atoms] section identifies the MARTINI CG bead. The parameters are the same in all standard models, apart for the dihedral section at the bottom (changing for unperturbed or excited monomers). In CG_i-MD simulations designed to investigate the effect of the strength of the interactions, we decreased the original interaction between SC5 MARTINI beads (ε = 0.627 kcal mol^{-1}) to 0.75 ε, 0.5 ε and 0.1 ε.

```
[moleculetype]
; molname       nrexcl
  TUB         1

[atoms]
; id    type  resnr   residu   atom    cgnr    charge
  1     SC5     1     BENZ      B1      1        0
  2     SC5     1     BENZ      B2      2        0
  3     SC5     1     BENZ      B3      3        0
;
  4     SC5     2       BENZ     B4      4       0
  5     SC5     2       BENZ     B5      5       0
  6     SC5     2       NENZ     N6      6       0
  7     SC5     2       NENZ     N7      7       0
  8     SC5     2       BENZ     B8      8       0
  9     SC5     2       BENZ     B9      9       0
 10     SC5     2       BENZ     B10    10       0
 11     SC5     2       BENZ     B11    11       0
 12     SC5     2       BENZ     B12    12       0
 13     SN0     2       NEND     N13    13       0
;
 14     SC5     4       BENZ     B4     14       0
 15     SC5     4       BENZ     B5     15       0
 16     SC5     4       NENZ     N6     16       0
 17     SC5     4       NENZ     N7     17       0
 18     SC5     4       BENZ     B8     18       0
 19     SC5     4       BENZ     B9     19       0
 20     SC5     4       BENZ     B10    20       0
 21     SC5     4       BENZ     B11    21       0
 22     SC5     4       BENZ     B12    22       0
 23     SN0     4       NEND     N13    23       0
;
 24     SP0     3       PEG      P24    24       0
 25     SP0     3       PEG      P25    25       0
 26     SP0     3       PEG      P26    26       0
 27     SC1     3       ALK      A27    27       0
 28     SC1     3       ALK      A28    28       0
;
 29     SP0     3       PEG      P29    29       0
 30     SP0     3       PEG      P30    30       0
 31     SP0     3       PEG      P31    31       0
 32     SP0     3       PEG      P32    32       0
;
 33     SP0     3       PEG      P33    23       0
 34     SP0     3       PEG      P34    34       0
 35     SP0     3       PEG      P35    35       0
 36     SP0     3       PEG      P36    36       0
;
 37     SP0     3       PEG      P37    37       0
 38     SP0     3       PEG      P38    38       0
 39     SP0     3       PEG      P39    39       0
 40     SP0     3       PEG      P40    40       0
;
 41     SP0     3       PEG      P41    41       0
 42     SP0     3       PEG      P42    42       0
```

```
 43     SP0     3       PEG     P43    43       0
 44     SP0     3       PEG     P44    44       0

[bonds]
  1  2  1       0.27    22000
  2  3  1       0.27    22000
  3  1  1       0.27    22000
;
  2  4  1       0.285   22000
  2  5  1       0.285   22000
;
  4  5  1       0.27    22000
  5  6  1       0.41    22000
  6  4  1       0.41    22000
;
  6  7  1       0.15    22000
;
  7  8  1       0.41    22000
  7  9  1       0.41    22000
  8  9  1       0.27    22000
;
 10  8  1       0.285   22000
 10  9  1       0.285   22000
;
 10 11  1       0.27    22000
 11 12  1       0.27    22000
 12 10  1       0.27    22000
;
 11 13  1       0.34    22000
 12 13  1       0.34    22000
;
 2   6  1       0.64    22000
 7  10  1       0.64    22000
10  13  1       0.546   22000
;
;
  3 14  1       0.285   22000
  3 15  1       0.285   22000
;
 14 15  1       0.27    22000
 15 16  1       0.41    22000
 16 14  1       0.41    22000
;
 16 17  1       0.15    22000
;
 17 18  1       0.41    22000
 17 19  1       0.41    22000
 18 19  1       0.27    22000
;
 20 18  1       0.285   22000
 20 19  1       0.285   22000
;
 20 21  1       0.27    22000
 21 22  1       0.27    22000
 22 20  1       0.27    22000
```

```
;
 21 23  1       0.34    22000
 22 23  1       0.34    22000
;
 3  16  1       0.64    22000
17  20  1       0.64    22000
20  23  1       0.546   22000
;;;
;;;
 1  24  1       0.27    22000
;
24  25  1       0.32    12000
24  26  1       0.32    12000
;
25  27  1       0.28    12000
26  28  1       0.28    12000
;
27  29  1       0.32    12000
27  33  1       0.32    12000
28  37  1       0.32    12000
28  41  1       0.32    12000
;
29  30  1       0.32     12000
30  31  1       0.32     12000
31  32  1       0.32     12000
;
33  34  1       0.32     12000
34  35  1       0.32     12000
35  36  1       0.32     12000
;
37  38  1       0.32     12000
38  39  1       0.32     12000
39  40  1       0.32     12000
;
41  42  1       0.32     12000
42  43  1       0.32     12000
43  44  1       0.32     12000

[angles]
;
1 2 4     2     125       300
1 2 5     2     175       300
1 3 14    2     125       300
1 3 15    2     175       300
3 2 4     2     175       300
3 2 5     2     125       300
2 3 14    2     175       300
2 3 15    2     125       300
;
11 10 8     2     125     300
11 10 9     2     175     300
21 20 18    2     125     300
21 20 19    2     175     300
12 10 8     2     175     300
12 10 9     2     125     300
```

```
22 20 18    2     175     300
22 20 19    2     125     300
;
13 10  7   2     180      500
23 20 17   2     180      500
;
6  7  10   2    118.0      1200
16 17 20   2    118.0      1200
7  6  2    2    118.0      1200
17 16 3    2    118.0      1200
;;
;;
2  1  24   2    140.0      120
3  1  24   2    140.0      120
;
1  24 25   2    122.0       40
1  24 26   2    122.0       40
;
24 25 27   2    126.0       70
24 26 28   2    126.0       70
;
25 27 29   2    110.0       20
25 27 33   2    110.0       20
26 28 37   2    110.0       20
26 28 41   2    110.0       20
;
27 29 30   2    100.0       30
27 33 34   2    100.0       30
28 37 38   2    100.0       30
28 41 42   2    100.0       30
;
29 30 31   2    125.0       90
30 31 32   2    125.0       90
33 34 35   2    125.0       90
34 35 36   2    125.0       90
37 38 39   2    125.0       90
38 39 40   2    125.0       90
41 42 43   2    125.0       90
42 43 44   2    125.0       90
;
25 24 26   2     90        120
29 27 33   2    130         70
37 28 41   2    130         70

[dihedrals]
4 5 6 2       2      0    200
14 15 16 3    2      0    200
8 9 7 10      2      0    200
18 19 17 20   2      0    200
11 12 13 10   2      0    200
21 22 23 20   2      0    200
;
8 9 11 12   9      140.0    4  1
18 19 21 22 9      140.0    4  1
8 11 9 12   9      140.0    4  1
```

```
18 21 19 22 9      140.0    4  1
;
1 3 4 5     9      140.0    4  1
1 2 14 15   9      140.0    4  1
1 4 3 5     9      140.0    4  1
1 14 2 15   9      140.0    4  1
;
4  5  6  7    9    180.0    6  2
9  8  7  6    9    180.0    6  2
14  15 16 17  9    180.0    6  2
19  18 17 16  9    180.0    6  2

; CNNC DIHEDRAL – native unperturbed CG tails (the number of unperturbed tails in
each monomer depends on the percentage of cis in the tubule)
2 6 7 10    9        180   64   2
3 16 17 20  9        180   64   2
2 6 7 10    9        0.0   30   1
3 16 17 20  9        0.0   30   1
```

OR:

; CNNC DIHEDRAL – standard excited S* *trans* tails, **CG_{S*}** (the number of excited *trans* tails in each monomer depends on the percentage of *cis* in the tubule)

```
2 6 7 10    9        180   64   2
3 16 17 20  9        180   64   2
2 6 7 10    9        0.0   30   1
3 16 17 20  9        0.0   30   1
2 6 7 10    8        0    220  ; 280 instead of 220 to win crowding in NVE CG-MD runs
3 16 17 20  8        0    220  ; 280 instead of 220 to win crowding in NVE CG-MD runs
```

OR:

; CNNC DIHEDRAL – dynamic toy model **CG_1** (dihedral changed in all tails in the tubule)

```
;2 6 7 10    9      180.0   20  1
;3 16 17 20  9      180.0   20  1
```